ELSEVIER

Thermochimica Acta 322 (1998) 77–82

thermochimica acta

Some comments about a correct estimation of the kinetic exponent for non-isothermal solid-state processes using Augis and Bennett method

J. Málek[a,*], J.M. Criado[b], F.J. Gotor[b], J. Šesták[c]

[a] *Joint Laboratory of Solid State Chemistry of the Academy of Sciences of the Czech Republic and University of Pardubice, Studentská 84, 532 10 Pardubice, Czech Republic*
[b] *Instituto de Ciencia de Materiales de Sevilla C.S.I.C., Avda. Americo Vespucio s/n, Isla Cartuja, 41 071 Sevilla, Spain*
[c] *Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 53 Prague, Czech Republic*

Received 29 December 1997; received in revised form 15 June 1998; accepted 30 June 1998

Abstract

The method of estimation of kinetic exponent of the Johnson–Mehl–Avrami (JMA) model from non-isothermal DTA or DSC data introduced by Augis and Bennett has been analyzed. It is shown that this method gives reasonably accurate estimations provided that it has been checked by an independent method that the data really correspond to the JMA model. Otherwise, the Augis and Bennett method can lead to wrong interpretation of experimental data. A simple testing method which allows verification of the applicability of this method is proposed. These methods were successfully applied to analysis of non-isothermal crystallization of $Ge_{0.3}Sb_{1.4}S_{2.7}$ glass. © 1998 Elsevier Science B.V.

Keywords: Crystallization processes; DSC; DTA; Johnson–Mehl–Avrami model; Kinetics

1. Introduction

Twenty years ago Augis and Bennett [1] suggested a convenient method of calculation of kinetic exponent, m, for the Johnson–Mehl–Avrami (JMA) model from non-isothermal DTA or DSC data. The method is based on a simple equation:

$$m = \frac{2.5RT_p^2}{E_a \Delta T} \quad (1)$$

where T_p is the maximum of DTA or DSC peak, ΔT the peak halfwidth and E_a the activation energy. This method became quite popular (more than 130 citation of original paper [1] to date) and it is frequently used for the estimation of parameter m from non-isothermal data [2–6]. However, the JMA model was developed to describe nucleation-growth processes in isothermal conditions and it can be applied to the description of non-isothermal DTA or DSC data only in a limited number of special cases. From this point of view the applicability of the JMA model should be carefully examined before the Augis and Bennett method is used.

The aim of this paper is to analyze practical limits of validity of Eq. (1) in non-isothermal kinetics of solid-state processes.

2. Theory

The theoretical basis for the description of isothermal solid-state transformations involving both nuclea-

---

*Corresponding author. Fax: +420-40-48-400; e-mail: malek@pol.upce.cz

PII: S0040-6031(98)00491-2

tion and growth phases was formulated by Johnson and Mehl [7], Avrami [8,9] and Kolmogorov [10]. The resulting equation describes the time dependence of the fractional extent of the process, α, and it is known as the Johnson–Mehl–Avrami equation:

$$\alpha = 1 - \exp[-(Kt)^m] \tag{2}$$

where K and m are constants with respect to time t. For some simple cases of solid-state transformation it is possible to find a characteristic value of the kinetic exponent m [11,12].

By differentiation of Eq. (2) with respect to time the isothermal transformation rate equation is obtained:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = Km(1-\alpha)[-\ln(1-\alpha)]^{1-1/m} \tag{3}$$

It has been shown [12,13] that the validity of Eqs. (2) and (3) can be extended to non-isothermal conditions provided that a new crystalline phase grows from a constant number of nuclei and all nucleation is completed prior to crystal growth in macroscopic scale. Usually, it is expected that the rate constant K exhibits a simple Arrhenius temperature dependence $K(T)=A\ \exp(-E_a/RT)$. The rate equation for non-isothermal conditions then can be expressed:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = A\exp(-E_a/RT)f(\alpha) \tag{4}$$

where $f(\alpha)=m(1-\alpha)\ [-\ln(1-\alpha)]^{1-1/m}$ is the kinetic function for the JMA model.

Usually, it is assumed that the rate ($\mathrm{d}\alpha/\mathrm{d}t$) is proportional to the measured quantity (temperature difference for DTA or heat flow for DSC technique). Fig. 1 shows a typical DTA or DSC peak associated with a constant scan rate experiment. At the half maximum of this peak we can write the following condition using Eq. (4):

$$A\exp(-E_a/RT_1)f(\alpha_1) = A\exp(-E_a/RT_2)f(\alpha_2) \tag{5}$$

Eq. (5) can be rewritten after converting it into logarithmic form and assuming that $T_1T_2 \cong T_p^2$

$$\frac{RT_p^2}{E_a\Delta T} = \left[\ln\left(\frac{f(\alpha_1)}{f(\alpha_1)}\right)\right]^{-1} \tag{6}$$

where $\Delta T=T_2-T_1$ is the peak halfwidth. This equation is formally identical with Eq. (1) assuming that $\{\ln[f(\alpha_1)/f(\alpha_2)]\}^{-1}\cong m/2.5$. This assumption not seems to be so straightforward as stated in Ref.[1]. Therefore, we will examine it in more detail in Section 3.

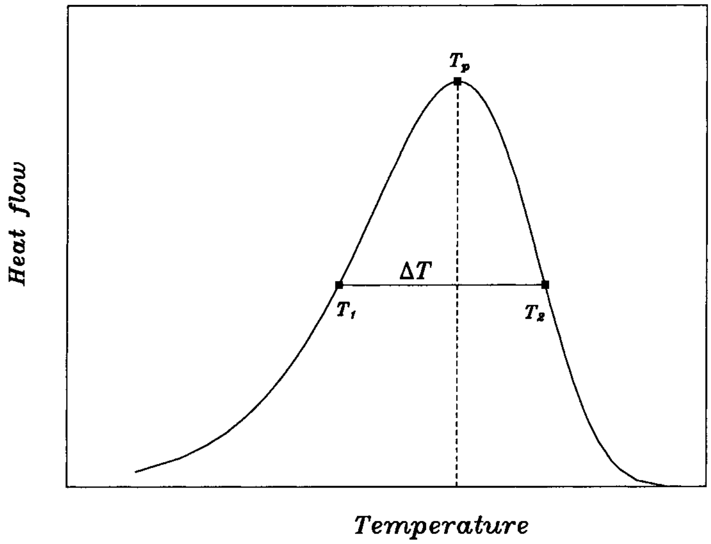

Fig. 1. Analysis of a typical DSC curve according to the method suggested by Augis and Bennett [1].

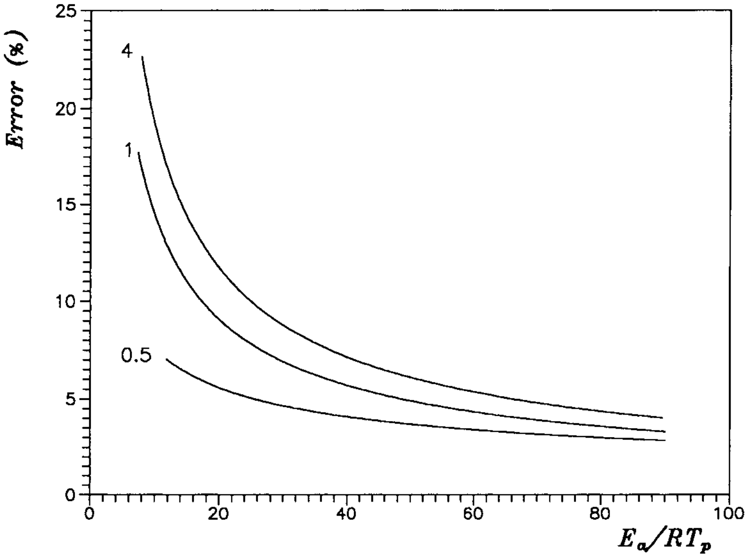

Fig. 2. Error of kinetic exponent m (calculated using (Eq. (1)) as a function of reduced activation energy. The numbers correspond to the values of parameter m of theoretically calculated DSC curves used for analysis as shown in Fig. 1.

3. Results and discussion

Theoretical DSC curves can be obtained by numerical solution of the differential Eq. (4). Fig. 2 shows an error of estimation of kinetic exponent m if these DSC curves calculated for the JMA model are analyzed using Eq. (1). The error is defined in the following way:

$$\mathrm{Error}\,(\%) = \frac{m_{\mathrm{calc}} - m}{m} \times 100 \qquad (7)$$

where m is the true value of kinetic exponent and m_{calc} the value calculated from Eq. (1). It is seen that the error decreases with the reduced activation energy, E_a/RT_p, and increases with the value of parameter m. Nevertheless, it is below 10% for $m \leq 4$ and $E_a/RT_p \geq 30$. These conditions are usually fulfilled for most practical cases where the JMA equation can be applied. It seems, therefore, that Eq. (1) can provide reasonably accurate estimation of the parameter m for most cases of non-isothermal solid-state processes. However, as anticipated in Section 1, the JMA equation can be applied to the description of non-isothermal data only in a limited number of special cases and the kinetic model corresponding to a particular data set is usually not known 'a priori'. Eq. (1) always provides a value of kinetic exponent for any DTA or DSC peak. Nevertheless, if the analyzed DTA or DSC curve does not correspond to the JMA model then the Augis and Bennett method can lead to a wrong interpretation of experimental data. Therefore, it seems that the validity of the JMA model should carefully be examined before any practical application of Eq. (1) is made. A very simple and reliable method testing the applicability of the JMA model is based on the mathematical properties of the $z(\alpha)$ function which can easily be obtained by a simple transformation of DTA or DSC data [14]:

$$z(\alpha) = \left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) T^2 \qquad (8)$$

It can be shown that the function $z(\alpha)$ has a maximum at α_p^∞ which should be confined to the interval $0.62<\alpha_p^\infty<0.64$ for the JMA model [14]. Strictly speaking, only in this case can the Augis and Bennett method be applied and Eq. (1) gives reliable value of exponent m. It was found [15–19], however, that in many cases crystallization processes in non-isothermal conditions cannot be described by the JMA model ($\alpha_p^\infty \ll 0.62$) and that the empirical Sestak–Berggren (SB) model [20] provides a more satisfactory descrip-

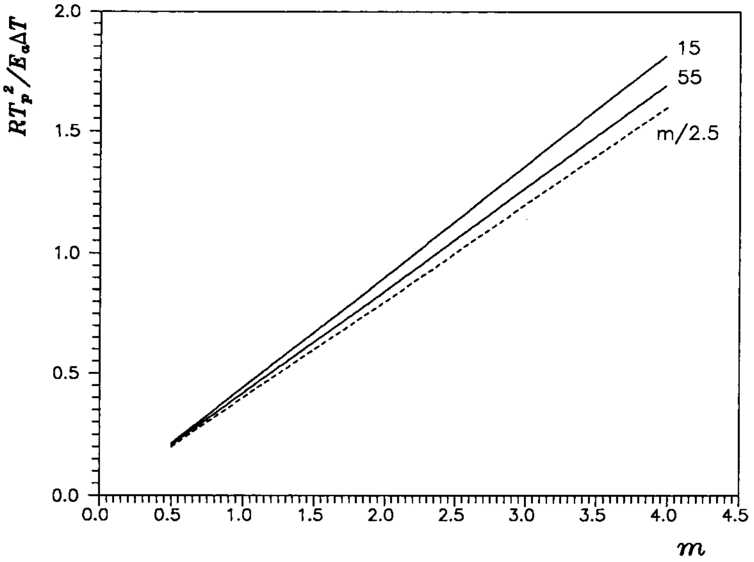

Fig. 3. The dependence of parameter $RT_p^2/E_a\Delta T$ as a function of the kinetic exponent m for the JMA model. Full lines were obtained for theoretically calculated DSC curves for E_a/RT_p=15 and 55. Broken line corresponds to Eq. (1).

tion of experimental data. In these cases, Eq. (1) evidently cannot be applied for the estimation of a meaningful parameter m.

According to Eq. (1), the term $RT_p^2/E_a\Delta T$ should be a linear function of the kinetic exponent m for the JMA model. Augis and Bennett [1] claimed that the slope of such a plot should be equal to 1/2.5. In fact this slope is greater and it varies slightly with a reduced activation energy, being 1/2.18 for E_a/RT_p=15 and 1/2.35 for E_a/RT_p=55. These plots, obtained by analysis of theoretically calculated DSC curves, are shown in Fig. 3. It seems, therefore, that Eq. (1) should rather be written in the following form:

$$m = \frac{cRT_p^2}{E_a\Delta T} \tag{9}$$

where c is a parameter which depends on the reduced activation energy as shown in Fig. 4. The value of c=2.44 corresponds to infinite reduced activation energy ($E_a/RT_p \to \infty$) and it is still considerably lower than the value of 2.5 reported by Augis and Bennett [1]. If the kinetic exponent m for the JMA model is calculated using Eq. (9) instead of Eq. (1) then the error mentioned above (see Fig. 2 and corresponding discussion) will be practically eliminated.

In any practical application of Augis and Bennett method of analysis of real data, the accuracy of the estimated parameter m also depends on the experimental errors which affect the correct determination of T_p and ΔT. It is also very important to have a correct determination of the activation energy which should be invariant with respect to fractional conversion α (this is also essential for other methods of determination of the kinetic exponent [22]). The isoconversional method of calculation of E_a [21] is recommended as it provides the possibility of verifying this invariance. While the Augis and Bennett method of estimation of the parameter m of the JMA model is valid under the specific aforementioned conditions, a more deterministic method of evaluation of this parameter is usually preferred. An outline of such methods can be found, for example, in Refs. [12,22–24].

Fig. 5 shows non-isothermal DSC data corresponding to crystallization of bulk $Ge_{0.3}Sb_{1.4}S_{2.7}$ glass [25]. The normalized $z(\alpha)$ function calculated using Eq. (8) is shown in the inset. The maximum of this function agrees with the value predicted for the JMA model and, therefore, the Augis and Bennett method can be used for the estimation of the value of kinetic exponent. From Fig. 5, we find the peak temperature of 656.4 K and the peak halfwidth of 16.6 K, respec-

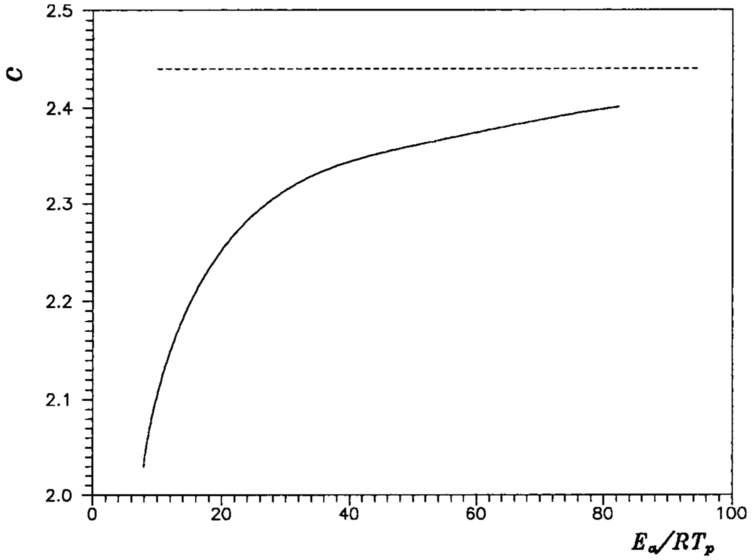

Fig. 4. The dependence of parameter c in Eq. (9) as a function of reduced activation energy. Broken line shows a limiting value for $E_a/RT_p \to \infty$.

tively. The value of activation energy reported previously [25,26] is 160 kJ/mol and, therefore, $E_a/RT_p=29.3$. From Fig. 4 this value of the reduced activation energy corresponds to $c=2.31$. Then the value of the kinetic exponent estimated using Eq. (9) was found to be $m=3.1$. This value is very close to a

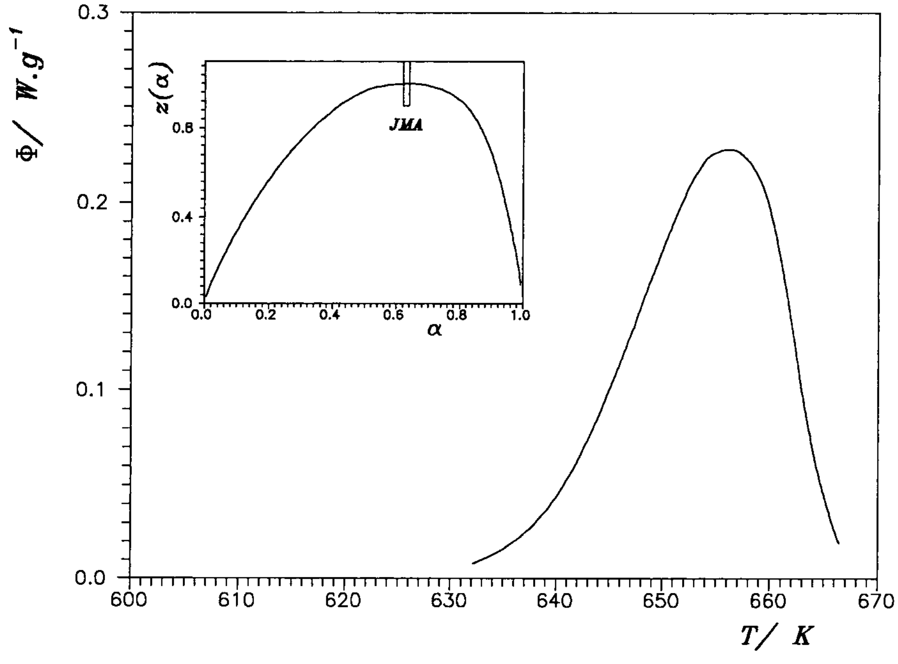

Fig. 5. DSC curve of crystallization of bulk $Ge_{0.3}Sb_{1.4}S_{2.7}$ glass measured at heating rate 5 K/min. Inset shows the normalized $z(\alpha)$ dependence calculated from DSC data using Eq. (8). The position of the maximum typical for the JMA model is marked with broken lines.

previously reported value (m=3.05) obtained by other methods [25] and it is also in agreement with observed growth of spherulitic crystals of Sb_2S_3 phase. A somewhat higher value of kinetic exponent (m=3.37) is obtained from original Augis and Bennett formula expressed by Eq. (1).

4. Conclusions

The method of estimation of kinetic exponent of the JMA model from the shape of DTA or DSC curve introduced by Augis and Bennett has been analyzed. It is shown that Eq. (1) reported in the original paper of Augis and Bennett can provide reasonably accurate estimation of kinetic exponent (within 10% error) though the more precise Eq. (9) gives even better results. Nevertheless, this simple method of estimation of the kinetic exponent is valid only in the case that the analyzed DTA or DSC data really correspond to the JMA model. Otherwise, the Augis and Bennett method can lead to wrong interpretation of experimental data. A simple testing method which allows to verify the applicability of the JMA model is suggested.

These methods have been successfully applied to analysis of non-isothermal crystallization of bulk $Ge_{0.3}Sb_{1.4}S_{2.7}$ glass.

Acknowledgements

This work was supported by the Grant Agency of the Czech Republic under grants No.104/97/0589 and 203/96/0184.

References

[1] J.A. Augis, J.E. Bennett, J. Therm. Anal. 13 (1978) 283.
[2] S.H. Hong, G.L. Messing, J. Am. Ceram. Soc. 80 (1997) 1551.
[3] A. Ozturk, J. Mater. Sci. 32 (1997) 2623.
[4] C.S. Ray, Q.Z. Yang, W.H. Huang, D.E. Day, J. Am. Ceram. Soc. 79 (1996) 3155.
[5] J.L. Besson, H. Lemercier, T. Rouxel, G. Trolliard, J. Non-Cryst. Solids 211 (1997) 1.
[6] K.H. Lee, D.A. Hirschfeld, J.J. Brown, J. Am. Ceram. Soc. 79 (1996) 597.
[7] W.A. Johnson, R.F. Mehl, Trans. Am. Inst. Miner. (Metall.) Eng. 135 (1939) 416.
[8] M. Avrami, J. Phys. Chem. 7 (1939) 1103.
[9] M. Avrami, J. Phys. Chem. 8 (1940) 212.
[10] A.N. Kolmogorov, Izvestia. Akad. Nauk USSR, Ser. Math. 1 (1937) 355.
[11] J.W. Christian, The Theory of Transhormations in Metals and Alloys, 2nd edn., Pergamon, New York, 1975.
[12] D.W. Henderson, J. Non-Cryst. Solids 30 (1979) 301.
[13] T.J.W. DeBruijn, W.A. DeJong, P.J. Van Den Berg, Thermochim. Acta 45 (1981) 315.
[14] J. Málek, Thermochim. Acta 267 (1995) 61.
[15] J. Málek, J. Non-Cryst. Solids 107 (1989) 323.
[16] J. Málek, V. Smrčka, Thermochim. Acta 186 (1991) 153.
[17] J. Málek, Y. Messaddeq, S. Inoue, T. Mitsuhashi, J. Mat. Sci. 30 (1995) 3082.
[18] J. Málek, S. Matsuda, A. Watanabe, T. Ikegami, T. Mitsuhashi, Thermochim. Acta 267 (1995) 181.
[19] J. Málek, A. Watanabe, T. Mitsuhashi, Thermochim. Acta, 282–283 (1996) 131.
[20] J. Šesták, G. Berggren, Thermochim. Acta 3 (1971) 1.
[21] H.L. Friedman, J. Polym. Sci. Part C 6 (1964) 183.
[22] J. Málek, Thermochim. Acta 200 (1992) 257.
[23] J. Šesták, Thermophysical Properties of Solids, Their Measurements and Theoretical Analysis, Elsevier, Amsterdam, 1984.
[24] T. Ozawa, Bull. Chem. Soc. Jpn. 57 (1984) 639.
[25] J. Málek, E. Černošková, R. Švejka, J. Šesták, G. Van der Plaats, Thermochim. Acta, 280–281 (1996) 353.
[26] N. Ryšavá, L. Tichý, Č. Barta, A. Tříska, H. Tichá, Phys. stat. sol. (a) 87 (1985) K13.