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Thermochimica Acta 288 (1996) 97–104

thermochimica
acta

A new method for the derivation of activation energies from experiments performed at constant heating rate

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Received 24 April 1996; accepted 26 June 1996

Abstract

The Ozawa, Kissinger and Boswell isoconversion methods for obtaining activation energies, E_a , from experiments performed at constant heating rate belong to one group of methods. It is shown that from these three methods the Kissinger method is generally the most accurate. Based on the analysis of the approximation errors made in this group of methods, a new isoconversion method is obtained, which takes the form:

$$\ln \frac{\beta}{T_f^{1.8}} = -A \frac{E_a}{k_B T_f} + \text{constant}$$

where $A = 1.0070 - 1.2 \cdot 10^{-5} E_a$ (E_a in kJ/mol), β is the heating rate and T_f is the temperature at a fixed amount transformed. Hence, similar to Ozawa, Boswell and Kissinger's methods it is based on obtaining the slope of a logarithmic function containing the heating rate vs. $1/T$. The new method is shown to be significantly more accurate than the others.

Keywords: Activation energy; Isoconversion method; Kissinger method; Non-isothermal analysis; Ozawa method.

1. Introduction

Thermally activated transformation processes in the solid state can be investigated by isothermal experiments or non-isothermal experiments at constant heating rate. The latter is the case with, for instance, differential scanning calorimetry (DSC) and non-isothermal dilatometry. For non-isothermal analysis at constant heating rate a mean activation energy, E_a , can be derived using (amongst other methods) a Kissinger-type isoconversion method (see for instance Ref. [1]). However, these methods are

subject to approximations which can introduce significant inaccuracies in the determination of E_a .

In this work the accuracy of the so-called Kissinger and Ozawa [2] methods are investigated. It will be shown that the approximations used in the derivation of these methods introduce significant inaccuracies. A new method for the derivation of activation energies is presented. It is shown that this method is an order of magnitude more accurate than the Kissinger and Ozawa methods.

2. Classical isoconversion methods for determination of E_a

Generally the transformation rate during a reaction is assumed to be the product of two functions, one depending solely on the temperature, T , and the other depending solely on the fraction transformed:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where α is the fraction transformed:

$$\alpha = x(t)/x_{\text{eq}}(T) \quad (2)$$

$x(t)$ is the amount transformed, x_{eq} is the maximum amount that can transform before (metastable) equilibrium is reached, i.e. $x_{\text{eq}} = x(t \rightarrow \infty, T)$. For $k(T)$ usually an Arrhenius expression is assumed to be valid, i.e.:

$$k(T) = k_0 \exp[-E_a/k_B T] \quad (3)$$

where k_0 is a constant, E_a is the activation energy of the process, which is assumed to be constant, and k_B is Boltzmann's constant. From Eqs. (1)–(3) follows immediately that for transformation studies performed at constant temperature, T_i , E_a can be obtained from the well known relation (see for instance ref. [1]):

$$\ln t_f = \frac{E_a}{k_B T_i} + C_1 \quad (4)$$

where t_f is the time needed to reach a certain fraction transformed, and C_1 is a constant which depends on the reaction stage and on the kinetic model. Thus E_a can be obtained from two or more experiments at different T .

For transformation studies performed at constant heating rate, methods for determining E_a can be derived as follows. Eq. (1) is integrated by separation of variables:

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{k_0}{\beta} \int_0^{T_f} \exp\left(-\frac{E_a}{k_B T}\right) dT = \frac{k_0 E_a}{\beta k_B} \int_{y_f}^{\infty} \frac{\exp(-y)}{y^2} dy = \frac{k_0 E_a}{\beta k_B} p(y_f) \quad (5)$$

where $y = E_a/k_B T$, $y_f = E_a/k_B T_f$, T_f is the temperature at a fixed state of transformation, and β is the heating rate. Various ways of approximating $p(y)$ have been applied

in the literature (see refs. [1,2,3,4,5]). Integrating in parts and truncating the series by assuming $y_f \gg 1$ results in the following approximation for p (see ref. [1]):

$$p(y) \cong p_K(y) = \frac{\exp(-y)}{y^2} \quad (6)$$

The assumption $y_f \gg 1$ is reasonable, since for the vast majority of solid state reactions (and many other reactions) $15 < y_f < 60$. By taking the logarithm of Eq. (5) and using Eq. (6) one obtains:

$$\ln \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \ln \frac{k_o E_a}{k_B} + \ln \frac{1}{\beta y_f^2} - y_f \quad (7)$$

At constant fraction transformed, α , this leads to:

$$\ln \frac{\beta}{T_f^2} = -\frac{E_a}{k_B T_f} + C_2 \quad (8)$$

C_2 and subsequent C_3, C_4, C_5 are constants which depend on the reaction stage and on the kinetic model. According to Eq. (8) plots of $\ln(T_f^2/\beta)$ versus $1/T_f$ should result in straight lines, the slope of the straight lines equalling E_a/k_B . This method is usually referred to as the Kissinger method. Adoption of a specific reaction model, as various authors have done in the past [6,7,8], is not required to derive Eq. (8).

An alternative method is the Ozawa method (see e.g. ref. [2]). This method is obtained by approximating $p(y)$ as follows:

$$\log p(y) \cong \log p_O(y) = -2.315 + 0.4567y \quad (9)$$

This approximation is known as Doyle's approximation. By taking the logarithm of Eq. (5) and using Eq. (9) this results in:

$$\ln \beta = -1.0518 \frac{E_a}{k_B T_f} + C_3 \quad (10)$$

A comparison of the Ozawa and Kissinger methods shows that they both comply to the following equation:

$$\ln \frac{\beta}{T_f^s} = -A \frac{E_a}{k_B T_f} + C_4 \quad (11)$$

where s is a constant, and A is a constant which depends on the choice of s . In the case of Kissinger's method $s = 2$ and $A = 1$, whilst for the Ozawa method $s = 0$ and $A = 1.0518$. Also Boswell [3] proposed a (less known) method which can be represented by Eq. (11), using $s = 1$ and $A = 1$. Also for Eq. (11) a corresponding approximation of $p(y)$ should exist. Insertion in Eq. (5) will verify that this approximation has the general form:

$$p(y) \cong p_S(y) = \frac{\exp(-Ay + B)}{y^s} \quad (12)$$

where B is a constant depending on s . Just as Eq. (11) is a generalised form incorporating Eqs. (8) and (10), one can consider Eq. (12) to be a generalised form incorporating Eqs. (6) and (9).

At this point it should be noted that apart from the isoconversion methods of Kissinger, Ozawa and Boswell other methods for the derivation of activation energies exist. The method proposed first by Friedman [9] does not use any approximations and is therefore mathematically exact (see also ref. [10]). Apart from requiring temperatures at a fixed α (as the above methods) this method also requires $d\alpha/dT$ at fixed α . If $d\alpha/dT$ at fixed α can be measured accurately Friedman's method is advisable. However, the latter can be difficult to obtain for several experimental methods. (For DSC experiments it is sensitive to the baseline stability.) In this paper only methods of the type presented in Eq. (11) are considered.

To assess the accuracy of the different approximations for $p(y)$ first $p(y)$ was calculated by converting the integral into a summation (with 2000 steps) and subsequently the values of A and B for a best fit of p_s to $p(y)$ for $15 \leq y \leq 60$ were calculated by linear regression of $\ln(py^s)$ vs. y (i.e. different values of A and B are obtained for different values of s). The values obtained for A are presented in Fig. 1. In the same figure also a measure for the quality of the fit is presented. This quantity, Q , is defined as the integral of $(p_s(y)/p(y) - 1)^2$ for $15 \leq y \leq 60$. The fraction p_s/p is presented in Fig. 2. Figs. 1 and 2 show that the best approximation of $p(y)$ using Eq. (12) is obtained for s equalling about 1.8 to 1.9. For $s = 2$ one obtains $A = 0.998$. Hence, in the range of y values concerned, the Kissinger method will on average underestimate E_a by 0.2% (see also ref. [11]). The approximations which lead to Boswell's method ($s = 1$) and especially the one which leads to Ozawa's method ($s = 0$) are clearly much less accurate, and to obtain an accurate activation energy it is imperative that tables of correction factors are used. (For the case of Ozawa's method correction factors have been given in ref. [12].) For s around 1.9, the values for A obtained from the fitting procedure are

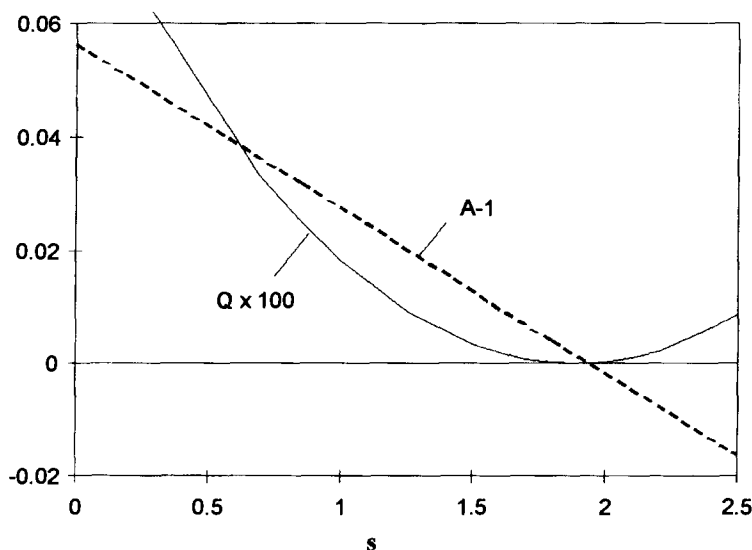


Fig. 1. Correction factor A (from Eq. (12)) needed to obtain the best approximation of the function $p(y)$ for $15 \leq y \leq 60$ and the resulting quality parameter, Q , for a best fit of $p_s(y)$ to $p(y)$, both as a function of s .

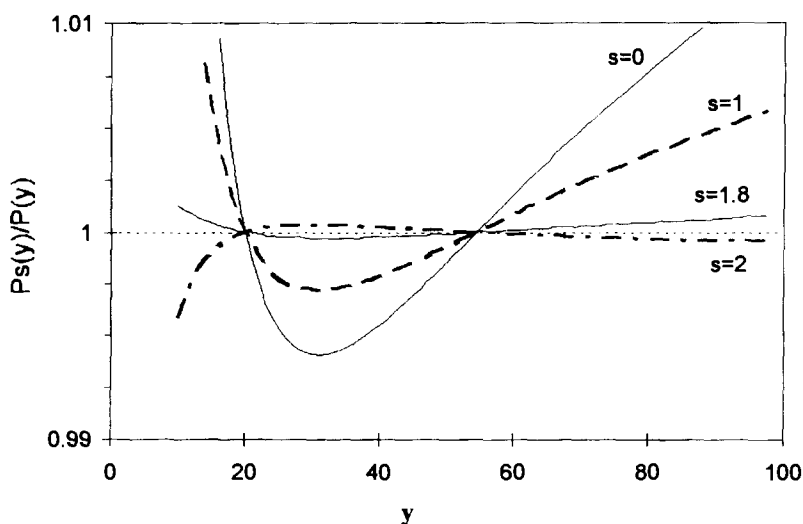


Fig. 2. The ratio of $p(y)$ (from Eq. (5)) and its approximation $p_s(y)$ (Eq. (12)) as a function of y for several values of s . The best approximation is obtained when this ratio is approximately constant, i.e. for $s \approx 1.9$.

close to unity and hence it follows that Eq. (11) with s equalling about 1.8 to 2 and $A = 1$ is a reasonably accurate method for obtaining activation energies. For $s = 1.94$ the fitting procedure results in $A = 1$ and hence these parameters should give the best result with Eq. (11) and $A = 1$. Within the interval of y values studied the accuracy of this method is better than Kissinger's method. However, an even more accurate method can be obtained.

3. A new isoconversion method for determining E_a

To obtain this new method the following general expression for $f(\alpha)$ is used (see e.g. refs. [1,13]):

$$f(\alpha) = (1 - \alpha)^p \left[\ln \frac{1}{(1 - \alpha)} \right]^q \quad (13)$$

where p and q are constants. It is noted that Eq. (13) can take account of both homogeneous n -th order reaction kinetics ($q = 0$, reaction order $n = p$) and Johnson–Mehl–Avrami–Kolmogorov (JMAK) reaction kinetics ($p = 1$ and Avrami exponent $m = [1 - q]^{-1}$). In the following it is assumed that incubation times are negligibly small. Using Eqs. (1)–(3) and (13), transformation curves (i.e. α as a function of T) were generated using a step by step method (i.e. considering small intervals ΔT), for $1 \leq p \leq 3$, $1 \leq m \leq 3$, $50 \leq E_a \leq 300$ kJ/mol, 1 K/min $\leq \beta \leq 100$ K/min, whilst k_0 was chosen such that $250 \leq T_f \leq 1000$ K. The vast majority of solid state reactions studied in the literature fall within these parameters. From the curves activation energies were calculated for $0.02 \leq \alpha \leq 0.9$.

As was explained above in principle various isoconversion methods for the calculation of E_a can be obtained using Eq. (11) with s around 1.8 to 2 and A equalling about unity. It is considered that allowing A to vary with heating rate can further improve the accuracy of the method. Hence, several values of s in the range 1.7 to 2 were tried and an optimised A was estimated via a linear regression analysis of the obtained slopes of $\ln(T_f^s/\beta)$ versus $1/k_B T_f$. It was found that within the range of parameters studied the following expression yielded a very accurate reproduction of the activation energy of the reaction, with a minimum variation of measured activation energy with heating rate and α :

$$\ln \frac{\beta}{T_f^{1.8}} = -A \frac{E_a}{k_B T_f} + C_5 \quad (14)$$

with

$$A = 1.0070 - 1.2 \cdot 10^{-5} E_a \quad (E_a \text{ in kJ/mol}), \quad (15)$$

Hence, to obtain the activation energy with this new method the slope of a plot of $\ln(T_f^{1.8}/\beta)$ versus $1/k_B T_f$ should be calculated, whilst A can be evaluated using this slope as a first approximation for E_a . Note that A obtained from Eq. (15) for the range of E_a values studied is close to the one obtained from Fig. 1 of 1.004.

To compare the accuracy of the different isoconversion methods, curves generated with Eq. (13) are used. The reaction parameters (see Table 1) are chosen to model often studied, well known reactions as well as hypothetical reactions which probe the limits of the range of parameters used. Examples from the first group are reaction B which models GP-zone formation in a hypothetical Al-based alloy and reaction E which models γ' formation in a Fe-1 mass%N alloy [14]. In Table 1 the average activation energies as obtained for $\alpha = 0.56$ and β between 1 and 100 K/min are presented. Inspection of Table 1 reveals that Kissinger's method is about one order of magnitude more accurate than Ozawa's method. Other authors came to similar conclusions [4,15]. It should however be noted that activation energies obtained with Ozawa's method can be corrected using a table of correction factors as a function of y (see Flynn [12]). Application of these tables to correct values in Table 1 (using y at T_p)

Table 1

E_a calculated by different methods normalised by the value of E_a that was used as input. Transformation curves were generated using Eq. (13). T_p is the temperature at maximum reaction rate for $\beta = 15$ K/min.

	Reaction Parameters				E_a (calculated)/ E_a		
	m	p	T_p in K	E_a in in kJ/mol	Ozawa Method	Kissinger Method	Eqs. ((14), (15))
Reaction A	1.4	1.4	610	48	1.134	0.984	0.999
Reaction B	1.4	1.4	350	58	1.042	0.997	1.000
Reaction C	3	3	700	96	1.061	0.995	1.000
Reaction D	1.4	1.4	1000	96	1.108	0.989	1.001
Reaction E	3	1	540	193	0.997	1.000	1.000
Reaction F	2	2	700	289	0.988	0.999	1.000

reproduces the correct activation energy within about 0.2%. As expected from the calculated A value of 0.998 for $s = 2$, Kissinger's method still underestimates E_a by a few tenths of a percent. The deviations are especially large for smaller y values. The new method (Eqs. (14) and (15)) is about 5 times more accurate than Kissinger's method, bringing the average accuracy of the determination of E_a to about 0.05%. The new method does not suffer from declining accuracy at decreasing y values.

For all methods considered the obtained values for E_a vary (slightly) with β , i.e. plots obtained on the basis of Eqs. (8), (10) and (14) are not perfectly straight. Further, for all methods considered the obtained values for E_a vary (slightly) with α . These variations result from the variations of the accuracy of the various approximations of $p(y)$ with y (see Fig. 2). However, the variations in E_a are smallest for the new method (Eqs. (14) and (15)) and they amount to about 0.1% in the range of α and β considered. The variations of E_a with α and β for the next best method (the Kissinger method) are about factor 5 larger.

Note that the new method is based on an approximation of $p(y)$ which is more accurate than the other methods considered (see Fig. 2). Hence, although Eq. (13) was used to generate some practical examples, the conclusions concerning the accuracy of the methods considered should hold irrespective of the transformation model $f(\alpha)$ used. Also, even though the accuracy will degrade somewhat when y is outside the range studied (15 to 60), still the new method should be the most accurate of the methods considered.

It might be worthwhile to stress again that this new method is designed to be used at constant values of α . Even though the stage at maximum rate of transformation is in good approximation at constant α (see refs. [1,16]) using this stage will inevitably introduce some inaccuracies which depend on the operating reaction model (see e.g. ref. [17]).

4. Conclusions

A new isoconversion method for obtaining activation energies from experiments performed at constant heating rate is presented. Similar to Ozawa and Kissinger's methods it is based on obtaining the slope of a logarithmic function containing the heating rate vs. $1/T$. The new method is more accurate than the other two.

Acknowledgments

This work is financed in part by the EC Human Capital and Mobility project. The author is grateful to Dr. A.-M. Zahra for stimulating discussions.

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