

Peak shape methods for general order thermoluminescence glow-peaks: A reappraisal

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Abstract

This paper presents a reappraisal of the well known peak shape expressions for calculating the activation energy E in a thermoluminescence (TL) glow-peak. This study leads to new insights as to the meaning of the coefficients used in the original equations. The reappraisal leads to new equations for the coefficients of the peak shape expressions which contain the general order parameter b , instead of the experimentally determined geometrical shape factor which is used in the original equations. Previously only the coefficients for first and second order kinetics were determined on the basis of existing theory and the coefficients for intermediate kinetics order were determined empirically using a linear interpolation–extrapolation method. In the present work the improved peak shape coefficients are evaluated in analytical form as a function of the kinetic order b , by using the general order kinetics expression for the TL intensity. The intrinsic errors in the newly derived expressions for E are evaluated and their relevance to experimental work is discussed in detail. A method for a further improvement of the accuracy of the peak shape methods is suggested.

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1. Introduction

The shape of a thermoluminescence (TL) glow-peak is the basis of important and convenient methods for calculating the trapping parameters of distinct energy levels within the crystal. These methods are based on measurements of a few points on the glow-peak, shown in Fig. 1. Early work on the development of such expressions concentrated on the development of convenient expressions for calculating the activation energy E of trapping levels [1–3]. The term peak shape methods is reserved in the TL literature for such methods, although there are other methods for finding E which are also based on the glow-peak

shape (i.e. curve fitting methods) [4,5]. The seminal work by Chen [6] is a reference point in the derivation of the peak shape methods. Chen [6] summarized all pre-existing methods and gave a detailed methodology for deriving the coefficients of the expressions for first and second order kinetics only.

The coefficients used in the peak shape methods for the intermediate kinetic orders were also evaluated by Chen [7] by (i) evaluating the coefficients for first order kinetics, (ii) calculating the coefficients for second order kinetics and (iii) using a linear interpolation–extrapolation method to obtain expressions for the intermediate kinetic orders as a function of the symmetry factor μ_g , which was found to be between 0.42 and 0.52 for first and second order kinetics respectively.

The expressions derived by Chen have been used extensively over the last 35 years. Although the intermediate

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glow-peaks derived using activation energies in the region 0.1–1.6 eV and frequency factors in the region between 10^5 and 10^{13} s^{-1} [6]. Their values can be estimated as a function of the kinetic order by producing synthetic glow-peaks using Eq. (2).

In order to derive the peak shape formulae using Eqs. (6)–(8), one has to evaluate the terms I_m/n_0 , n_m/n_0 and I_m/n_m from the analytical TL expressions.

3. Derivation of I_m/n_0 , n_m/n_0 and I_m/n_m

3.1. Derivation of I_m/n_0

From Eq. (2) considering $I(T_m) = I_m$ we obtain

$$\frac{I_m}{n_0} = n_0^{b-1} s' \exp\left(-\frac{E}{kT_m}\right) \left[1 + \frac{(b-1)s'n_0^{b-1}}{\beta} \int_{T_0}^{T_m} \exp\left(-\frac{E}{kT'}\right) dT'\right]^{-\frac{b}{b-1}}. \quad (10)$$

Using the exact condition for the TL peak maximum given by Eq. (3), we have after some algebra:

$$\frac{I_m}{n_0} = \left[n_0^{b-1} s' e^{-\frac{E}{kT}}\right]^{-\frac{1}{b-1}} \left[\frac{bkT_m^2}{\beta E}\right]^{-\frac{b}{b-1}}. \quad (11)$$

Using the approximate condition for the TL peak maximum given by Eq. (5), yields:

$$\frac{I_m}{n_0} = \left[\frac{\beta E}{kT_m^2} \frac{1}{1 + (b-1)\Delta_m}\right]^{-\frac{1}{b-1}} \left[\frac{bkT_m^2}{\beta E}\right]^{-\frac{b}{b-1}}, \quad (12)$$

and after some algebra one obtains

$$\frac{I_m}{n_0} = b^{-\frac{b}{b-1}} \left[\frac{1}{1 + (b-1)\Delta_m}\right]^{-\frac{1}{b-1}} \left[\frac{kT_m^2}{\beta E}\right]^{-1} \quad (13)$$

and finally,

$$\frac{I_m}{n_0} = b^{-1} \left[\frac{b}{1 + (b-1)\Delta_m}\right]^{-\frac{1}{b-1}} \left(\frac{\beta E}{kT_m^2}\right). \quad (14)$$

3.2. Derivation of n_m/n_0 and I_m/n_m

Solving Eq. (1) for n_m we have

$$-\int_{n_0}^{n_m} \frac{dn}{n^b} = \frac{s'}{\beta} \int_{T_0}^{T_m} \exp\left(-\frac{E}{kT'}\right) dT'. \quad (15)$$

From Eq. (15) after some algebra we obtain

$$n_m = n_0 \left[1 + \frac{(b-1)s'n_0^{b-1}}{\beta} \int_{T_0}^{T_m} \exp\left(-\frac{E}{kT'}\right) dT'\right]^{\frac{1}{1-b}}. \quad (16)$$

Using the exact condition for the maximum given by Eq. (3) one obtains for the term n_m/n_0 :

$$\frac{n_m}{n_0} = \left[\frac{bs'n_0^{b-1}kT_m^2}{\beta E} \exp\left(-\frac{E}{kT_m}\right)\right]^{-\frac{1}{b-1}}. \quad (17)$$

Using the approximate condition for the maximum given by Eq. (5) one obtains

$$\frac{n_m}{n_0} = \left[\frac{b}{1 + (b-1)\Delta_m}\right]^{-\frac{1}{b-1}}. \quad (18)$$

According to Halperin and Braner [3] the quantity n_m/n_0 , which represents the ratio of the high temperature half integral of a glow-peak over its total integral is the geometrical symmetry factor, let us say μ'_g of a glow-peak, which differs very slightly from the commonly used symmetry factor μ_g defined above. According to Halperin and Braner [3] glow-peaks with a symmetry factor around $(1 + \Delta_m)/e$ are of first order and glow-peaks with symmetry factor $(1 + \Delta_m)/2$ (see Eq. (18), for $b = 2$) are of second order. Obviously the symmetry factor of intermediate kinetic orders can be obtained from Eq. (18) for given values of b and Δ_m . For a given order of kinetics, the symmetry factor is not a fixed number but rather a very slowly varying quantity with the parameters (E, s) , i.e. a pseudo-constant.

Historically, the notation μ_g was used for the symmetry factor n_m/n_0 and not for the ratio δ/ω . However, in this paper we use the commonly used notation of $\mu_g = \delta/\omega$.

By dividing Eq. (14) over Eq. (18) one obtains

$$\frac{I_m}{n_m} = \frac{1}{b} \frac{\beta E}{kT_m^2}. \quad (19)$$

4. Methods based on the total width (ω)

Eq. (6) can be re-written as

$$\frac{I_m}{\beta n_0} = \frac{C_\omega}{\omega}. \quad (20)$$

Using Eq. (14) we obtain

$$\frac{I_m}{\beta n_0} = b^{-1} \left[\frac{b}{1 + (b-1)\Delta_m}\right]^{-\frac{1}{b-1}} \left(\frac{E}{kT_m^2}\right), \quad (21)$$

and finally combining Eqs. (20) and (21) we have

$$E = C_\omega \cdot b \left[\frac{b}{1 + (b-1)\Delta_m}\right]^{\frac{1}{b-1}} \cdot \frac{kT_m^2}{\omega}. \quad (22)$$

Since $(b-1)\Delta_m$ is less than unity, the following approximation, which introduces an error of less than 1%, can be used

$$(1 + (b-1)\Delta_m)^{\frac{1}{b-1}} \cong 1 + \frac{b-1}{b-1} \Delta_m = 1 + \Delta_m, \quad (23)$$

$$E = C_\omega \cdot b^{\frac{b}{b-1}} \left[\frac{1}{1 + \Delta_m}\right] \cdot \frac{kT_m^2}{\omega}, \quad (24)$$

or

$$E(1 + \Delta_m) = C_\omega \cdot b^{\frac{b}{b-1}} \cdot \frac{kT_m^2}{\omega}, \quad (25)$$

Table 1

The numerical values as a function of the kinetic order of the part $f_a(b)$ of the coefficients in peak shape methods expressions given by Eqs. (26), (28) and (34)

b	$f_\omega(b) = b^{b/(b-1)}$	$f_\delta(b) = b$	$f_\tau(b) = b(b^{1/(b-1)} - 1)$	$b_\tau(b) = \left(\frac{b^{1/(b-1)}}{b^{1/(b-1)} - 1}\right)$
1.0	2.7200	1.0	1.778	1.5820
1.1	2.8531	1.1	1.753	1.6275
1.2	2.9860	1.2	1.786	1.6719
1.3	3.1171	1.3	1.817	1.7154
1.4	3.2467	1.4	1.847	1.7581
1.5	3.3750	1.5	1.875	1.8000
1.6	3.5020	1.6	1.902	1.8412
1.7	3.6280	1.7	1.928	1.8817
1.8	3.7528	1.8	1.953	1.9218
1.9	3.8768	1.9	1.970	1.9600
2.0	4.0000	2.0	2.000	2.0000

and finally by solving for E ,

$$E = C_\omega \cdot b^{\frac{b}{b-1}} \cdot \frac{kT_m^2}{\omega} - 2kT_m. \quad (26)$$

The last equation shows that the coefficient of the term kT_m^2/ω consists of two terms, C_ω and $f_\omega(b) = b^{b/(b-1)}$. The quantity C_ω is the respective triangle assumption pseudo-constant which has to be evaluated by simulation, whereas the values of $f_\omega(b)$ depend on the kinetic order b and are listed in Table 1. This equation is of the same form as the well-known Chen expression, but it contains explicitly the kinetic order b and is derived here from analytical expressions, while previously it was obtained using a linear interpolation–extrapolation technique.

5. Methods based on the high temperature half-width (δ)

Eq. (7) can be re-written as

$$\frac{I_m}{\beta n_m} = \frac{C_\delta}{\delta} \quad (27)$$

and by taking into account Eq. (19) one obtains

$$E = C_\delta \cdot b \cdot \frac{kT_m^2}{\delta}. \quad (28)$$

The coefficient of the term kT_m^2/δ consists of two terms, C_δ and $f_\delta(b) = b$. The term C_δ is the respective triangle assumption pseudo-constant which has to be evaluated by simulation, whereas the values of $c_\delta(b)$ are fixed numbers for a given b . The evaluated values of $f_\delta(b)$ are listed in Table 1.

6. Methods based on the low temperature half-width (τ)

Eq. (8) can be re-written as

$$\frac{n_0}{n_m} - 1 = \frac{\tau}{C_\tau} \frac{I_m}{\beta n_m}. \quad (29)$$

Replacing the terms $I_m/\beta n_m$ and n_0/n_m from Eqs. (19) and (18) respectively, one obtains after some algebra

$$E_\tau = C_\tau \cdot b \cdot \left[\left(\frac{b}{1 + (b-1)A_m} \right)^{\frac{1}{b-1}} - 1 \right] \cdot \frac{kT_m^2}{\tau}. \quad (30)$$

Taking into account Eqs. (23), (30) becomes

$$E_\tau = C_\tau \cdot b \cdot \left[\left(\frac{b^{\frac{1}{b-1}}}{1 + A_m} \right) - 1 \right] \cdot \frac{kT_m^2}{\tau}. \quad (31)$$

By using the approximation below, which introduces an error of less than 1%.

$$\frac{b^{1/(b-1)}}{1 + A_m} \cong b^{1/(b-1)}(1 - A_m). \quad (32)$$

Eq. (31) after some manipulation gives:

$$E_\tau = C_\tau \cdot b \cdot \frac{kT_m^2}{\tau} \cdot \left(b^{\frac{1}{b-1}} - 1 \right) - C_\tau \cdot b \cdot \frac{kT_m^2}{\tau} \cdot \left(b^{\frac{1}{b-1}} - 1 \right) \cdot \frac{b^{\frac{1}{b-1}}}{b^{\frac{1}{b-1}} - 1} \cdot \frac{2kT_m}{E_\tau}. \quad (33)$$

The first term in this equation is the dominant term in determining the value of E_τ , while the second term represents a small correction. If the E_τ appearing in the second term of the right hand side of Eq. (33) is replaced by the first term of the right hand side of Eq. (33), then with a loss of less than 1% in accuracy, Eq. (33) can be written as

$$E_\tau = C_\tau \cdot b \cdot \left(b^{\frac{1}{b-1}} - 1 \right) \cdot \frac{kT_m^2}{\tau} - \left(\frac{b^{1/(b-1)}}{b^{1/(b-1)} - 1} \right) \cdot (2kT_m). \quad (34)$$

The first coefficient in the last equation consists of two terms, C_τ and $f_\tau(b) = b(b^{1/(b-1)} - 1)$. The term C_τ is the respective triangle assumption pseudo-constant which has to be evaluated by simulation, whereas the values of $f_\tau(b)$ are fixed numbers for a given b . The evaluated values of $f_\tau(b)$ are listed in Table 1. Similarly the second coefficient $b_\tau(b) = (b^{1/(b-1)})/(b^{1/(b-1)} - 1)$ is a fixed number for given kinetic order and its values are also listed in Table 1.

7. Numerical simulation

The numerical simulation of synthetic glow-peaks was performed by using very broad regions of the trapping parameters, in order to cover as many practical cases as possible. For the sake of simplicity the Rasheedy version [9] of the general order equation is used in which $n_0 = N$, one can use directly the value of s in s^{-1} . The activation energy region was varied between 0.7 eV and 2 eV in steps of 0.1 eV (14 values). The frequency factor was inserted in the form $s = \exp(A)$ with A ranging between 16 and 46 in steps of 1 (30 values), covering a region between 10^7 and $10^{20} s^{-1}$. From all possible glow-peaks corresponding to the (E, s) pairs in these wide regions of (E, s) , only those having their glow-peak maximum temperature in the practical range 200–800 K were considered.

The kinetic order was varied from 1.1 to 2 in steps of 0.1. The general order expression given by Eq. (2), does not hold for $b = 1$. However, it holds for values of b which are very

close to 1. It was found that for $b = 1.0005$ the general order expression given by Eq. (2) approximates the TL intensity for first order kinetics accurately, up to the fifth significant digit [10]. Therefore the value of $b = 1.0005$ was chosen to represent the case of first order kinetics through the general order kinetics expression. In total, 420 synthetic glow-peaks were produced for each one of the 11 kinetic orders. The mean values evaluated and listed in subsequent sections are the average of more than 400 values.

In order to ensure an accurate determination of the various parameters, a very small temperature step is necessary. In the present simulation the TL intensity was evaluated every 0.005 K; this corresponds to 1.2×10^5 points being evaluated for each glow-peak.

7.1. Evaluation of C_ω , C_δ and C_τ

From Eqs. (26), (28) and (34) it is seen that in order to evaluate the coefficients in front of the peak shape methods, the values of the pseudo-constants C_ω , C_δ and C_τ must be found.

For the simulation of synthetic glow-peaks the exponential integral appearing in Eq. (2) was not approximated by the usual asymptotic series, since the software used contains this integral as a built-in function.

The values of the pseudo-constants C_ω , C_δ obtained from the simulation are listed in Table 2, whereas Fig. 2 shows their behavior as a function of the symmetry factor. The presentation of these pseudo-constants as a function of the symmetry factor is preferable to using the kinetic order b , since the symmetry factor is an experimentally measured quantity.

During the simulations described in this paper it is possible to perform two tests. The first test concerns Eqs. (22), (28) and (30). This test evaluates the output values of activation energy using the values of the pseudo-constants C_ω , C_δ , C_τ and T_m evaluated within the same simulation. The aim here is to test the accuracy of the above equations. The results showed that the output activation energies values coincide with the input E values, ensuring the correctness of these equations.

The second test concerns Eqs. (22) and (30). For the derivation of these Equations two approximations were used,

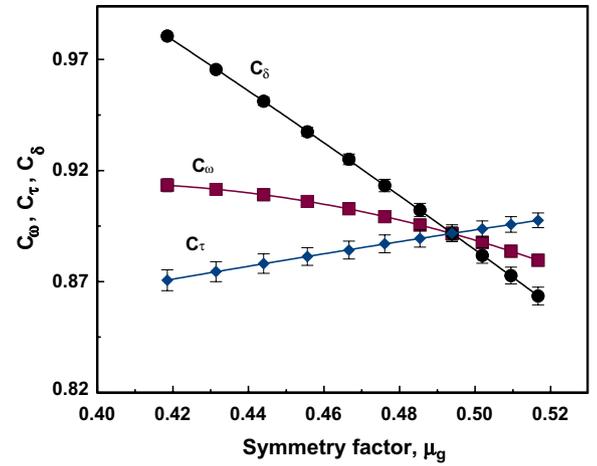


Fig. 2. The triangle assumption pseudo-constants C_ω , C_δ and C_τ as a function of the symmetry factor.

given by Eqs. (23) and (32). The second test, therefore, evaluates output values of the activation energies using the individual values of the pseudo-constants C_ω and C_τ evaluated during the simulation, aiming to estimate the influence of these approximations. The agreement between the input and output E values is estimated by the error $\frac{E_{in}-E_{out}}{E_{in}} \times 100$, which is shown in Fig. 3. The left-hand side figure concerns the ω expression described by Eq. (22) and the right-hand side of the figure concerns the τ expression from Eq. (30). Note that each one of the figures contains 3200 (E, s) pairs. As it is seen from the figures, in the majority of cases the errors are less than 0.5% for the case of ω and less than 0.4% for the case of τ . These small percent errors represent the influence of the approximations given by Eqs. (23) and (32).

7.2. Evaluation of c_ω , c_δ , c_τ and b_x

The general form of the peak shape methods given by Chen [7,5] is

$$E_x = c_x \cdot \frac{kT_m^2}{\alpha} - b_x \cdot (2kT_m), \quad (35)$$

where the index α stands for ω , δ and τ .

Table 2

The values of the triangle assumption pseudo-constants C_ω , C_δ and C_τ resulting as the mean values of all (E, s) pairs from the simulations along with the mean values of symmetry factor, μ_g , as a function of the kinetic order

b	μ_g	C_ω	C_δ	C_τ
1.0	0.4185 ± 0.0034	0.9134 ± 0.0029	0.9806 ± 0.001	0.8706 ± 0.0047
1.1	0.43139 ± 0.0036	0.9115 ± 0.0025	0.9655 ± 0.001	0.8745 ± 0.0045
1.2	0.4440 ± 0.0036	0.9091 ± 0.0020	0.9512 ± 0.0018	0.8781 ± 0.0044
1.3	0.4556 ± 0.0037	0.9061 ± 0.0017	0.9374 ± 0.002	0.8813 ± 0.004
1.4	0.4666 ± 0.0037	0.9028 ± 0.0014	0.9251 ± 0.0024	0.8842 ± 0.004
1.5	0.4761 ± 0.0038	0.8992 ± 0.0009	0.9133 ± 0.0028	0.8870 ± 0.004
1.6	0.4854 ± 0.0037	0.8955 ± 0.0006	0.9022 ± 0.003	0.8894 ± 0.0039
1.7	0.4939 ± 0.0040	0.8916 ± 0.0003	0.8916 ± 0.003	0.8918 ± 0.0038
1.8	0.5019 ± 0.0037	0.8877 ± 0.0002	0.8818 ± 0.0035	0.8937 ± 0.0036
1.9	0.5094 ± 0.0037	0.8837 ± 0.0005	0.8724 ± 0.0038	0.8957 ± 0.0035
2.0	0.5167 ± 0.0030	0.8796 ± 0.0008	0.8635 ± 0.004	0.8946 ± 0.0033

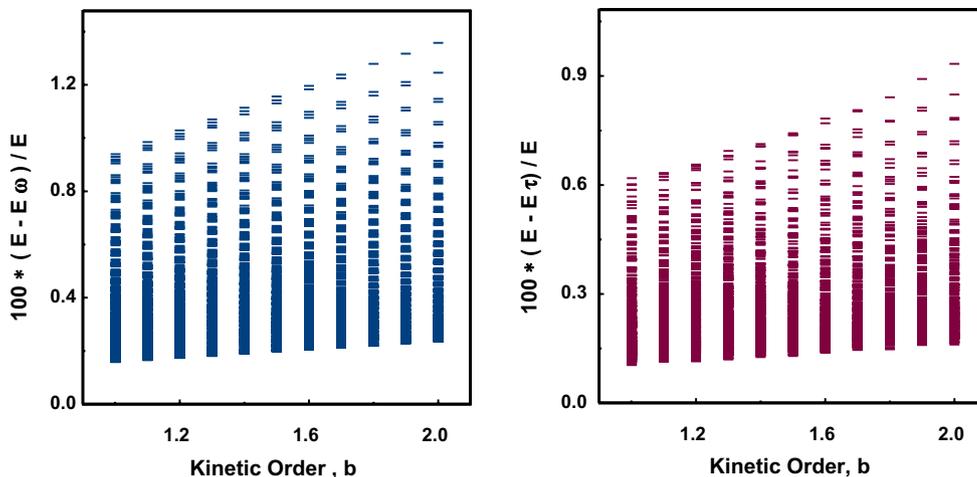


Fig. 3. The error $\frac{E-E_{\omega,\tau}}{E} \times 100$ of activation energies E_{ω} and E_{τ} as a function of the kinetic order. E represents the input values whereas the $E_{\omega,\tau}$ values were evaluated through Eqs. (22) and (30), respectively.

Chen [6,7] evaluated the coefficients c_x and b_x for first and second order kinetics and used an interpolation–extrapolation method to evaluate the values for intermediate order kinetics. His final expressions are

$$c_{\omega} = 2.52 + 10.2(\mu_g - 0.42) \quad b_{\omega} = 1, \tag{36}$$

$$c_{\delta} = 0.976 + 7.3(\mu_g - 0.42) \quad b_{\delta} = 0, \tag{37}$$

$$c_{\tau} = 1.51 + 3(\mu_g - 0.42) \quad b_{\tau} = 1.58 + 4.2(\mu_g - 0.42). \tag{38}$$

Using the values of the pseudo-constants C_{ω} , C_{δ} and C_{τ} , which were evaluated in the simulation and are listed in Table 2, the new values for the coefficients c_x and b_x are evaluated through Eqs. (26), (28) and (34). Their values as a function of kinetic order are listed in Table 3.

The new values of c_x and b_x are compared with the original expressions of Chen in Figs. 4–7. In these figures it is seen that the new values of the coefficients evaluated in the present work are slightly non-linear as a function of the symmetry factor. On the other hand the values of the coefficients derived by Chen lie on a straight line which is very close to the non-linearity obtained in the present work. The differences are due to the interpolation–extrapolation method used during their evaluation. The agreement in

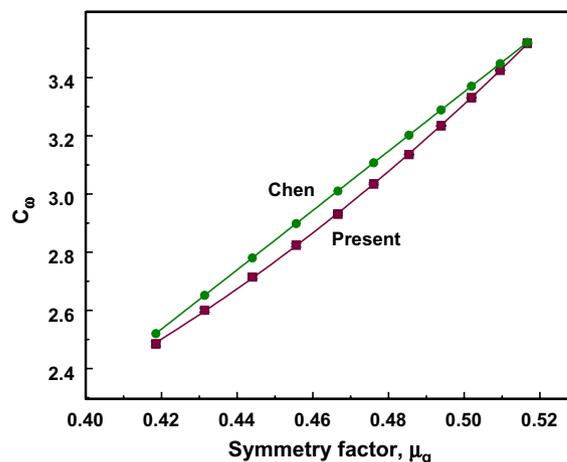


Fig. 4. The net values of the peak shape methods coefficients c_{ω} of the ω based method, as they were evaluated by Chen and in the present work, as a function of the symmetry factor.

Table 3
The net values of the peak shape methods coefficients as a function of the kinetic order

b	c_{ω}	c_{δ}	c_{τ}	b_{τ}
1.0	2.4845 ± 0.0079	0.9806 ± 0.0011	1.4955 ± 0.0081	1.5820
1.1	2.6006 ± 0.0071	1.0620 ± 0.0011	1.5330 ± 0.0079	1.6275
1.2	2.7146 ± 0.0060	1.1414 ± 0.0022	1.5683 ± 0.0079	1.6719
1.3	2.8244 ± 0.0053	1.2186 ± 0.0026	1.6013 ± 0.0073	1.7154
1.4	2.9311 ± 0.0045	1.2951 ± 0.0034	1.6329 ± 0.0074	1.7581
1.5	3.0348 ± 0.0030	1.3699 ± 0.0042	1.6631 ± 0.0075	1.8000
1.6	3.1360 ± 0.0021	1.4435 ± 0.0048	1.6916 ± 0.0074	1.8412
1.7	3.2347 ± 0.0009	1.5157 ± 0.0051	1.7194 ± 0.0073	1.8817
1.8	3.3314 ± 0.0006	1.5872 ± 0.0063	1.7453 ± 0.0070	1.9218
1.9	3.4259 ± 0.0019	1.6581 ± 0.0072	1.7645 ± 0.0069	1.9600
2.0	3.5184 ± 0.0032	1.7387 ± 0.0080	1.7952 ± 0.0066	2.0000

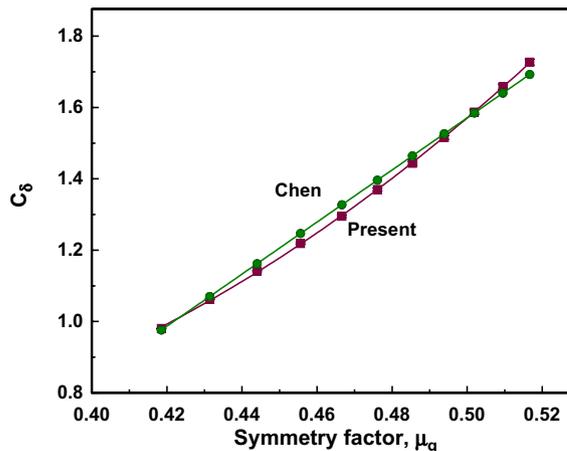


Fig. 5. The net values of the peak shape methods coefficients c_{δ} of the δ based method, as they were evaluated by Chen and in the present work, as a function of the symmetry factor.

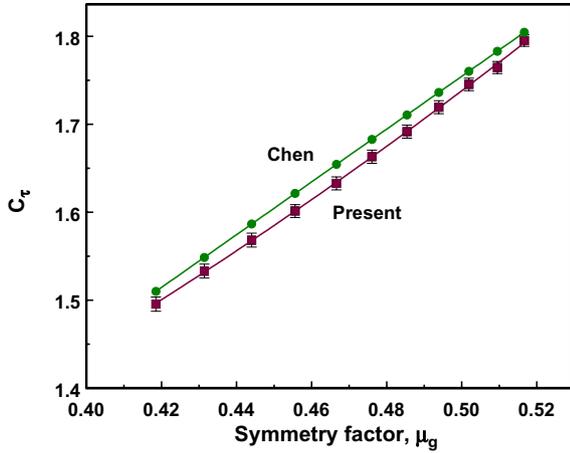


Fig. 6. The net values of the peak shape methods coefficients c_τ of the τ based method, as they were evaluated by Chen and in the present work, as a function of the symmetry factor.

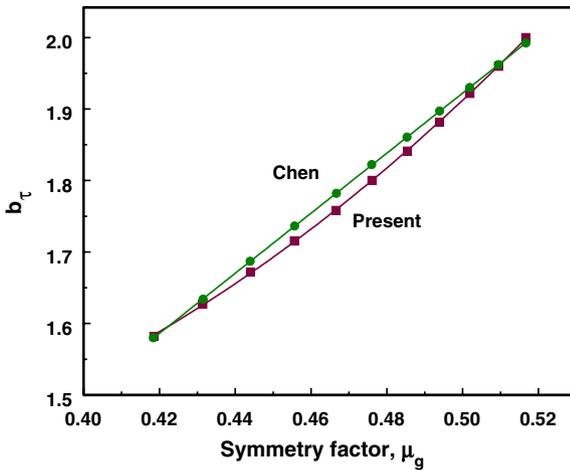


Fig. 7. The net values of the peak shape methods coefficients b_τ of the τ based method, as they were evaluated by Chen and in the present work, as a function of the symmetry factor.

these figures explains why the expressions developed by Chen give very accurate values for the trapping parameters.

7.3. Comparison of the newly obtained expressions with those of Chen

The application of the general form Eq. (35) is now possible using the c_a , b_a values shown in Table 3 for each kinetic order b . Under this situation a comparison is possible of the resulting E values from Eq. (35) using both the newly obtained values of c_a , b_a and those of Chen derived from Eqs. (36)–(38) using the symmetry factors of Table 2.

The comparison is performed by simulating synthetic glow-peaks using the same (E, s) regions described above.

Fig. 8 shows the results concerning the ω method. The horizontal line passes through an average value of the results in the present study. In order to understand this behavior one has to look at Fig. 4. The coefficient c_ω of

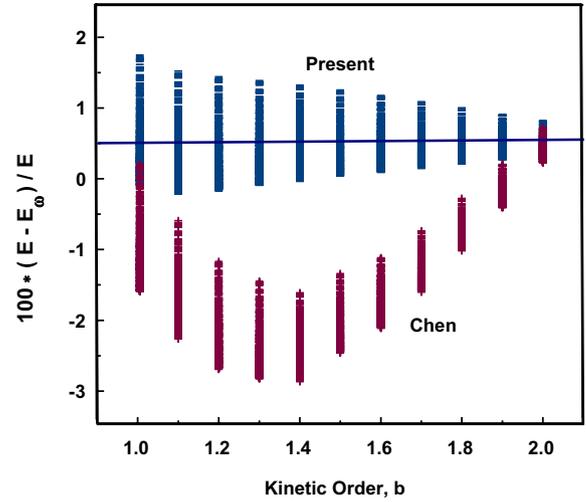


Fig. 8. The error $\frac{E-E_\omega}{E} \times 100$ of the activation energies E_ω , as a function of the kinetic order. E are the input values, whereas the E_ω values were evaluated through Eq. (35) using the Chen coefficients and the newly obtained coefficients, which are listed in Table 3. The horizontal line passes symmetrically through the results of the present work. At each kinetic order the errors values of 370 simulated (E, s) pairs are plotted.

the present study follows the open curve as a function of the symmetry factor and give results passing through the average line, whereas the Chen coefficients are a strictly linear function of the symmetry factor and follow a parabolic shape.

Fig. 9 shows the results concerning the δ method. The behavior is very similar to the previous case.

Fig. 10 shows the results concerning the τ method. The horizontal lines at -0.5% to 0.5% define a region where the two sets of coefficients give the same accuracy. Looking at Fig. 6 one can see that both sets of coefficients follow a

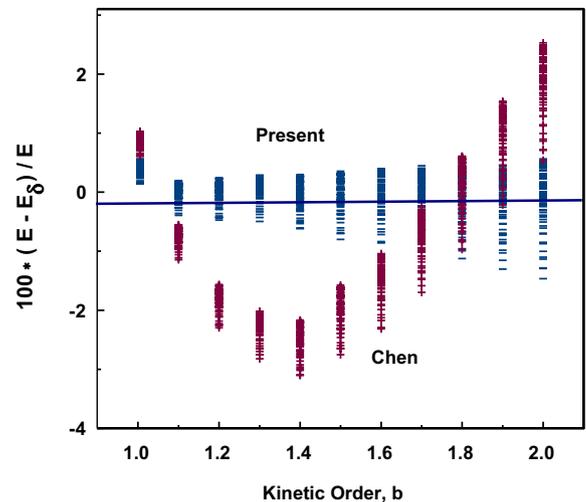


Fig. 9. The error $\frac{E-E_\delta}{E} \times 100$ of activation energies E_δ as a function of the kinetic order. The E are the input values, whereas the E_δ values were evaluated through Eq. (35) using the Chen coefficients and the newly obtained coefficients, which are listed in Table 3. The horizontal line passes symmetrically through the results of the present work. At each kinetic order the errors values of 370 simulated (E, s) pairs are plotted.

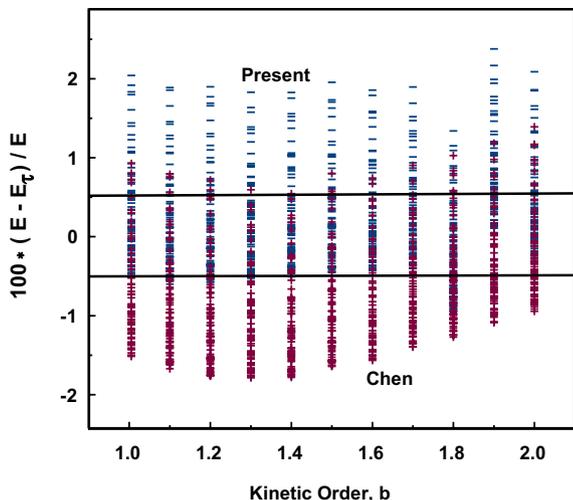


Fig. 10. The error $\frac{E-E_t}{E} \times 100$ of activation energies E_t as a function of the kinetic order. E are the input values, whereas the E_t values were evaluated through Eq. (35) using the Chen coefficients and the newly obtained coefficients, which are listed in Table 3. The horizontal lines pass through the $\pm 0.5\%$ errors containing values of both sets of coefficients. At each kinetic order the errors values of 370 simulated (E, s) pairs are plotted.

parallel behavior, which is reflected exactly in the behavior of Fig. 10. The reason is that except in the central common region, the accuracy of the Chen coefficients is below the demarcation line of -0.5% and the accuracy of the newly derived coefficients is above the demarcation line of $+0.5\%$.

7.4. Accuracy of the peak shape methods

The peak shape expressions found in this paper estimate the activation energy E with an accuracy better than 0.5% in the majority of (E, s) pairs. However, this accuracy is obtained using a simulation where the temperature is evaluated with an accuracy of 0.005 K. The situation, however, is very different in experimental situations, where the experimental accuracy in the temperature measurement may be larger than 1 K.

The experimental quantities which have to be experimentally measured in order to evaluate the activation energy E are T_m , T_1 , and T_2 . The errors of these quantities are propagated to the errors of E through Eq. (35).

The total probable error of a function depended upon x_i quantities, $\Phi = f(x_i)$ is [11]:

$$\Delta\Phi = \pm \left[\left(\frac{\partial f}{\partial x_1} \cdot \delta x_1 \right)^2 + \left(\frac{\partial f}{\partial x_2} \cdot \delta x_2 \right)^2 + \dots + \left(\frac{\partial f}{\partial x_n} \cdot \delta x_n \right)^2 \right]^{\frac{1}{2}}. \quad (39)$$

Then the relative error will be:

$$\sigma = \pm \frac{\Delta\Phi}{\Phi}. \quad (40)$$

Applying the error propagation formula, Eq. (39), the total errors for ω , δ , τ and μ_g will be, respectively,

$$\Delta\omega = \pm \left[(\Delta T_2)^2 + (-\Delta T_1)^2 \right]^{\frac{1}{2}}, \quad (41)$$

$$\Delta\delta = \pm \left[(\Delta T_2)^2 + (-\Delta T_m)^2 \right]^{\frac{1}{2}}, \quad (42)$$

$$\Delta\tau = \pm \left[(\Delta T_m)^2 + (-\Delta T_1)^2 \right]^{\frac{1}{2}}, \quad (43)$$

$$\Delta\mu_g = \pm \frac{\delta}{\omega} \left[\left(\frac{\Delta\delta}{\delta} \right)^2 + \left(-\frac{\Delta\omega}{\omega} \right)^2 \right]^{\frac{1}{2}}. \quad (44)$$

On the other hand the total error of E_a derived by applying Eq. (39) to Eq. (35) is,

$$\Delta E_a = \pm E_a \left[\left((1 - b_a \Delta_m) \cdot \frac{\Delta c_a}{c_a} \right)^2 + \left(\frac{\Delta T_m}{2T_m} \right)^2 + \left((1 - 2b_a \Delta_m) \cdot \frac{\Delta\alpha}{\alpha} \right)^2 + (\Delta_m \Delta b_a)^2 \right]^{\frac{1}{2}}, \quad (45)$$

where $\Delta_m = 2k T_m / E_a$. The coefficient parameters c_a and b_a are included, since they are composite parameters consisting of fixed and dependent quantities. The coefficients c_a in Eq. (35) consist of two terms, the term C_a from the triangle approximation, whose error is estimated from the simulation and of the term $f_a(b)$, which is a function of the kinetic order. The error of c_a is therefore $\Delta c_a = f_a(b) \Delta \varpi C_a$. The values of ΔC_a for ω , δ and τ are listed in Table 2. In the case of the simulations the error Δb_a is zero, since b_a depends only on b and therefore it is a fixed number for a given order of kinetics. However, this term is included because in Chen's τ method the b_τ is expressed as function of the symmetry factor, which introduces an additional source of error.

It is usually said [5] that the τ based methods yield more accurate results than the other peak shape methods. By examining Eq. (45), a first estimate about the accuracy of each of the ω , δ and τ methods can be obtained. The difference in the accuracy of the 3 peak shape methods comes from the first and third terms of Eq. (45). The most accurate method should be the one for which these two terms are minimized. In the case of the δ method, which does not contain the term b_a , ($b_a = 0$), these terms have their largest value and therefore this method is expected to be less accurate than the other two expressions. On the other hand $b_a = 1$ for the ω method and greater than 1 for the τ method. Therefore, the two terms are minimized for the τ method which is expected to be the most accurate. Summarizing, the relative accuracy of the three methods is as follows:

$$\Delta E_\tau < \Delta E_\omega < \Delta E_\delta. \quad (46)$$

However, this is an ideal case and holds only when, additionally, $\Delta\tau/\tau < \Delta\omega/\omega < \Delta\delta/\delta$. Furthermore, the experimental glow-peaks are not usually clean peaks. In most cases satellites may be present, which can easily be thermally pre-cleaned at the lower part of the peak and not at the high temperature side. The order of accuracies under these circumstances is inverted.

During practical applications the coefficients of the peak shape methods are considered to be constants which do not affect the error evaluation of the activation energy. However, as was shown in the present work, these coefficients are not constants but rather pseudo-constants which carry their own intrinsic errors. Therefore, any family of peak shape methods will possess an intrinsic error coming from the accuracy of its coefficients and this error is in addition to any errors deriving from the experimental accuracy of the variables T_m , T_1 and T_2 appearing in these expressions. In order to explore this intrinsic error let us assume that the errors in T_m , ω , τ and δ , i.e. the quantities ΔT_m and Δa are zero. In this case Eq. (45) gives:

$$\frac{\Delta E_a}{E_a} = \pm(1 - b_a A_m) \cdot \frac{\Delta c_a}{c_a}. \quad (47)$$

The relative error in Eq. (47) is an intrinsic minimum limit which depends upon the error in the triangle assumption pseudo-constants C_a , (i.e. C_ω , C_δ and C_τ), the values of which are evaluated from the simulation with Eqs. (6)–(8). It must also be noted that this limit holds also in the case where the coefficients c_a are expressed as a function of μ_g . The reason is that the symmetry factor for a given order of kinetics is not a fixed number but rather is also a pseudo-constant as seen from Eq. (18).

The general behavior of the error in Eq. (45) is simulated for ΔE_ω , ΔE_δ and ΔE_τ . In order to simplify the simulation it is assumed that: (i) $\Delta T_1 = \Delta T_2 = \Delta T_m$ and (ii) the error ΔC_x of all C_x is taken equal to a typical value of 0.4% obtained during the simulations.

The results are shown in Fig. 11. The straight lines are the obvious results obtained when the first term of Eq. (45) (or Eq. (47)), which represents the limit discussed above, is omitted by setting $\Delta C_x = 0$. However, taking into account the first term of Eq. (45) with a typical value of $\Delta C_x = 0.4\%$, then Fig. 11 shows that the error in E can not be less than 0.35–0.4%, up to $\Delta T = 0.1$ K.

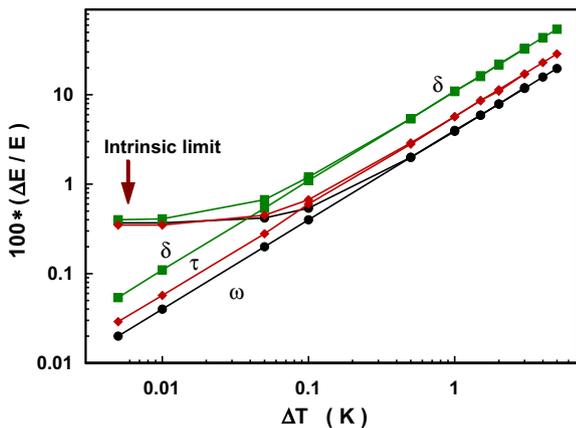


Fig. 11. The straight lines correspond to the errors obtained from Eq. (45) when the first term, which represents the intrinsic error limit (also Eq. (47)), is omitted, i.e. $\Delta C_x = 0$. The arrow shows the intrinsic error limit of 0.35–0.4%, obtained, when the first term of Eq. (45) is taken into account considering $\Delta C_x = 0.4\%$.

Another observation is that the accuracy of ω method is better than that of the τ method above 0.1 K. This can be understood from the first assumption $\Delta T_1 = \Delta T_2 = \Delta T_m$ stated above. Since ω is almost double the value of τ , the value of $\Delta\omega/\omega$ is much lower than the value of $\Delta\tau/\tau$ and therefore the error in E_ω will be lower.

If one wants to evaluate the error in E when using the Chen coefficients, one must take into account that in this case the terms c_a , b_a are expressed as a function of μ_g , as seen in Eqs. (36)–(38). By applying the error propagation formula given by Eq. (39) it is found that $\Delta c_\omega = 10.2 \Delta\mu_g$, $\Delta c_\delta = 7.3 \Delta\mu_g$, $\Delta c_\tau = 3 \Delta\mu_g$ and $\Delta b_\tau = 4.2 (2k T_m) \Delta\mu_g$.

The most practical result, however, which emerges from the above error analysis is that the errors in E increase linearly with ΔT . Therefore, the experimental error in temperature must be lowered as much as possible. In practice it is rather easy to achieve a very low error in T , although this is not usually done during experimental work. First of all one has to achieve a very good thermal contact between the sample and the heating element and to use a low rate of heating, not greater than 1 K/s, in order to avoid possible temperature lag effects. The crucial point to consider is the sampling time in photon counting systems, which must be set as short as possible. For example in the RisøTL/OSL reader having an Analog to Digital Converter (ADC) of 2^{13} channels, a TL readout up to 400 °C with 1 K/s gives a temperature increment, ΔT of 0.045 K.

As was discussed above, the intrinsic error limit of 0.35–0.4% in E is set by the accuracy of the triangle assumption pseudo-constants C_ω , C_δ and C_τ which are evaluated by the simulation. The intrinsic error limit under discussion shown in Fig. 11 is evaluated by considering an average relative error of 0.4%. Although this error is very low when one considers the very broad (E, s) regions used, it can be lowered even more as follows.

Let us assume for example that one applies one of the peak shape methods using the newly obtained coefficients and evaluates the trapping parameters $E \pm \Delta E$ and $s \pm \Delta s$. Even if one has extremely low errors in T , one can not achieve accuracy better than the intrinsic error limit of 0.35–0.4% evaluated above. It is very easy, however, to decrease this error limit by re-evaluating the triangle assumption pseudo-constants in an (E, s) region restricted within the limits $E \pm \Delta E$, $s \pm \Delta s$ obtained. In fact, since the triangle assumption pseudo-constants vary extremely slowly, a single simulation using the experimentally obtained E and s values, is enough to obtain a new highly improved pseudo-constant value C_a . Then using Eq. (47) one can find that the intrinsic error limit of 0.35–4% could be decreased by at least a factor of five, with a corresponding increase in the accuracy of E .

The above error evaluation approach is necessary if one wishes to gain all the benefits of the peak shape methods when they are applied to experimental results. However, there is another field of research where the above approach should be very useful. This is the field of simulations involving TL models and TL effects (i.e. super-linearity,

pre-dose effect, etc.) by the numerical solution of the differential equations governing the TL process [5,10]. During such simulations the quality of the resulting TL glow-peak can be continuously tested using the peak shape methods. It must be noticed, however, that the derivation of the peak shape methods is based on the Randall–Wilkins [12] and Garlick–Gibson [13] kinetic models, for which the quasi-equilibrium condition is satisfied. In the case of general order kinetics of May and Partridge [8] the respective equation can not be derived from the original set of simultaneous equations describing the TL process. However, since the general order equation coincides with second order for $b=2$ and approximates first order for $b \sim 1.0005$, it is assumed that it is an equation for which the quasi-equilibrium condition is satisfied too. Therefore, these models are expected to describe accurately only those simulated glow-peaks for which the quasi-equilibrium condition is satisfied. In cases deviating from the quasi-equilibrium conditions, one might expect that the output activation energy values E evaluated by the peak shape methods will deviate from the input E values used in the models, in a manner depending upon the degree of satisfaction of the quasi-equilibrium conditions.

The present work indicates another very effective way of testing glow-peaks resulting from the numerical solution of the differential equations, by evaluating the equivalent analytical expressions and making a direct glow-peak comparison. This can be done as follows. Once the glow-peak is derived during the simulations, its symmetry factor n_m/n_0 is evaluated as the ratio of the high temperature half glow-peak over the total integral of the glow-peak. Then using Eq. (18) the corresponding kinetic order b is iteratively evaluated, to an accuracy depending upon the number of terms in the asymptotic series and the analytical glow-peak is evaluated using Eq. (2).

A final reason why the above suggested approach is ideal for comparing glow-peaks derived from the analytical TL expressions with those derived from the numerical solution of the differential equations, is that in the simulations one can control the temperature to any desired accuracy.

8. Conclusions

The peak shape methods for general order kinetics are reappraised in detail. The peak shape method coefficients are given a theoretical foundation on the basis of analytical expressions as a function of the kinetic order b . Furthermore the very good accuracy of the approximate Chen coefficients is easily understood by inspection of Figs. 4–7.

A numerical simulation of synthetic glow-peaks was performed in an activation energy region between 0.7 eV and 2 eV in steps of 0.1 eV (14 values), a frequency factor region between 10^7 and 10^{20} s^{-1} (30 values) and kinetics order between 1 and 2 (11 values). The newly derived peak shape method coefficients contain the general order parameter b , instead of the experimentally determined geometrical shape factor which is used in the original equations.

The errors of the peak shape methods are studied in detail and an error evaluation procedure is described, which allows one to gain all the benefits of the peak shape methods when they are applied to experimental results. A method for further improvement of the accuracy of the evaluation of the activation energy is also suggested.

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