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Calculation of parameters from glow curves for the mixed-order kinetics

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Abstract

A new method for the calculation of parameters is proposed. The method is based on determination of the glow curve maximum and effective values of the half-width and part of the half-width on the higher temperature side. A relation between the symmetry factor as a function of the corresponding constant $\alpha = n_0/(h + n_0)$ and the correction factor Δ is obtained. An approximate symmetry factor function is derived, which enables analytical calculation of the parameters: activation energy E , constant α , and pre-exponential factor $s^{(h)}$. An iterative procedure is developed for more precise calculation of these parameters. The new method is checked for some characteristic values of the parameters. The connection between the models of general and mixed-order kinetics has been described theoretically.

1. Introduction

The general order kinetics does not cover all possible cases of TL kinetics found experimentally. The conditions for general model kinetics are difficult to reveal in practice because there are no actual materials for which one could accurately claim that there is only one type of traps and recombination centres. Most real materials contain additional deep traps so that the thermal stability of trapped charge is greater than that for the TL signal being monitored [1, 2].

$$I = -\frac{dn}{dT} = \frac{s'}{R}n(n+h)\exp\left(-\frac{E}{kT}\right) \quad (1)$$

where at a time t (s), I ($\text{cm}^{-3} \text{s}^{-1}$) is the TL intensity, n (cm^{-3}) is the electron trap concentration, h (cm^{-3}) is the initial electron inactive trap concentration, s' ($\text{cm}^3 \text{s}^{-1}$) is the pre-exponential factor, T (K) is the material temperature, R (K s^{-1}) is the heating rate, E (eV) is the energy position of a single active trap, and k (eV K^{-1}) is the Boltzmann constant. As shown for the

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second order kinetics [3], the calculation of the term h that is multiplied by s' is impossible. Therefore, it is more convenient to introduce, instead of the pre-exponential factor s' , a new pre-exponential factor $s^{(h)} = s^{(h)} = s'h$.

The electron trap concentration and the TL intensity for glow peaks of mixed order kinetics are given by relations in general forms:

$$n = \frac{h\alpha}{\exp\left[\frac{s^{(h)}}{R} \int_{T_0}^T \exp\left(-\frac{E}{kT'}\right) dT'\right] - \alpha} \quad (2)$$

and

$$I = \frac{s^{(h)}h\alpha \exp\left[\frac{s^{(h)}}{R} \int_{T_0}^T \exp\left(-\frac{E}{kT'}\right) dT'\right]}{\left\{\exp\left[\frac{s^{(h)}}{R} \int_{T_0}^T \exp\left(-\frac{E}{kT'}\right) dT'\right] - \alpha\right\}^2} \exp\left(-\frac{E}{kT}\right) \quad (3)$$

where n_0 (cm^{-3}) is the initial electron active trap concentration and $\alpha = n_0/(h+n_0)$ is constant.

In order to simplify the presentation of equation (3), we introduce the replacement

$$IT = \frac{s^{(h)}}{R} \int_0^T \exp\left(-\frac{E}{kT'}\right) dT' \quad (4)$$

then expression (3) can be presented in the following form:

$$I = \frac{s^{(h)}h\alpha \exp(IT)}{[\exp(IT) - \alpha]^2} \exp\left(-\frac{E}{kT}\right). \quad (5)$$

2. Calculation of the pre-exponential factor $s^{(h)}$

The validity of the parameter for the maximum values of the curve can be obtained after calculating the first derivate of the function and then putting it equal to zero:

$$\begin{aligned} s^{(h)}h\alpha[\exp(IT_m) - \alpha]^2 \exp(IT_m) \exp\left(-\frac{E}{kT_m}\right) \left[\frac{s^{(h)}}{R} \exp\left(-\frac{E}{kT_m}\right) + \frac{E}{kT_m^2}\right] \\ = \frac{2h\alpha}{R} \left[s^{(h)} \exp(IT_m) \exp\left(-\frac{E}{kT_m}\right)\right]^2 [\exp(IT_m) - \alpha]. \end{aligned} \quad (6)$$

After some mathematics, one obtains an equation which can be used for the calculation of the parameters of TL processes according to the model of mixed-order kinetics. Such an expression has already been given in [4]:

$$[\exp(IT_m) - \alpha] \left[\frac{s^{(h)}}{R} \exp\left(-\frac{E}{kT_m}\right) + \frac{E}{kT_m^2}\right] - \frac{2s^{(h)}}{R} \exp(IT_m) \exp\left(-\frac{E}{kT_m}\right) = 0 \quad (7)$$

if we put $T = T_m$ in equation (3), we get

$$I_m = \frac{s^{(h)}h\alpha \exp(IT_m)}{[\exp(IT_m) - \alpha]^2} \exp\left(-\frac{E}{kT_m}\right). \quad (8)$$

From this equation and equation (7) after some mathematics, we obtain the following expression:

$$\frac{s^{(h)}}{R} \exp\left(-\frac{E}{kT_m}\right) + \frac{E}{kT_m^2} = \frac{2I_m}{Rh\alpha} [\exp(IT_m) - \alpha]. \quad (9)$$

For $T = T_m$ equation (2) can be written as follows:

$$n_m = \frac{h\alpha}{\exp(IT_m) - \alpha}. \quad (10)$$

After substituting this expression in equation (9), we get

$$\frac{s^{(h)}}{R} \exp\left(-\frac{E}{kT_m}\right) + \frac{E}{kT_m^2} = \frac{2I_m}{Rn_m}. \quad (11)$$

Now, one can introduce the parameter δ_{eff} [5], which can be directly obtained from the experimental curve. This curve has already been given earlier:

$$\delta_{\text{eff}} = \int_{T_m}^{\infty} i \, dt = \frac{Rn_m}{I_m}. \quad (12)$$

After replacing the parameter δ_{eff} , in expression (11) one obtains

$$s^{(h)} = R \left(\frac{2}{\delta_{\text{eff}}} - \frac{E}{kT_m^2} \right) \exp\left(\frac{E}{kT_m}\right). \quad (13)$$

This is a very important expression since it allows an analytical and precise calculation of the pre-exponential factor when the activation energy E is known as well as geometrical parameters, which can be read off or determined from the experimental curve.

3. Calculation of the trap activation energy

After some rearrangements in the previous equations, one can obtain an expression for calculation of the activation energy of activated traps. First, we take an expression to calculate the value of the symmetry factor [6], which is defined as a ratio of trapped charge carriers in active traps at maximum n_m determined by equation (10) to the initial concentration n_0 :

$$\mu_s = \frac{n_m}{n_0} = \frac{h\alpha / (\exp(IT_m) - \alpha)}{h\alpha / (1 - \alpha)} = \frac{1 - \alpha}{\exp(IT_m) - \alpha}. \quad (14)$$

When this equation is rearranged and using equation (7), we get

$$\frac{s^{(h)}}{R} \exp\left(-\frac{E}{kT_m}\right) [\alpha(1 - 2\mu_s) - 1] + (1 - \alpha) \frac{E}{kT_m^2} = 0. \quad (15)$$

From this equation and equation (13) we get the following expression:

$$(2kT_m^2 - E\delta_{\text{eff}})[\alpha(1 - 2\mu_s) - 1] = (1 - \alpha)E\delta_{\text{eff}}. \quad (16)$$

After some rearrangements, we get an expression for the activation energy of a trap:

$$E = \frac{1 - \alpha(1 - 2\mu_s)}{1 - \alpha(1 - \mu_s)} \frac{kT_m^2}{\delta_{\text{eff}}} = C \frac{kT_m^2}{\delta_{\text{eff}}}. \quad (17)$$

We can see that the expression for the activation energy of a trap has the same form as the expression for the activation energy calculation but according to the model of general order kinetics [5]. This means that this type of relation can be used for activation energy calculation in both cases. In our case the coefficient C is a function of the symmetry factor μ_s since the factor α depends on μ_s .

4. Calculation of the order of kinetics

The symmetry factor for TL glow curves is obtained by using the model of general order kinetics. For the limiting values of this model one obtains models of the first and second order kinetics. In the region between these two models one can assume that the orders of kinetics are between 1 and 2. This means that the corresponding symmetry factor, obtained by using the model of mixed order kinetics, can be attributed to the corresponding order of kinetics.

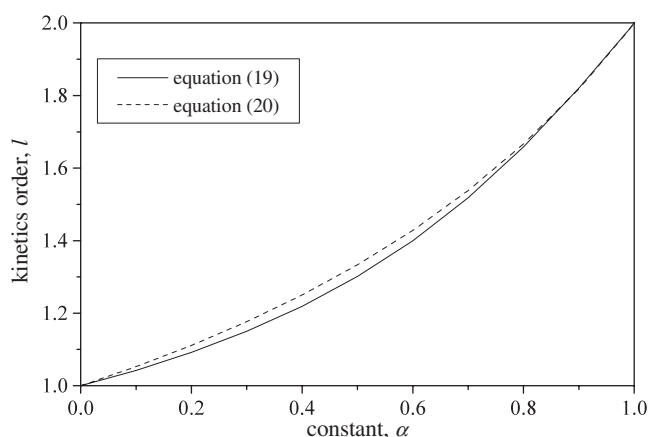


Figure 1. Order of kinetic versus constant α according to relations (19) and (20).

However, since there is no unique value for the symmetry factor that corresponds to only one value of the kinetics order, the question remains as to what criterion is to be used to connect kinetics order with the corresponding α parameter. This parameter in a way replaces the order parameter in the model of mixed order kinetics. If we consider the equation for activation energy calculation according to the general order kinetics [5]

$$E = \frac{lkT_m^2}{\delta_{\text{eff}}} \quad (18)$$

then for the order of kinetics according to the model of mixed order kinetics we get the following:

$$l = \frac{1 - \alpha(1 - 2\mu_s)}{1 - \alpha(1 - \mu_s)}. \quad (19)$$

From the above expressions one can see that $l = 1$ for $\alpha = 0$, in other words the model of first order kinetics, which is always the case when $h \gg n_0$, or for $\alpha = 1$ we get $l = 2$, which is the case when $h \ll n_0$. This is in complete correlation with the symmetry factor values as well as with the limiting values. If we now take $2\mu_s \approx 1$ and $\alpha < 1$ then we get $|\alpha(1 - 2\mu_s)| \ll 1$, and if we take $\mu_s \approx 0.5$ in the first approximation then we get

$$l = \frac{2}{2 - \alpha}. \quad (20)$$

Kinetics order versus constant α plots are shown in figure 1. Calculations were made using equations (19) and (20), respectively. These curves were obtained empirically earlier [7, 8].

5. Calculation of the symmetry factor

If $T = T_m$ in equation (4), then we obtain

$$IT_m = \frac{s^{(h)}}{R} \int_0^{T_m} \exp\left(-\frac{E}{kT'}\right) dT'. \quad (21)$$

Approximating the integral in equation (21) by using the well known expression

$$\int_{T_0}^T \exp\left(-\frac{E}{kT}\right) dT \cong T \exp\left(-\frac{E}{kT}\right) \sum_{n=1}^{\infty} \left(\frac{kT}{E}\right)^n (-1)^{n-1} n! \quad (22)$$

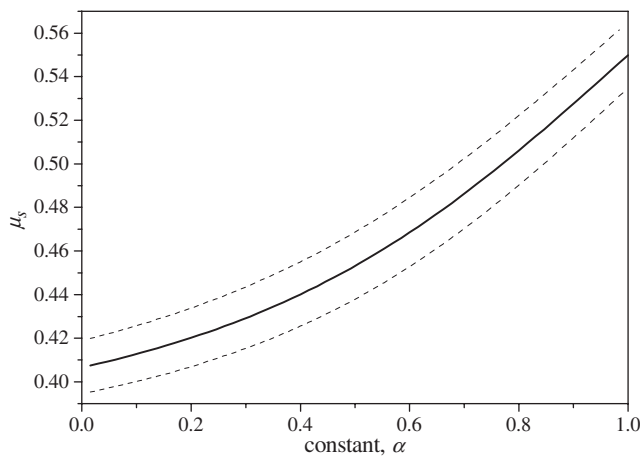


Figure 2. Dependence of the symmetry factor μ_s on the constant α for three values, $\Delta_m = 0.07$ (top curve), $\Delta_m = 0.1$ (middle curve) and $\Delta_m = 0.13$ (bottom curve).

and substituting the first two terms in to expression (21) and after some rearranging, we get

$$IT_m = \frac{s^{(h)} k T_m^2}{R E} \exp\left(-\frac{E}{k T_m}\right) (1 - \Delta_m). \quad (23)$$

Here, $\Delta_m = 2kT_m/E$. After substituting the expression factor (13) in equation (23) and some rearrangements, we get

$$IT_m = \left(\frac{2kT_m^2}{\delta_{\text{eff}} E} - 1\right) (1 - \Delta_m) \quad (24)$$

and when we introduce (17) into the previous expression we get

$$IT_m = \left[\frac{1 - \alpha}{1 - \alpha(1 - 2\mu_s)}\right] (1 - \Delta_m). \quad (25)$$

After substitution in (14), we get a final expression for the symmetry factor:

$$\mu_s = \frac{1 - \alpha}{\exp\left\{\left[\frac{1 - \alpha}{1 - \alpha(1 - 2\mu_s)}\right] (1 - \Delta_m)\right\} - \alpha}. \quad (26)$$

The dependence of the symmetry factor on the constant α for some characteristic values of Δ_m is shown in figure 2 [9]. These functions can be used for approximate calculations of α using some values of the symmetry factor.

If we use the approximation (20), then the expression for the symmetry factor becomes significantly simple:

$$\mu_s = \frac{1 - \alpha}{\exp[(1 - \alpha)(1 - \Delta_m)] - \alpha}. \quad (27)$$

From equation (27), if $\alpha \rightarrow 0$, we get $\mu_s \approx (1 + \Delta_m)/e$, which corresponds to the approximation for the first order kinetics [6, 9]. The value of the symmetry factor cannot be calculated since the numerator and denominator for this value are equal to zero. Therefore, the limiting value is calculated using equation (26). After differentiating numerator and denominator, we get

$$\mu_s \xrightarrow{\alpha \rightarrow 1} \frac{2\mu_s}{1 - \Delta_m + 2\mu_s}. \quad (28)$$

If, by using the same procedure, the limiting value of equation (27) is calculated as $\mu_s \approx [1 + (\Delta_m/2)]/2$, and if this value is substituted in (28) and the same procedure is repeated, then we get the following values:

$$\mu_s \xrightarrow{\alpha \rightarrow 1} \frac{1 + \Delta_m/2 + \Delta_m/4 + \Delta_m/8 + \Delta_m/16 + \dots}{2} \rightarrow \frac{1 + \Delta_m}{2}. \quad (29)$$

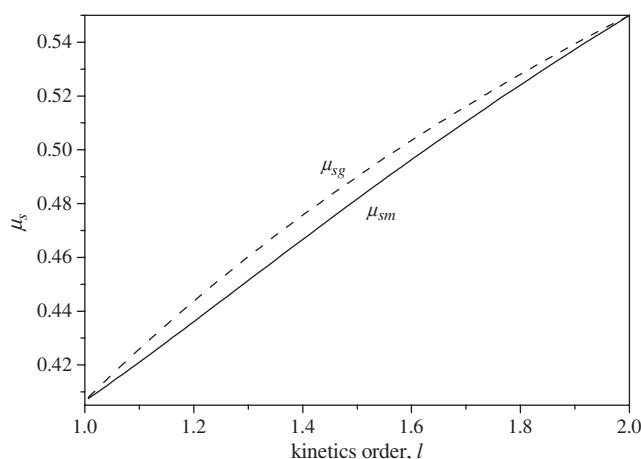


Figure 3. Dependence of the symmetry factor for models of general order (μ_{sg}) and mixed order (μ_{sm}) kinetics on order of kinetics l .

This expression corresponds to the value that is considered as an approximation of the second order kinetics [6, 9]. This iterative method of evaluation of limiting value also shows the method of evaluation of the symmetry factor for a certain value of Δ_m . When some calculated value of the symmetry factor for general order kinetics [5] is compared with the calculated symmetry factor for the model of mixed order kinetics, for the same values of kinetics order and Δ_m , one can notice their similarities and their differences. In figure 3, these values of the symmetry factor are shown for $\Delta_m = 0.1$ (0.07).

6. Procedure for calculation of parameters

The procedure for the calculation of parameters consists of the following steps: first for the normalized experimental curve δ_{eff} and ω_{eff} are calculated where ω_{eff} is the integral of the whole normalized glow curve [5], and then μ_s is calculated from the ratio of these two values. From the same curve, T_m is also determined. From the value of the curve $\mu_s(\alpha)$ for $\Delta_m = 0.1$, an approximate value of the constant α is obtained. From this value and the values of other parameters, using equation (17), an approximate value of the activation energy E is determined. Now, the value of Δ_m is evaluated, which is very close to its exact value. This makes it possible, by using a second iterative, to work out the constant α , which is very close to its exact value. Now again the calculation is made and more accurate values of E and Δ_m are obtained. Iterations can be repeated until the desired accuracy is achieved. The parameter $s^{(h)}$ is determined from equation (13). The accuracy of the obtained results depends primarily on the accuracy of the initial parameters, that is the accuracy of the read values of TL intensities from the experimental curve. The described iterative procedure gives the accuracy of α and E below 1%. The values obtained from the curves simulated by a computer with the parameters $E = 1$ keV, $s = 10^{10}$, $N = 10^{10} \text{ cm}^{-3}$, $R = 1 \text{ K s}^{-1}$, and different values of concentrations of inactive traps, that is, concentration of free carriers in the traps $h = H$, occupancy of active traps f , and different values of the constant α are given in table 1.

7. Discussion

The proposed calculation of TL parameters using the model of mixed order kinetics is based on initial parameters proposed by Halperin and Braner [6] and Chen [9]. Since an approximation in the calculation of the temperature integral (22) was used, this calculation is also approximate.

Table 1. Values of the parameters obtained from the glow curves simulated by computer.

h (cm ⁻³)	f (%)	α	l	E_c (keV)	ε_E (%)	α_c	ε_α (%)	$s_c^{(h)}$	ε_s (%)
1×10^{10}	0.25	0.2	1.103	0.9978	-0.22	0.2002	0.10	9.42×10^9	-5.80
1.67×10^9	0.25	0.6	1.412	0.9976	-0.24	0.5941	-0.98	1.59×10^9	4.79
2.53×10^7	0.25	0.99	1.991	0.9985	-0.15	0.9938	0.38	1.51×10^7	-40.32
2×10^{10}	0.50	0.2	1.098	0.9971	-0.29	0.1918	-4.10	1.87×10^{10}	-6.50
3.33×10^9	0.50	0.6	1.406	1.0022	0.22	0.6051	0.85	3.49×10^9	4.80
5.05×10^7	0.50	0.99	1.987	1.0007	0.07	0.9908	0.08	4.76×10^7	-5.74
3×10^{10}	0.75	0.2	1.095	1.0020	0.20	0.2076	3.80	3.15×10^{10}	7.00
5×10^9	0.75	0.6	1.402	0.9998	-0.02	0.6001	0.02	4.98×10^9	-0.40
7.58×10^7	0.75	0.99	1.987	0.9964	-0.36	0.9838	-0.63	1.11×10^8	46.44
4×10^{10}	1.00	0.2	1.093	0.9994	-0.06	0.1985	-0.75	3.94×10^{10}	-1.50
6.67×10^9	1.00	0.6	1.400	1.0035	0.35	0.6086	1.42	7.18×10^9	7.65
1.01×10^8	1.00	0.99	1.981	0.9987	-0.13	0.9861	-0.39	1.35×10^8	33.66

The accuracy of this calculation can be improved by using a large number of terms in a series, which approximates the temperature integral. Increasing the number of terms in a series, which is not difficult to achieve, can increase the accuracy of calculation of the parameter α . In each case, however, iteration should be used in the calculation in order to get as near as possible to the exact solution. In the majority of cases, two or three iterations are necessary to get close to the exact solution. The results in table 1 show that the relative error less than 0.5% is easily achieved in order to get the activation energy of a trap. It turns out that the relative error in evaluation of the parameter α varies in accordance with the magnitude of the parameter. When the values of parameter α are near to zero, the relative error can be rather large since the deviations can be of the same order of magnitude as the value of the parameter. The relative error of the calculation decreases with increasing α value. The deviations of calculated values of α_c on one or the other side from the exact values are independent of the method of calculation but depend on the approximate values $\mu_s(\alpha, \Delta_m)$ used for the determination. The largest relative errors are obtained when the pre-exponential factor is determined. This can be expected because of the use of an exponential function for the evaluation of this factor, equation (13), which considerably enlarges the deviations. However, for the majority of calculations this value is below 10% except for cases when the parameter α is nearly one. For these cases, it is shown that in the calculation of the parameters close to the mentioned value of α singularities appear for $\mu_s \approx 0.5$ and $\alpha \approx 1$.

Therefore, even small changes in values of the parameters have a considerable influence on calculations of other parameters and especially on the $s^{(h)}$ parameter. Also, it should be pointed out that the value of temperature for the maximum T_m should be determined with high precision since it has a considerable influence on the accuracy of calculations and this is the consequence of the exponential function in the expression used. The values of the parameter can be obtained applying the method of calculation used for the model of second order kinetics. Therefore, from the previous discussion one can notice limitations of this method of calculation, which appear near to the above mentioned points, and they may appear in all types of calculations and fittings when the above mentioned equation is used. The change of order of kinetics in the case of general order kinetics depends on the change in ratio $r = \gamma_l/\gamma_i$, where γ_l and γ_i are the probability of retrapping and the probability of luminescent recombination, respectively. In the case of mixed order kinetics, this change depends on the ratio $\alpha = n_0/(h + n_0)$, where n_0 and h are concentrations of free carriers in active and inactive traps, respectively. Furthermore, there is a supposition that the probability of luminescent recombination and probability of

retrapping are approximately the same and that the point where the concentration of inactive traps equals zero should be the common point for the model of general order kinetics and the model of the mixed order kinetics. Theoretically, in the model of mixed order kinetics the values of parameters at this point are achieved as limiting values since the equation describing mixed order kinetics is not defined at this point.

This practically means that the application of both models for general order kinetics and second order kinetics near this point can give better results.

It can be concluded that, similarly to the model of general order kinetics, deviations of constant α values are relatively small for the given range of Δ_m , and they converge in the process of iteration. From figure 3 it can be seen that the symmetry factor versus kinetics order is linear within nearly the whole interval of the kinetics order values. Deviations from linearity take place near the value 2 of kinetics order.

8. Conclusion

A completely new method for the calculation of the glow curve parameters according to the model of mixed order kinetics has been developed. Based on this method it is possible to calculate all parameters, constant $\alpha = n_0/(h + n_0)$, activation energy of traps and pre-exponential factor $s^{(h)} = s'/h$, which completely determine any curve of the stated model. The obtained high accuracy of the values of parameters depends much more on the accurate reading of data from the experimental curve than on the calculation method itself. The relative error for the activation energy of traps, when two iterations are used in calculation and when the temperature maximum of the curve is accurately determined to three decimal places, is below 0.5%. For the value of α it is between 0.5 and 5%, depending on the value of the parameter, which could be very close to zero, and in that case the value for the relative error is higher. Also, the relative error is higher near $l = 2$, i.e. $\alpha = 1$ due to indefiniteness in equations used for calculations. The relative error in determination of the $s^{(h)}$ parameter is high because of the exponential function in the expression used for the calculation. It is below 10% for most calculations. The calculation accuracy can be increased by increasing the number of the order in equation (22), which approximates the value of the temperature integral, or by increasing the number of derived iterations.

Expressions for the calculation of the energy and order of kinetics were obtained theoretically, so that some empirical expressions [4] and procedures [7, 8] used up to now are theoretically confirmed. Also, the difference between the model of mixed order and the model of general order kinetics via differences in the symmetry factor, for the same values of the parameters l and Δ_m , has been shown.

Further ways to determination of kinetic parameters of the TL process based on the existing models have been opened up.

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