International Journal of Luminescence and applications
Vol6 (3) September, 2016, pages 156-160

# On the two heating rate method of determination of the activation energy of TL peaks under different heating schemes

**M Karmakar[1], S K Azharuddin[2], B Ghosh[2] and S D Singh[3*]**

[1]Acharya Prafulla Chandra College, New Barrackpore, Kolkata – 700 131
[2]Department of Physics, Jadavpur University, Kolkata- 700 032
[3]Department of Physics, Manipur University, Canchipur, Imphal-795003
Email : dorendrajit@yahoo.co.in; mahua_apc@yahoo.com

***Abstract***

*In the present paper, we consider the application of the Booth's method and another variant of two heating rate method suggested by Pagonis. The Booth's method is based on the shift of the TL peak temperature with change of heating rate and another variant is related with shift of peak intensity with heating rate. We have considered the applicability of the method for non- first order kinetic peaks with temperature dependent frequency factor.*

***Key words***: ***Thermoluminescence, activation energy, two-heating rates method, proportional error***

## 1.INTRODUCTION

Thermoluminescence (TL) is a well-established technique that is widely applied in dosimetry, archeological dating and for detecting changes in defect concentration in insulators [1,2]. The underlying premise of TL emission is that the exposure of a material to the ionizing radiation causes a redistribution of charges in the defect centres within the material. When the material is heated at a controlled heating scheme, the TL is emitted as a temperature dependent set of peaks collectively known as a glow curve. Activation energy ($E$) is one of the important parameters connected with a typical peak of a glow curve. The stability of a peak is decided by its activation energy which is crucial for dating purposes.

Booth method [3] is a particular type of the simple two different heating rates method [1,2] for the determination of activation energy ($E$) of TL peak. Recently Pagonis et al [4] suggested another variant of two-heating rates method hereafter called Pagonis method for the determination of activation energy for TL peaks. In the present paper we plan to adjudge the suitability of the Booth and Pagonis method for the determination of activation energy of a TL peak.

## 2. METHODOLOGY

The TL intensity I(T) of a first order (b=1) TL peak is given by

$$I(T) = sn_0 \exp\left(-\frac{E}{kT}\right)\exp\left[-\frac{s}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right)dT'\right] \quad (1)$$

whereas for a non-first order TL peak one can write

$$I(T) = sn_0 \exp\left(-\frac{E}{kT}\right)\times \left[1+(b-1)\frac{s}{\beta}\int_{T_0}^{T} \exp\left(-\frac{E}{kT'}\right)dT'\right]^{-\frac{b}{b-1}} \quad (2)$$

International Journal of Luminescence and applications
Vol6 (3) September, 2016, pages 156-160

where $n_0$ is the initial number of trapped electrons, $s$ is the of frequency factor and $b$ is the order of kinetics. $\beta$ is the heating rate corresponding to the linear heating scheme

$$T = T_0 + \beta t \tag{3}$$

where T is the temperature at any time t and $T_0$ is the initial temperature at t=0 , k is the Boltzmann constant

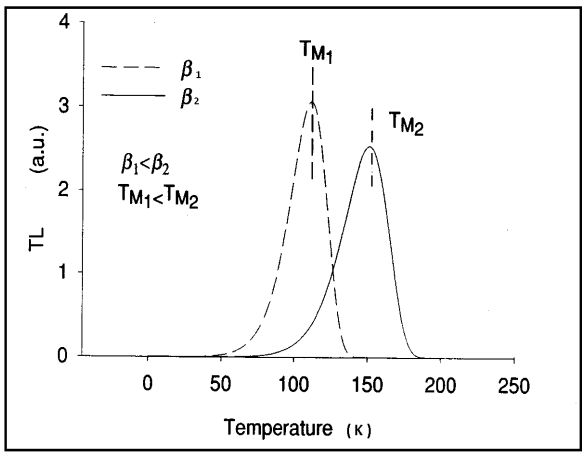


**Fig. 1 : Schematic diagram of two-heating rate method**

The peak temperature $T_m$ corresponding to maximum intensity $I_m$ of a TL peak for $b=1$ (Eqn. 1) is given by

$$\frac{\beta E}{kT_m^2} = s\exp\left(-\frac{E}{kT_m}\right) \tag{4}$$

Whereas for general order kinetics the corresponding maximum intensity condition can be expressed as

$$\left[1+(b-1)\frac{s}{\beta}\int_{T_0}^{T_m}\exp\left(-\frac{E}{kT'}\right)dT'\right] = \frac{bskT_m^2}{\beta E}\exp\left(-\frac{E}{kT_m}\right) \tag{5}$$

Now using the asymptotic expression of the integral $\int_{T_0}^{T_m}\exp\left(-\frac{E}{kT}\right)dT$ one can write [4]

$$\int_{T_0}^{T_m}\exp\left(-\frac{E}{kT}\right)dT = \frac{kT_m^2}{E}\exp\left(-\frac{E}{kT_m}\right)\left[1-\frac{2kT_m}{E}\right] \tag{6}$$

Whereas without any loss of generality $T_0$ may be replaced by 0 [5] so that eqn. (4) can be expressed as

$$\frac{\beta E}{kT_m^2} = s\exp\left(-\frac{E}{kT_m}\right)\left[1+(b-1)\frac{2kT_m}{E}\right] \tag{7}$$

It can be easily shown that for experimental TL peaks, the second term within the parenthesis can be neglected compared to unity so that both for first order and non-first order peaks eqn.(4) for maximum can be expressed as

$$\frac{\beta E}{kT_m^2} = s\exp\left(-\frac{E}{kT_m}\right) \tag{8}$$

If we consider two different heating rates ( $\beta_1, \beta_2$ ) activation energy as calculated by Booth method is given by [3], where $T_{m1}$ and $T_{m2}$ are corresponding peak temperatures (Fig. 1).

$$E_B = k\frac{T_{m1}T_{m2}}{T_{m1}-T_{m2}}\ln\left[\left(\frac{\beta_1}{\beta_2}\right)\left(\frac{T_{m2}}{T_{m1}}\right)^2\right] \tag{9}$$

Using equation (1) and (2) the expression for $\ln I_m$ for $b=1$ and $b\neq 1$ are given by [4]

$$\ln I_m = -\frac{E}{kT_m} + \ln sn_0 - \frac{s}{\beta}\frac{kT_m^2}{E}\left[1-\frac{2kT_m}{E}\right] \qquad b=1 \tag{10}$$

$$\ln I_m = -\frac{E}{kT_m} + \ln sn_0 - \frac{b}{b-1}\ln\left[1+(b-1)\frac{s}{\beta}\frac{kT_m^2}{E}\left(1-\frac{2kT_m}{E}\right)\right] \quad b \neq 1 \tag{11}$$

It has been shown by Pagonis et al [4] that the third term in equations (10) and (11) can be neglected in comparison with the first two terms so that both equations (10) and (11) can be expressed as

$$\ln I_m \cong -\frac{E}{kT_m} + \ln sn_0 \tag{12}$$

Now we consider two different heating rates ($\beta_1, \beta_2$) and $I_{m1}$ and $I_{m2}$ are the corresponding peak intensities. The activation energy as calculated by the method proposed by Pagonis et al [4]

$$E_P = \frac{kT_{m1}T_{m2}}{T_{m1}-T_{m2}}\ln\frac{I_{m1}}{I_{m2}} \tag{13}$$

In case of temperature dependent frequency factor,where

$$s = s_0 T^a \quad \text{with} -2 \le a \le 2 \tag{14}$$

the TL intensity of a glow peak is given by

$$I(T) = n_0 s_0 T^a \exp(-E/kT) \times \exp\left(-\frac{E}{kT} - (s_0/\beta)\int_{T_0}^{T} T'^a \exp(-E/kT')dT'\right) \quad b = 1 \tag{14}$$

$$I(T) = n_0 s_0 \exp(-E/kT) \times \left\{1+\frac{(b-1)s_0}{\beta}\int_{T_0}^{T} T'^a \exp(-E/kT')dT'\right\}^{-\frac{b}{b-1}} \quad b \neq 1 \tag{15}$$

The maxima condition for TL peaks corresponding to the first order and non-first order kinetics are given respectively by

$$\frac{\beta E}{kT_m^2} - \frac{s}{\beta}T_m^a \exp\left(-\frac{E}{kT_m}\right) + \frac{a}{T_m} = 0 \tag{16}$$

And

$$\frac{\beta E}{kT_m^2} + \frac{a}{T_m} = \frac{bs_0 T_m^a \exp(-E/kT_m)}{\left[1+s_0\frac{(b-1)}{\beta}\right]\int_{T_0}^{T_m} T^a \exp(E/kT')dT'} \tag{17}$$

Equations (16) and (17) can be used to determine peak temperature $T_m$ and eqn. (12) is used to determine maximum intensity $I_m$.

## 3.RESULTS AND DISCUSSION

In order to compute the errors involved in different methods such as proposed by Booth [3] and Pagonis et al [4] we have computed $T_m$ and $I_m$ using relevant equations (14-17) for particular values of $E$, $s$ and $\beta$. Using the computed values of $T_m$ and $I_m$ for two heating rates we have computed activation energies $E_B$ and $E_P$ by using respectively the method of Booth [3] and Pagonis et al [4].After computing $E_B$ and $E_P$, we compute the percentile

proportional error $\delta_B (= \frac{|E - E_B|}{E} \times 100\%)$ and $\delta_P (= \frac{|E - E_P|}{E} \times 100\%)$ in determination of activation energy by Booth[3] and Pagonis method[4]. The plot of $\delta_B$ and $\delta_P$ with variation of $b$ ( $1 \le b \le 2.5$ ) for a=-2,0,2 and for $E$ =1 eV , $s_0$ =$10^{12}$ units is depicted in Figure 2.

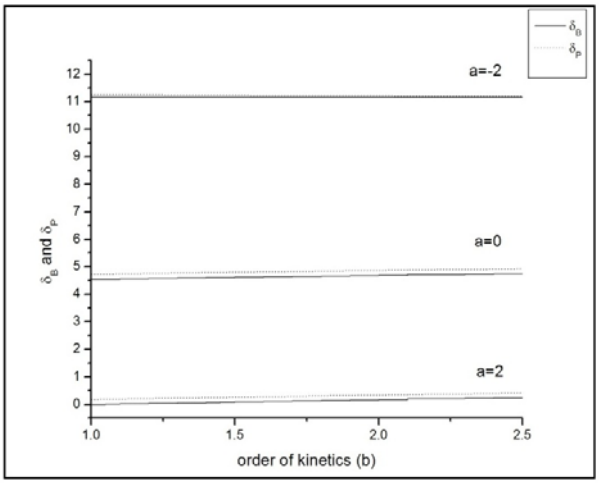


**Fig 2. Variation of $\delta_B$ and $\delta_P$ with order of kinetics for different values of 'a' in Computer simulated glow curve ( E=1 eV, s=$10^{12}$ units)**

In all the cases $\delta_B$ and $\delta_P$ is constant with $b$ . $\delta_P$ is marginally larger than $\delta_B$ . We have run computer codes for a value of $E$ ranging from 0.1 eV to 1.6 eV. $\delta_B$ and $\delta_P$ in all the cases have been found insensitive to the input value of $E$ used in the calculation. In Figure 3, we present the variation of $\delta_B$ and $\delta_P$ as a function of $\log s_0$ for $b = 2$ and $E$ = 1 eV. It is found that $\delta_B$ increases with $\log s_0$ . The values of $\delta_B$ and $\delta_P$ is greater for a=-2 than for a=0 and 2. For a=-2 , $\delta_B$ decreases from 22% to about 11%, whereas $\delta_P$ decreases from 22.5% to 11.2% as $\log s_0$ increases from 8 to 12. For a=0 , $\delta_B$ decreases from 0.3% to 0.17 11% whereas $\delta_P$ decreases from 0.6% to 0.34% as $\log s_0$ increases from 8 to 12. For a=2 ,

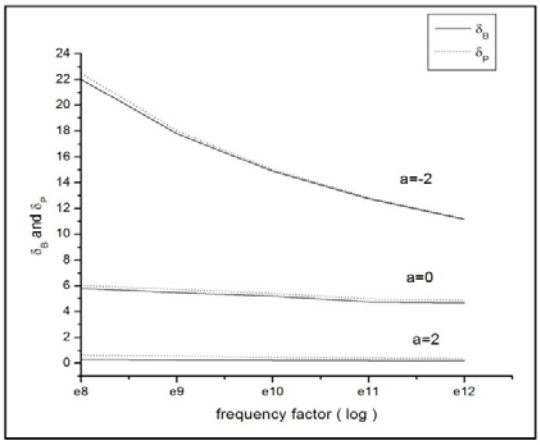


**Fig. 3 : Variation of $\delta_B$ and $\delta_P$ with $\log s_0$ for different values of 'a' in Computer simulated glow curve( E=1 eV, b=2)**

decreases from 0.6% to 0.34% as $\log s_0$ increases from 8 to 12. For a=2 , $\delta_B$ decreases from 5.8% to about 4.68% whereas $\delta_P$ decreases from 6% to 4.86% with the same variation of $\log s_0$ . It is to be noted that both Booth method and that due to Pagonis et al [4] underestimate the value of $E$ .

We now adjudge the suitability of our findings by considering experimental 376 K TL peak of $Ba_{0.92}SO_4$:$Dy_{0.04}Mn_{0.04}$ annealed at 873 K and irradiated with 300 Gy γ-ray dose [5]. The values of $E_B$ and $E_P$ are presented in Table 1,along with the values $E_{cf}$ obtained by rigorous curve fitting method[2]. If we consider $E_{cf}$ as the standard or reference value of activation energy, it may be

noted that in accordance with our findings both $E_B$ and $E_P$ are larger than $E_{cf}$ and the value of $E_B$ and $E_P$ are approximately within the range predicted by us.

**Table 1. Proportional errors in the determination of $E_B$ and $E_P$ in eV in experimental case [7]**

| $E_B$ | $E_P$ | $E_{cf}$ | $\delta_B(\%)$ | $\delta_P(\%)$ |
|---|---|---|---|---|
| 1.085 | 1.091 | 1.08 | 0.463 | 1.02 |

## 4. CONCLUSION

In the present work, we have analysed the suitability of the two variants of the two heating rates method for the calculation of activation energy namely one proposed by Booth[3] and the other proposed by Pagonis et al[4] both for temperature independent and temperature dependent frequency factors in TL. The percentile proportional error involved are larger for the case of temperature dependent frequency factor than for temperature independent frequency factor. The applicability of the present findings has been tested by considering an experimental TL peak of $Ba_{0.92}SO_4:Dy_{0.04}Mn_{0.04}$. In future we plan to extend the present work to other heating schemes namely hyperbolic and exponential heating schemes.

## References

1. R. Chen and V. Pagonis, Thermally and Optically stimulated luminescence: A simulation approach Wiley: (Chicester, UK)2011
2. R. Chen and S.W.S McKeever Theory of Thermoluminescence and Related Phenomenon) World Scientic( Singapore)1997
3. A. H. Booth Canad. J. Chem. 32(1954)214
4.V. Pagonis, G. Kitis, C. Furetta, Numerical and Practical Exercises in Thermoluminescence; Springer, New York (USA) 2006
5.Yengkhom Rangeela Devi Ph. D Thesis 2013 Manipur University