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# On the general-order kinetics of the thermoluminescence glow peak

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**Abstract.** Previous workers have suggested an equation for the general-order kinetics of an isolated thermoluminescence (TL) glow peak which cannot be explained by the usual first- or second-order kinetics. The difficulty with respect to the general-order equation is related to the dimension of the pre-exponential factor which has an unacceptable meaning. Also, the frequency factor  $S$  in the case of the general-order equation is found to vary in the same sample when the dose is varied. The unacceptable meaning of the dimensions of the pre-exponential factor as well as the variation in  $S$  as a function of the dose guide us to suggest a new TL general-order equation which seems to overcome the previously mentioned difficulties.

## 1. Theoretical background

### 1.1. First-order kinetics

The model that we start with to explain the thermoluminescence (TL) kinetics is the model of Randall and Wilkins (RW) [1], where they considered the occurrence of a TL peak due to the thermal release of electrons from traps and their subsequent recombination with holes trapped in recombination centres. Two other assumptions implied by RW are firstly that only one trapping state and one kind of centre are involved and secondly that electrons thermally released from traps recombine rather quickly with trapped holes, i.e. no retrapping or trapping into other traps or recombination into other recombination centres is allowed and substantial accumulation of electrons in the conduction band is assumed to be impossible. The energy depth of the ground state of this trap is  $E$  (eV) below the bottom of the conduction band. At a time  $t$  (s), the temperature of the material is  $T$  (K), and the single-electron trap contains  $n$  ( $\text{cm}^{-3}$ ) electrons. The rate of release of electrons per unit time at a temperature  $T$  (K) is given by

$$-dn/dt = nS \exp(-E/kT) \quad (1)$$

where  $k$  ( $\text{eV K}^{-1}$ ) is Boltzmann's constant and  $S$  ( $\text{s}^{-1}$ ) the frequency factor. If the sample is heated so that the temperature rises at a linear rate  $R$ , i.e.  $dT = Rdt$ , then

$$dn/n = -(S/R) \exp(-E/kT) dT. \quad (2)$$

The equation describing TL for first-order kinetics is then given by

$$I = -\frac{dn}{dt} = n_0 S \exp\left(\frac{-E}{kT}\right) \exp\left[-\frac{S}{R} \int_{T_0}^T \exp\left(\frac{-E}{kT'}\right) dT'\right]. \quad (3)$$

This is the expression for the TL glow intensity  $I$  from electrons trapped at a single trapping level. Curve a in figure 1 shows a computed first-order TL glow peak based on equation (3).

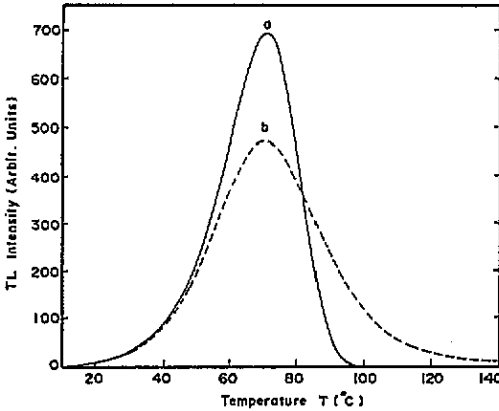


Figure 1. Computed TL glow peaks according to equations (3) and (6) for (a) first- and (b) second-order kinetics, respectively. The curves are computed with  $E = 0.9$  eV,  $S = 3 \times 10^{12} \text{ s}^{-1}$ ,  $n_0 = N = 10^4 \text{ cm}^{-3}$  and  $R = 2 \text{ K s}^{-1}$ .

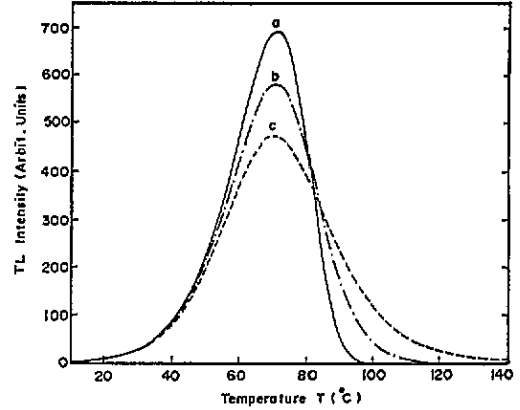


Figure 2. Computed TL glow peaks according to equation (15) for the following orders of kinetics: curve a,  $b = 1.0008$ ; curve b,  $b = 1.4$ ; curve c,  $b = 2$ . The curves are computed with  $E = 0.9$  eV,  $S = 3 \times 10^{12} \text{ s}^{-1}$ ,  $n_0 = N = 10^4 \text{ cm}^{-3}$  and  $R = 2 \text{ K s}^{-1}$ .

### 1.2. Second-order kinetics

For the case of equal retrapping and recombination probabilities, the rate of release of electrons per unit time at a temperature  $T$  (K) is given by [2]

$$-dn/dt = (n^2 S/N) \exp(-E/kT) \quad (4)$$

where  $N$  ( $\text{cm}^{-3}$ ) is the concentration of traps. All other terms remain as previously defined. If the sample is heated so that the temperature rises at a linear rate  $R$ , i.e.  $dT = R dt$ , then

$$-dn/n^2 = (S/NR) \exp(-E/kT) dT. \quad (5)$$

The equation describing TL for second-order kinetics according to equation (5) is given by

$$I = n_0^2 S \exp\left(\frac{-E}{kT}\right) / N \left[1 + \frac{n_0 S}{NR} \int_{T_0}^T \exp\left(\frac{-E}{kT'}\right) dT'\right]^2. \quad (6)$$

The computed TL glow peak of second-order kinetics is depicted in figure 1, curve b. Equation (6) may be written as [3]

$$I = n_0^2 S' \exp\left(\frac{-E}{kT}\right) / \left[1 + \frac{n_0 S'}{R} \int_{T_0}^T \exp\left(\frac{-E}{kT'}\right) dT'\right]^2 \quad (7)$$

where  $S' = S/N$  is known as the pre-exponential factor which has the units  $\text{cm}^3 \text{ s}^{-1}$ .

### 1.3. General-order kinetics

In several cases the shape of the glow peak does not conform to either the first- or second-order glow curves expected from equations (1) and (4), respectively. This led to the suggestions [4-11] of a general case for which the rate of releasing electrons from its trap level may be written as

$$-dn/dt = n^b S' \exp(-E/kT) \quad (8)$$

where  $b$  is the order of the kinetics and  $S'$  the pre-exponential factor which has units of  $\text{cm}^{3(b-1)} \text{s}^{-1}$ . Usually  $b$  is assumed to be between 1 and 2, but sometimes it can exceed this range [12]. Note that the constant  $S'$  in equation (8) is not identical with  $S'$  in equation (7); in the former it has units of  $\text{cm}^{3(b-1)} \text{s}^{-1}$ , and in the latter units of  $\text{cm}^3 \text{s}^{-1}$ . In a special case, when  $b = 2$ ,  $S'$  in equation (8) reduces to  $S'$  of the second-order kinetics [3]. The solution of equation (8) for a linear heating rate  $R$  and for  $b \neq 1$  is shown to be [6]

$$I = S n_0 \exp\left(\frac{-E}{kT}\right) \left/ \left[ 1 + \frac{(b-1)S}{R} \int_{T_0}^T \exp\left(\frac{-E}{kT'}\right) dT' \right]^{b/(b-1)} \right. \quad (9)$$

where  $S$  defined by Chen [12] has units of  $\text{s}^{-1}$ :

$$S = S' n_0^{(b-1)}. \quad (10)$$

The difficulty with respect to equation (8) is related to the meaning of the pre-exponential factor  $S'$ . The units of  $S'$  according to equation (8) should be  $\text{cm}^{3(b-1)} \text{s}^{-1}$ , i.e. the dimensions change with the order  $b$ . In order to bypass this difficulty, the magnitude  $S$  has been defined in equation (10) and has units of  $\text{s}^{-1}$ . Another difficulty should be noted, however, namely that the frequency factor  $S$  in equation (10) is constant for a given sample and dose (i.e. given  $n_0$ ) but would vary in the same sample when the dose is varied [12].

### 2. New calculations of the general-order kinetics

In order to overcome the difficulties appearing in equations (8) and (10) for the general-order kinetics the following rearrangements will be considered.

Firstly the rate equations (1) and (4) in the case of the first- and second-order kinetics, respectively, will be rewritten in the following forms: for the first-order kinetics,

$$-dn/dt = (n^1/N^0) S \exp(-E/kT) \quad (11)$$

and, for the second-order kinetics,

$$-dn/dt = (n^2/N^1) S \exp(-E/kT). \quad (12)$$

Secondly, the comparison between equations (11) and (12) may guide us to rewrite the rate equation in the general case in the following form:

$$-dn/dt = (n^b/N^{b-1}) S \exp(-E/kT). \quad (13)$$

This, certainly, includes the better-known first-order  $b = 1$  and second-order  $b = 2$  cases given by equations (1) and (4), respectively. It is worthwhile noting that the

frequency factor  $S$  appearing in equation (13) has units of  $s^{-1}$  similar to the frequency factor in the first- and second-order kinetics without any difficulty related to the dimension problem appearing in equation (8). Also, the value of  $S$  in equation (13) is seen to be independent of the change in the absorbed dose (i.e. change in  $n_0$ ). On integration of equation (13), one obtains

$$n = n_0 / \left[ 1 + \frac{S(b-1)(n_0/N)^{(b-1)}}{R} \int_{T_0}^T \exp\left(\frac{-E}{kT'}\right) dT' \right]^{1/(b-1)} \quad (14)$$

where  $R = dT/dt$  is the heating rate and  $n_0$  is the initial concentration of electrons in the traps;

$$I = n_0^b S \exp\left(\frac{-E}{kT}\right) / N^{b-1} \left[ 1 + \frac{S(b-1)(n_0/N)^{(b-1)}}{R} \int_{T_0}^T \exp\left(\frac{-E}{kT'}\right) dT' \right]^{b/(b-1)}. \quad (15)$$

Putting  $b = 2$ , equation (15) easily gives the second-order kinetics equation (cf equation (6)). Following Chen [6], equation (15) is not valid for the case  $b = 1$ ; it can easily be shown that it reduces to equation (2) when  $b \rightarrow 1$ .

Figure 2 shows the TL glow peaks due to equation (15), for  $b = 1.0008, 1.4$  and  $2$ .

### 3. Conclusion

We have presented in this paper a modification of the general-order equation in the case of TL glow peaks which cannot be described by first- or second-order kinetics. The new equation (equation (15)) includes three parameters: the thermal activation energy or trap depth  $E$  (eV), the frequency factor  $S$  ( $s^{-1}$ ) and the order  $b$  of kinetics. The strange units of the pre-exponential factor, namely  $cm^{3(b-1)} s^{-1}$ , and the variation in the frequency factor with respect to the increase in the absorbed dose,  $S = S' n_0^{(b-1)}$ , have been eliminated by using an empirical formula based on the equations describing the rate of releasing electrons from its trap levels in the case of first- and second-order kinetics.

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