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RECENT DEVELOPMENTS IN THERMOLUMINESCENCE KINETICS: APPLICATIONS TO OTHER THERMALLY STIMULATED PROCESSES

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ABSTRACT

Recent thermoluminescence (TL) studies indicate that many kinetic properties are not in accord with the well known 1st and 2nd order TL kinetic equations. For example, the usual equations do not describe: 1) the shape of certain single glow peaks. 2) The shape of glow peaks in many glow curves containing more than one glow peak. 3) The dependence of the peak temperature, the FWHM, the shape, and other properties on the premeasurement dose. However, the properties of some single glow peaks are precisely described, or closely approximated by, the more general basic equation from which the usual 1st and 2nd order equations are obtained as special cases. Furthermore, glow curves containing more than one glow peak are described by a system of equations that includes interactions between different types of traps and is a straightforward extension of the general one peak equation. This system--called Interactive Kinetics--accounts for most properties, and explains many anomalies, associated with glow curves containing more than one glow peak. It is particularly convenient for computerized analysis procedures. Lastly, it is suggested that other thermally stimulated processes depend on analogous interactions and are describable by similar sets of kinetic equations that are convenient for computer analysis.

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INTRODUCTION

Recent attempts to understand certain thermoluminescence results, especially measurements on the shape of both single glow peaks and peaks in glow curves containing more than one peak, have produced results demonstrating the usefulness of computerized numerical techniques as well as likely applications to other thermally stimulated processes. The recent developments, which can be regarded as a generalization of the well known 1st and 2nd order kinetics, will be described in some detail. Finally, possible relations to other thermally stimulated processes will be sketched. Thermoluminescence will be abbreviated TL.

TL KINETICS FOR A SINGLE GLOW PEAK

In a TL measurement a single thermally activated process leads to a glow curve containing one glow peak. This presentation will begin with the single peak equation originally considered by Randall and Wilkins[1] and Garlick and Gibson.[2] Background information is given by Braunlich,[3] and Chen and Kirsh.[4] This equation describes a simple system in which charges, electrons and (electronic) holes, have populated traps during a prior exposure to ionizing radiation at a temperature where thermally stimulated processes are negligible. Later, as the system is heated linearly the least strongly bound charges (e.g. the electrons) are untrapped and undergo a combination of two processes. First, the released charges may recombine at

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traps containing opposite sign charges (e.g. holes) and create luminescence. Second, and most importantly, the untrapped charges may be retrapped one or more times before recombining. In more general terms, this system is controlled by a thermally activated process that produces an observable part of the time but reestablishes the original state the remainder of the time. The general single glow peak equation is

$$I(t) = -\frac{dn}{dt} = n\ s\ \exp(-E/kT)\left(1 - \frac{\sigma_t(N-n)}{\sigma_t(N-n) + \sigma_r n_r}\right) \qquad (1)$$

In this, and below, the following apply: $I(t)$ = TL intensity at time t; n = trapped electron concentration at time t; n_0 = trapped electron concentration at time t = 0; s = preexponential, attempt-to-escape, frequency; E = thermal activation energy, in eV; N = trap concentration (traps/cm^3); k = Boltzmann's constant; T = temperature (°C for plots, K for computations); σ_t = cross section for electron retrapping; σ_r = cross section for light emitting electron-hole recombination; n_r = trapped hole concentration at time t (usually $n = n_r$); n_{r0} = trapped hole concentration at time t = 0; β = heating rate (degrees/unit time); and $\sigma = \sigma_t/\sigma_r$ = retrapping-recombination cross section ratio.

To emphasize differences between (1) and the cases described below this expression is called the General One-Trap or GOT equation. The usual n s exp(-E/kT) part describes the release of charges to the conduction band; the bracket gives the fraction of released charges not retrapped, i.e. the fraction contributing to TL. This equation should apply to numerous systems as it stands, not only in various approximations.

First Order TL Kinetics: As has been known since (1) was introduced, but emphasized in recent papers,[5-9] when retrapping is negligible $\sigma = 0$ and (1) becomes

$$I(t) = -dn/dt = s\ n^p \exp(-E/kT), \text{ with } p = 1. \qquad (2)$$

For linear heating $T = T_0 + \beta t$ and the familiar 1st order glow peak expression is obtained

$$I(T) = n_0\ s\ \exp(-E/kT)\exp\left(-\int_0^T \frac{s}{\beta} \exp(-E/kT)dT\right). \qquad (3)$$

Second Order TL Kinetics: If retrapping occurs and both $\sigma_t = \sigma_r$ and $n = n_r$ are assumed then p = 2 in (1) and the 2nd order expression is obtained

$$I(t) = -dn/dt = (n^2 s/N) \exp(-E/kT), \qquad (4)$$

Using $T = T_0 + \beta t$ the familiar 2nd order glow peak expression is obtained.

$$I(T) = \frac{n_0\ s^*\ \exp(-E/kT)}{\left(1 + \frac{s^*}{\beta} \int_0^T \exp(-E/kT)dt\right)^2} \text{ where } s^* = \frac{n_0}{N} s. \qquad (5)$$

Low Dose, i.e. Low Initial Trapped Charge: If the premeasurement trapped charge is low, $n \ll N$, or $n + \sigma(N-n) \approx \sigma N$, and (1) becomes

$$I(t) = -dn/dt = (n^2 s/N\sigma)\exp(-E/kT). \qquad (6)$$

This is precisely the same form as the 2nd order equation, i.e. (4), with one important difference. Instead of the lumped constant $s^* = s\ n_0/N$ it contains $s^0 = s\ n_0/\sigma N$. Thus if the 2nd order equation can be fitted--by a computerized procedure--to a measured glow curve, the lumped constant obtained can be either s^* or s^0; the procedure will not differentiate between them. Since $\sigma(=\sigma_t/\sigma_r)$ may be quite small (recent data[9] gave $\sigma \approx 10^{-5}$) many of the experimentally determined values of s that exceed the physically reasonable value of 10^{14} can be explained on the basis that s^0, not s^*, has been determined.

High Dose, i.e. High Initial Trapped Charge: If the premeasurement trapped charge is high N-n is small, and if $\sigma(=\sigma_t/\sigma_r) \ll 1$, i.e. recombination >> retrapping, then $n + \sigma(N-n) \approx n$. In this case the GOT expression is approximated by the 1st order equation; except in the high temperature "tail" occurring after most of the initial trapped charge has been released. This occurs after almost all of the glow curve has been recorded and is difficult to observe experimentally.

Properties of the GOT Equation: Almost all properties of the GOT equation and its 1st and 2nd order approximations are illustrated by Fig. 1. The curves were computed numerically; the GOT curves from (1) and the 1st and 2nd order ones from (3) and (5). Note that all curves have been adjusted to the same area. At high doses, i.e. n_0 values, the GOT and 1st order curves coincide, except in the hard-to-observe high temperature tail. At intermediate doses the GOT and 1st or 2nd order curves are not equivalent. And, at low doses the GOT and 2nd order curves superimpose.

Partial Order Kinetics: Well known are chemical and thermally stimulated processes described by partial or fractional order kinetics in which the exponent p in (2) is $\neq 1$ or 2. For (1) to include partial order kinetics it is necessary for the expression

$$n(1-\sigma(N-n)/(\sigma(N-n)+n)) \qquad (7)$$

to be equal to n^p where $p \neq 1$ or 2. By expanding (7) it can be shown that this cannot be done. However (7) can be closely approximated by n^p in restricted ranges. Thus TL data, e.g. Kathuria and Sunta,[10] analyzed by partial order kinetics that shows p increasing between 1 and 2 as the dose decreases is likely to be a case described by GOT kinetics.

TL KINETICS FOR SYSTEMS WITH MORE THAN ONE GLOW PEAK

The appearance of multipeak TL glow curves clearly indicates the presence of more than one thermally activated process; each one characterized by different kinetic parameters. Under special conditions, e.g. very small retrapping probability, the peaks may appear to be independent and described by one-peak kinetics. However, since the TL process includes uncorrelated charge migration the kinetics for individual peaks cannot be truly independent. The simplest possible case that includes interactions, applying to glow curves with more than one peak, is described by the equations

$$\frac{dn_i}{dt} = -n_i s_i e^{-E_i/kT} + \left(\sum_{i=1}^{j} n_i s_i e^{-E_i/kT}\right)\left(\frac{\sigma_i(N_i-n_i)}{n_r + \sum_{i=1}^{j} \sigma_i(N_i-n_i)}\right)$$

$$I(t) = -\frac{dn_r}{dt} = -\sum_{i=1}^{j} \frac{dn_i}{dt} \qquad \sigma_i = \sigma_{ti}/\sigma_r \qquad (8)$$

where the symbols are analogous to those above and j is the number of different peaks.

These equations have been studied using a two-step procedure. First, computerized solutions were obtained using nominal parameters. A typical example is shown in Fig. 2. Second, these solutions were regarded as data and fitted to the 1st and 2nd order equations, (3) and (5). A large number of results were obtained;[5-9] space is available to describe only a few. 1) A large fraction of the computed curves appear to be fitted by the 1st and/or 2nd order expressions, especially over the upper 60 percent or more. The deviations occur in the wings. Thus, many peaks appear to be 1st or 2nd order when it is known a priori that they are not. 2) The kinetic parameters, E and s, range from physically unrealistic low values, through reasonable values, to impossibly high values. This is a possible explanation for many questionable published values. 3) The peak temperatures, FWHM, etc., shift with premeasurement dose, in accord with measurements. 4) Curves of peak height vs. dose, and often peak area vs. dose, often exhibit superlinearity. Thus this "mysterious" phenomena is a natural consequence of the retrapping inherent in GOT and Interactive Kinetics. Overall, it appears that these more general kinetics apply to a number of different aspects of TL. They describe a number of features not explained by the usual 1st and 2nd order kinetics.

APPLICATIONS TO DATA ANALYSIS

Traditionally, data from TL and other thermally stimulated processes have been analyzed by a surprisingly large variety of methods.[3-4] Almost all are subject to inadequacies, especially undemonstrated assumptions. For example, often assumed are: 1) The kinetic order is known. 2) The peak shape is known and only the heating rate, peak temperature, and FWHM--not the entire curve--is used in the analysis. 3) The "stripping" techniques, used to separate low and high temperature peaks, do not alter the peaks. Many other inadequacies could be listed. Clearly, there are appreciable advantages in analyzing glow curves, and analogous curves, by fitting expressions to all significant data points using "best-fit" procedures, e.g. see Mattern et al.[11] However, it is important to choose equations that are suitable for numerical analysis; the determined constants, or lumped constants, must correspond to immediately recognizable individual, or group of, physical parameters. This is an inherent property of the GOT, 1st and 2nd order equations. The Interactive Kinetic equations were chosen for the analysis of multipeak data because they provided easily recognizable determined constants without sacrificing generality. In contrast, "rate-constant" equations often provide "best-fit" determined constants that are obscure functions of the physical parameters.

RELATION TO OTHER THERMALLY STIMULATED PROCESSES

The properties of TL systems with one or more glow peaks, sketched above, provide the basis for dividing thermally stimulated processes into two categories. First, those in which the thermally activated step leads directly to a physical observable. And second, processes in which the thermally activated step initiates the reaction, but there are intervening steps--which may occur only part of the time--that modify the appearance of the physical observable. Processes leading directly to an observable are likely to be described by a simple equation such as the well known 1st order equation. An example is dipole reorientation or relaxation. An example of a process with a thermal initiating step that may be followed by intervening steps is thermally stimulated conductivity in materials with one or more types of trapping levels. The released charge may be retrapped many times before being detected.

In general, the non-trivial complex kinetic situations, similar to the Interactive Kinetics given earlier, are usually describable only by systems of equations. As demonstrated above, to analyze these systems it is not necessary to analytically solve the equations involved. If every effort is made to formulate the equations in a way that preserves the identity of the physical parameters, numerical "best-fit" solutions can often provide (numerical) values of the required parameters.

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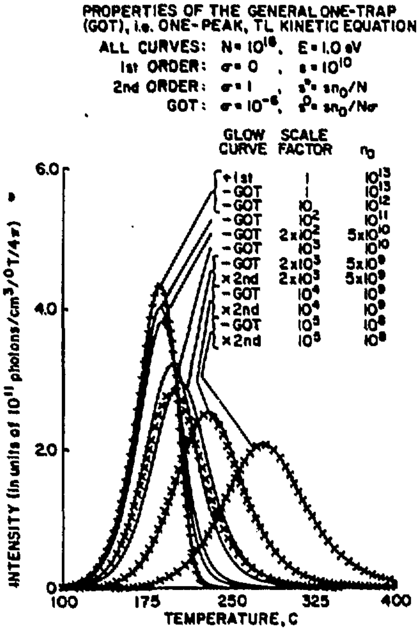

Fig. 1 Dependence of the GOT equation, (1) in the text, on premeasurement trapped charge (dose). At high doses it is approximated by 1st order kinetics, at low doses by 2nd order, and at intermediate doses by neither kinetics.

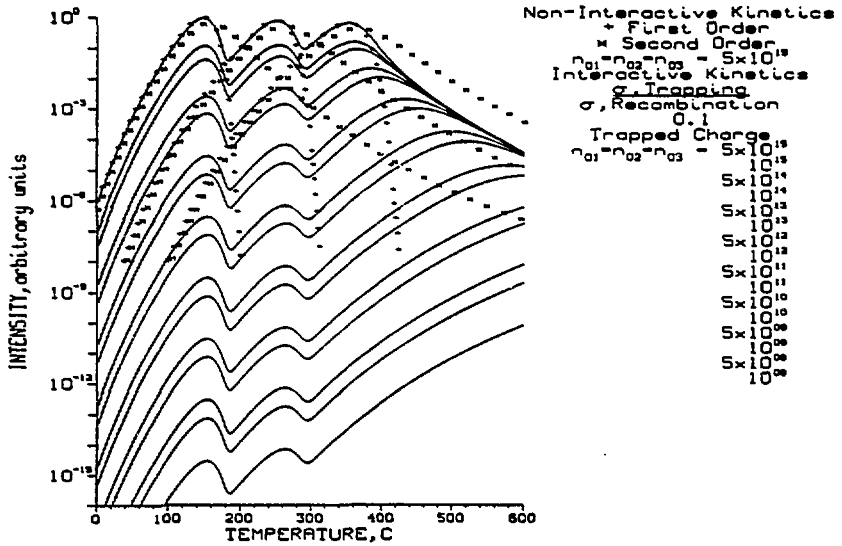

Fig. 2 Glow curves computed from Interactive Kinetics, equation (8) in the text, for the indicated premeasurement trapped charges (dose). Also shown are 1st and 2nd order glow curves computed from comparable parameters, see Ref. 5.