On the order of kinetics in the study of thermoluminescence

LETTER TO THE EDITOR

On the order of kinetics in the study of thermoluminescence

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Abstract. The definition of first-order, second-order and other possible kinetics in thermoluminescence are discussed in relation to a recent paper by Hagekyriakou and Fleming. The definitions offered for 'first-order kinetics' include 'classical' and 'pseudo'-first-order kinetics, all of which have the same properties and therefore are usually indistinguishable. Second-order kinetics are defined in a quite restrictive manner which leaves many intermediate cases which are neither of first nor of second order. The properties of the different kinetics in thermoluminescence peaks are compared as well as the kinetic order tests. The conclusions given by Hagekyriakou and Fleming are examined critically, and somewhat different conclusions are reached.

1. Introduction

In two recent papers, Hagekyriakou and Fleming (1982a, b) gave a set of criteria for determining the order of kinetics of thermoluminescence (TL) peaks. In a similar fashion to discussions previously given in the literature, some ambiguity seems to exist in the definitions of first- and second-order kinetics as related to TL theory. One of the purposes of the present Letter is to remove this ambiguity and to attempt to set a standard nomenclature in this field. In particular, it will be stressed that, in the general case, the kinetics may be of neither first- nor second-order kinetics and, in fact, the first- and second-order cases should be considered to be only limiting cases occurring when some special relations exist between the relevant trapping parameters. According to the present definition, cases referred to by Hagekyriakou and Fleming (1982a) as 'pseudo' first-order will be included in the general framework of first-order kinetics.

Hagekyriakou and Fleming (1982a) also give some tests to determine the kinetic order of the TL emission process. One of these (test 2) is based on the fact that the dependence on the dose of a first-order peak is expected to be such that the intensity of TL emission is proportional to the dose and that the shape of the peak remains the same for different initial concentrations of carriers in traps. It has not been proven, however, that similar situations may not occur with non-first-order peaks, although it is quite obvious that a distortion in the shape of the peak does occur in purely second-order cases. An example will be given of a non-first-order TL peak which does not change its shape with the amount of irradiation and which is expected to depend linearly on the

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excitation dose. More generally, it is argued that one should consider thoroughly the sensitivity of the method to identify deviations from the strict first-order property. The possible complications related to the combined effect of a number of TL peaks in a given temperature range will also be discussed briefly. Finally, the 'pseudo'-first-order kinetics from 'geminate' electron–hole recombination will be reconsidered in view of previous works (Chen and Halperin 1965, Land 1969, Chen 1976, Chen and Kirsh 1981).

2. Order of kinetics in TL theory

The term 'first-order kinetics' in TL theory has been taken from chemistry where a first-order reaction is said to be one in which the rate is directly proportional to the concentration of one reactant (Glasstone and Lewis 1960). In the first theoretical account of TL, Randall and Wilkins (1945) showed that a TL peak resulting from a single electron trapping state and a single kind of centre results in first-order kinetics if one assumes no retrapping of the electrons released. The equation governing the process in this case is

$$I(t) = - \, \mathrm{d}n/\mathrm{d}t = sn \exp(- E/kT) \tag{1}$$

where $I(t)$ is the emission intensity, n is the instantaneous concentration of trapped electrons (m^{-3}), t is the time (s), s is the pre-exponential (frequency) factor (s^{-1}), E is the activation energy (eV), k is Boltzmann's constant $(\mathrm{eV\,K}^{-1})$ and T is the absolute temperature (K). The fact that the assumption of no retrapping resulted in equation (1), in which $- \mathrm{d}n/\mathrm{d}t$ is proportional to n, made the Randall and Wilkins case a 'classical' first-order case among investigators dealing with TL, and, in some cases, the physical situation of 'negligible retrapping' has been termed 'first-order kinetics' (Hagekyriakou and Fleming 1982a). In fact, other physical circumstances may lead to a governing equation of the same form as equation (1); these were termed by the same authors 'pseudo'-first-order kinetics. So far this looks like a mere difference in taste concerning terminology; however, the more basic ambiguity starts when one deals with non-first-order cases. Hagekyriakou and Fleming (1982b) say that 'if the probability of retrapping before recombination is non-zero, we have second-order kinetics'. On the other hand, in their 1982a paper they say, following the chemical convention, that a reaction following second-order kinetics may be written as

$$- \, \mathrm{d}n/\mathrm{d}t = k_2 n(t) m(t) \tag{2}$$

where $n(t)$ and $m(t)$ are the concentrations of the reacting substances. As will be shown here, these two definitions are not necessarily identical and, since they are utilised alternatively by people in the field, an attempt should be made to establish an unambiguous terminology. The main point to be made is that the general shape of a TL curve is governed by a set of three simultaneous differential equations as given by Halperin and Braner (1960).

$$I(t) = - \, \mathrm{d}m/\mathrm{d}t = A_m m n_c \tag{3}$$

$$= - \, \mathrm{d}n/\mathrm{d}t = sn \exp(- E/kT) - n_c(N - n)A_n \tag{4}$$

$$= \mathrm{d}m/\mathrm{d}t = \mathrm{d}n/\mathrm{d}t + \mathrm{d}n_c/\mathrm{d}t \tag{5}$$

where n_c is the concentration of free electrons in the conduction band (m^{-3}) and A_n and A_m are the retrapping and recombination probabilities $(\mathrm{m}^3\,\mathrm{s}^{-1})$, respectively. Making a

conventional assumption (Halperin and Braner 1960, Shenker and Chen 1972) that the concentration of free electrons is much smaller than that of trapped electrons and that the rate of change of the former is much smaller than that of the latter, one gets the equation

$$I(t) = -\,\mathrm{d}n/\mathrm{d}t = s\exp(-E/kT)nmA_m/[mA_m + (N-n)A_n]. \tag{6}$$

This can be considered as a general single equation in the unknown functions n and m. It can be solved only when certain relations between n and m and the constant parameters are established. Thus, the first-order equation (1) is the case when recombination dominates,

$$A_m m \gg A_n(N-n), \tag{7}$$

and, using the relation $\mathrm{d}m/\mathrm{d}t \simeq \mathrm{d}n/\mathrm{d}t$ which results from equation (5) using the assumption mentioned, $|\mathrm{d}n_c/\mathrm{d}t| \ll |\,\mathrm{d}n/\mathrm{d}t|$.

In order that equation (6) will reduce to equation (2), which is one of the possibilities for defining second-order kinetics, one should assume that the denominator in equation (6) is constant. Garlick and Gibson (1948) asserted that $nA_m = nA_n$ whereas an alternative assumption is $N \gg n$ (excitation which is far from saturation) as well as $mA_m \ll A_nN$. One should remember, however, that since $m(t)$ and $n(t)$ are functions rather than parameters, these relations hold true at part of the TL peak and fail to do so at other parts.

An even more important point to be made is that many authors, including Hagekyriakou and Fleming (1982b), make the assumption that $n(t) = m(t)$ which, while assuming a constant denominator in equation (6), results in the equation

$$I(t) = s'\exp(-E/kT)n^2. \tag{8}$$

This is usually termed 'second-order equation' rather than the more general equation (2); s' is a constant with dimensions of $\mathrm{m}^3\,\mathrm{s}^{-1}$. The main question is related to the probability that the relation $n = m$ holds. At first sight, this seems very plausible as long as one considers only one trapping state and one kind of recombination centre. The likelihood that such a simple condition between n and m holds is, in fact, rather small in actual cases. The samples used for TL purposes usually have a large number of impurities and defects which may act as trapping states and luminescence centres. It is possible that in a certain temperature range mainly one kind of trap is releasing carriers and mainly one kind of centre is involved in recombination, but it is not plausible in most cases that the number of active electrons in traps is the same as that of holes in centres. The condition $m = n$ should usually be replaced by $m = n + c$ where c is a constant, positive or negative, which represents the net concentration of trapped carriers which are not involved in the particular peaks in question (see, e.g., Chen *et al* 1981). The main lesson of this discussion is that first- and second-order kinetics are only extreme cases and different kinds of intermediate cases are to be considered. These include the general-order kinetics (Chen 1969) and mixed-order kinetics (Chen *et al* 1981) as well as various other possibilities (see, e.g., Moharil 1982).

3. Dose dependence

Hagekyriakou and Fleming (1982a, b) rightly suggest that an important property of a first-order peak is that, at small radiation doses, the shape of the peak (or combination

of first-order peaks) is independent of the dose and the TL intensity varies linearly with the dose. The use of this as a test for first order should be applied very cautiously since the opposite, namely that this property is exclusive to first-order peaks, has not been proven. Even if such a proof were possible in principle (and apparently it is not), one should consider the sensitivity of this test to distinguish between first-order peaks which are strictly linear with the dose and whose shape does not vary and a non-first-order peak where the non-linearity and distortion may be very slight.

To exemplify this possibility, let us consider the following example. If one considers $n_c(t)$ as a known function, one can solve equation (3) (see Chen 1971) to yield

$$I(t) = A_m m_0 n_c(t) \exp\left(- A_m \int_0^t n_c(t') \, dt' \right). \tag{9}$$

It is plausible to think of a physical situation in which $n_c(t)$ is hardly dose dependent, say if the trapping states in question are close to saturation, whereas the recombination centre involved is far from saturation, which means that m_0 is practically linear with the dose. Examining equation (9) we can readily see that the TL peak will not change its shape with the varying dose and that each part of the peak including the maximum is linear with the dose. The peak should not be considered, however, to be a first-order peak since its shape may be strongly dependent on the shape of $n_c(t)$ and, therefore, $I(t)$ may be substantially different from the expected first-order curve.

4. Localised transitions

The subject of localised transitions has been discussed in the literature (Chen and Halperin 1965, Land 1969, Chen 1976, Chen and Kirsh 1981, Hagekyriakou and Fleming 1982b). Hagekyriakou and Fleming termed this situation where an electron recombines with a hole trapped in the centre in a close vicinity to that of the electron 'geminate' electron–hole recombination. The equations governing this situation are

$$I(t) = - \, dm/dt = pn_e \tag{10}$$

where p is the probability (s^{-1}) for an excited electron to recombine with the neighbouring hole and n_e is the instantaneous population of excited electrons, each of which can 'see' effectively only one trapped hole. The charge conservation equation

$$m = n + n_e \tag{11}$$

combined with the usual assumption $n_e \ll n$ reduces to

$$m = n, \tag{12}$$

which in this case should not be considered as a limiting assumption. The balance between excited and retrapped electrons can be written here as

$$- \, dn/dt = sn \exp(- E/kT) - sn_e, \tag{13}$$

the same coefficient s appearing in both terms due to the principle of detailed balance (Halperin and Braner 1960). Equations (10), (12) and (13) can be combined to yield

$$I = - \, dm/dt = [ps/(p + s)]m \exp(- E/kT). \tag{14}$$

It is obvious that, for all practical purposes, this is a first-order kinetics equation with an

effective frequency factor of $\bar{s} = ps/(p + s)$. It is readily seen that for $p \ll s$, $\bar{s} \to p$ whereas $p \gg s$ implies $\bar{s} \to s$. The former case may account for very low values of the measured frequency factor appearing in the literature. The main point to be made in this respect is that, since the results of a physical case represented by equation (14) are, in principle, indistinguishable from the 'usual' first-order case, there is no important reason to term them 'pseudo'-first-order kinetics.

5. Conclusion

The main points in this Letter can be summarised as follows.

(1) Any TL peak governed by an equation of the form (1) (or (14)) can be termed 'first-order kinetics peak', since the rate of change of the population of the relevant trapping state is proportional to the concentration. This may include the Randall–Wilkins case (negligible retrapping) and the case of localised (geminate) transitions as well as other possibilities (for example, see the discussion on extrinsic semiconductors, page 37 of Chen and Kirsh (1981)).

(2) Second-order peaks, represented by equation (8), are characterised by the fact that the rate of change of the population is proportional to n^2. This may be due to the Garlick and Gibson (1948) circumstances ($A_m = A_n$, $m = n$), to the dominating retrapping situation ($A_n N \gg A_m m_0$, $N \gg n_0$, $m = n$) and possibly to other cases as well.

(3) The first- and second-order kinetics should be considered only as extreme limiting cases whereas the general TL peak resulting from a single trapping state and a single kind of recombination centre is represented by equations (3)–(5). Cases like non-integer order of kinetics (Chen 1969), i.e. $-\mathrm{d}n/\mathrm{d}t \propto n^b$, $1 < b < 2$, and 'mixed'-order kinetics (Chen *et al* 1981), i.e. $-\mathrm{d}n/\mathrm{d}t = sn \exp(-E/kT) + s'n^2 \exp(-E/kT)$, may sometimes occur. One should keep in mind, however, that all these include simplifying assumptions and real experimental peaks may usually only be approximated by these two- or three-parameter cases. The fact is that the three simultaneous differential equations include eight relevant parameters.

(4) The important property of a first-order peak, namely that its shape does not vary with the initial value of trapping concentration n_0 and that at each point along the curve the TL intensity is proportional to n_0, cannot be used automatically in the reverse direction. If a TL peak exhibits a linear dependence of the maximum intensity of the dose with no appreciable shift of the maximum temperature with the dose, it cannot be taken as conclusive evidence that the kinetics are strictly of first order.

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Reply by J Hagekyriakou and R J Fleming

Chen has challenged some of the conclusions reached in two of our papers (Hagekyriakou and Fleming 1982a, b, hereafter referred to as I and II respectively) concerned with the determination of the kinetic order of the thermoluminescence (TL) emission mechanism in irradiated dielectrics. The purpose of this communication is to reply to the main points raised by Chen.

Since most of the disagreement seems to revolve around the definitions of kinetic order in the TL context, we first state these definitions. They are adapted from physical chemistry (Moore 1972).

(*a*) First-order kinetics are described by

$$I(t) = kn(t) \tag{1}$$

where $I(t)$ is the TL intensity at time t, $n(t)$ is the concentration of trapped electrons at time t and k is a constant, independent of time. To be precise, equation (1) states that the TL emission mechanism is first order in the concentration of trapped electrons. It is, of course, the filling of empty luminescent centres, i.e. their recombination with electrons, which brings about the TL emission. One can therefore always write

$$I(t) \propto -\mathrm{d}m(t)/\mathrm{d}t$$

where $m(t)$ is the concentration of empty luminescence centres at time t. Hence equation (1) implies

$$\mathrm{d}m(t)/\mathrm{d}t = -k_1 n(t) \tag{2}$$

where k_1 is independent of time. Making the usual assumptions that the concentration $n_c(t)$ of electrons in the conduction band is much less than $n(t)$, and that $\mathrm{d}n_c(t)/\mathrm{d}t < \mathrm{d}n(t)/\mathrm{d}t$, it follows that $\mathrm{d}m(t)/\mathrm{d}t = \mathrm{d}n(t)/\mathrm{d}t$. Hence, from (2),

$$I(t) \propto -\mathrm{d}n(t)/\mathrm{d}t = k_1 n(t). \tag{3}$$

Since the rate of release of electrons from traps will always be linearly proportional to $n(t)$, equation (3) implies a constant probability that an electron, having been released from a trap, will recombine with an empty luminescence centre. Note that, following Chen, we assume that all the electron traps have the same activation energy.

As mentioned in II, the 'popular' definition of first-order kinetics is zero retrapping, i.e. every electron, on escaping from a trap, recombines with a luminescence centre without first being retrapped. Obviously this is a particular case of equation (3), which we would expect to find very rarely, since a complete absence of retrapping is very unlikely in any dielectric, especially if it is largely amorphous. More importantly, one can readily specify conditions in which there is considerable retrapping but equation (1) still holds, for example the case described by Chen where each electron is retrapped in the same trap from which it escaped, and can 'see' only the luminescence centre nearest to it.