Review

Methods for kinetic analysis of thermally stimulated processes

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Several methods are known for the evaluation of the main kinetic parameters related to a thermoluminescence (TL) curve, namely the activation energy, the pre-exponential factor and the kinetic order. These methods can easily be applied under certain conditions to a series of related thermally stimulated phenomena which are governed by similar differential equations. These include thermally stimulated conductivity (TSC), thermally stimulated electron emission (TSEE), ionic thermocurrent (ITC), derivative thermogravimetry (DTG), differential thermal analysis (DTA), thermal desorption and other phenomena. The similarities and differences between these phenomena are considered and the applicability of the various methods to the different cases is discussed.

1. Introduction

In a number of phenomena, a certain property of a sample is measured as a function of temperature, when the sample is heated under a given heating scheme from a certain "low" temperature. In some of these phenomena the effect of interest appears only after the sample has been excited in one of various ways, while being held at the "low" temperature or during its cooling to this low temperature, prior to heating.

The following phenomena will be discussed: thermoluminescence (TL); thermally stimulated conductivity (TSC); thermally stimulated electron emission (TSEE); ionic thermoconductivity (ITC); thermal annealing; partial thermoremanent magnetization (PTRM); thermal desorption; evolved gas analysis (EGA); derivative thermogravity (DTG); differential thermal analysis (DTA); differential scanning calorimetry (DSC).

Some emphasis will be placed on thermoluminescence (TL), sometimes called thermally stimulated luminescence (TSL). A TL curve may be obtained when a solid sample, usually an insulator or semiconductor, is heated after having been exposed to various irradiations such as nuclear irradiation (α, β, γ irradiations and particle bombardment), X-rays, ultraviolet light and sometimes visible and infra-red light at low temperature. Energy absorbed by the sample is emitted, during the heating, as light in the form of a "glow curve". The position, shape and intensity of the glow peaks are related to the various parameters of the trapping states which are responsible for the TL.

The first theoretical treatment for a well isolated TL peak was given by Randall and Wilkins [1] who suggested the following equations

$$I = -C(\mathrm{d}n/\mathrm{d}t) = C.s.n \exp(-E/kT) \quad (1)$$

where I is the TL intensity, s the frequency factor (the pre-exponential factor) ($\sec^{-1}$), n the concentration of trapped electrons (cm^{-3}), T the absolute temperature, k Boltzmann's constant ($eV\,K^{-1}$), and C a proportionality factor which can be set equal to unity without any loss of generality as long as it remains constant with temperature (see below).

The solution of this equation gives, for the TL intensity, assuming $C = 1$ and using a linear heating scheme

$$I = n_0 s \exp(-E/kT)$$
$$\exp\left[-(s/\beta) \int_{T_0}^{T} \exp(-E/kT')\mathrm{d}T'\right] \quad (2)$$

where n_0 is the initial concentration of the trapped electrons, T_0 the initial "low" temperature, and β is the constant heating rate ($K \, sec^{-1}$), i.e. $T = T_0 + \beta t$.

Garlick and Gibson [2] suggested another approximation, more suitable for some of the glow peaks, which is represented by

$$I = -dn/dt = s'n^2 \exp(-E/kT) \qquad (3)$$

where s', the pre-exponential factor, is a constant with dimensions of $cm^3 \, sec^{-1}$ which should, therefore, not be referred to as the "frequency" factor. This case is usually called "second order kinetics", whereas the previous case is "first order kinetics". The solution of Equation 3 is

$$I = n_0^2 s' \exp(-E/kT)$$
$$\left[1 + (n_0 s'/\beta) \int_{T_0}^{T} \exp(-E/kT') dT' \right]^{-2}. \quad (4)$$

Equations 1 and 3 do not cover every possible isolated peak; this is apparently covered by a set of three simultaneous differential equations (see Section 2). Many authors [3–10] found it attractive and very useful to assume a "general" order kinetics, namely, assuming that the glow curve is governed by

$$I = -dn/dt = s'n^b \exp(-E/kT) \qquad (5)$$

where b is the kinetic order, and s' the pre-exponential factor in $sec^{-1} \, cm^{3(b-1)}$.

The pre-exponential factor s', while sometimes considered to be temperature independent, may in other cases be slightly dependent on temperature (e.g. T^2) [11–13]. Under appropriate conditions, thermally stimulated conductivity (TSC) (see Section 3) peaks would follow the same equation with s' proportional to T^a and where a is not necessarily 2 but rather has various values in the range $-2 \leqslant a \leqslant 2$ [14–15]. These values result from the various dependences on temperature of the cross-section for recombination [16–17]. Equation 5 and the dependence of s' on temperature were summed up by Razdan et al. [18] as follows:

$$I = -C \cdot dn/dt = Cs''T^a n^b \exp(-E/kT) \quad (6)$$

where $s' = s''T^a$, s'' being a constant.

Many methods for evaluating the activation energy of a glow curve were developed. Shalgaonkar and Narlikar [19] gave a review summing up many of these methods (see also [20]). Some methods

for evaluating the pre-exponential factor and the kinetic order were also given [4, 21] (for details see Section 2.1). Some of these methods were independently developed for other thermally stimulated processes. The main purpose of the present paper is to indicate the similarities (and differences) between the various phenomena, and especially to show that methods known to be suitable for analysis of TL peaks can quite easily be applied to many of the other cases. Thus, the analysis of a thermally stimulated peak would be the same, no matter what specific phenomenon is being investigated. In addition, some properties of the individual effects will be discussed.

2. Thermoluminescence
2.1. General theory
Halperin and Braner [12] wrote a set of three linear simultaneous equations to account for a single TL peak as follows

$$I = -dm/dt = A_m m n_c \qquad (7)$$
$$-dn/dt = sn \exp(-E/kT) - A_n(N-n)n_c \quad (8)$$
$$dn_c/dt = dm/dt - dn/dt, \qquad (9)$$

where N is the concentration of traps (cm^{-3}); n the concentration of electrons in traps (cm^{-3}); n_c the concentration of free electrons in the conduction band (cm^{-3}); A_m and A_n the recombination and retrapping probabilities ($cm^3 \, sec^{-1}$), respectively; and m is the concentration of holes in recombination centres (cm^{-3}). Here, the proportionality factor between the intensity I and $-dm/dt$ was set arbitrarily to unity, $I(T)$ would, therefore, be given in arbitrary units. These equations still deal with a single TL peak but are much more general than the Randall–Wilkins or Garlick–Gibson cases which assumed negligible and dominating retrapping, respectively. It is to be noted that the same equations are valid for the "inverse" case where the TL results from holes thermally released from hole traps into the valence band and subsequently recombining with electrons in centres. A by-product of a solution of this set of differential equations is $n_c = n_c(t)$, which is closely related to the conductivity (TSC) curve (see below). A slightly different set of equations has also been given by Halperin and Braner [12] for the case of electrons (or holes) which are thermally elevated to an excited state in the forbidden gap rather than the conduction (valence) band.

Halperin and Braner [12], as well as other workers [13, 22–25], looked for a solution to these equations, by assuming that

$$|dn_c/dt| \ll |dn/dt|; \qquad n_c \ll n \qquad (10)$$

which are reasonable in many cases. By doing so, Halperin and Braner found that

$$I = -dm/dt$$

$$= sn \exp(-E/kT) A_m \cdot m/[A_m m + A_n(N - n)]. \qquad (11)$$

It is important at this point to note the conditions for obtaining the first and second order kinetics equations from Equation 11. The Randall and Wilkins [1] case is known to be the case of negligible retrapping; under the present notation this would mean $A_m m \ll A_n(N - n)$, by which Equation 11 reduces to

$$I = -dm/dt = sn \exp(-E/kT). \qquad (12)$$

Using Conditions 10, Equation 9 reduces to $dn/dt = dm/dt$, and therefore Equation 12 becomes the regular first order case, namely Equation 1 with $C = 1$ as assumed above. The second order kinetics can result from Equation 11 by either of two sets of assumptions. A necessary condition in both cases is $n = m$, which is a quite restrictive condition by itself. In addition, Garlick and Gibson [2] assumed predominating retrapping which in our notation would be $A_n(N - n) \gg A_m m$. If we assume, in addition, that we are far from saturation, i.e. $N \gg n$, we get

$$I = -dn/dt = (sA_m/NA_n)n^2 \exp(-E/kT) \qquad (13)$$

which is Equation 3 with $s' = sA_m/NA_n$. Alternatively, if we assume in addition to $n = m$, equal recombination probabilities for centres and traps [26] (i.e. $A_m = A_n$), an equation equivalent to Equation 3, with $s' = s/N$, is again obtained.

It is evident that first and second order kinetics are only special cases whereas many TL single peaks are neither of first nor of second order. One way of analysing a TL peak, obtained using a linear heating function, is by considering its symmetry properties. The second order peaks are characterized by a practically symmetrical peak, whereas the first order peaks are asymmetrical, where τ – the half-width at the low temperature side of the peak – is almost 50% bigger than δ – the half-width towards the fall-off of the glow peak (see Fig. 1). An empirical way to deal with
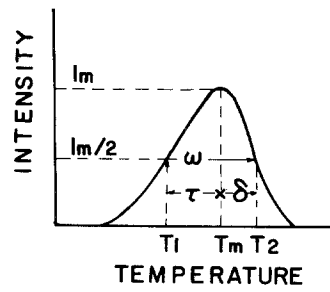

Figure 1 An isolated glow peak showing the parameters $\omega = T_2 - T_1, \tau = T_m - T_1, \delta = T_2 - T_m$.

intermediate cases is "general order" kinetics mentioned in Equation 5 with b being different from 1 or 2. This empirical approach [3–10] was found to be satisfactory for explaining the occurrence of various symmetry factors, $\mu_g = \delta/\omega$, where $\omega = \tau + \delta$ is the total half-width. The activation energies found by using this approach [4] were also satisfactory [27] (for details see Section 2.2).

It is of interest to note that equations identical with Equation 1 can be found where s is replaced by other constants having different physical meanings [28]. One possibility is to take Equation 7, which has quite general meaning (see Section 3), and to assume that the concentration of the conduction electrons depends exponentially on temperature and is only slightly affected by the excitation. This should fit the case of n-type semiconductors when the electrons from donor levels are released thermally into the conduction band and emit light, on recombination, at luminescence centres emptied during excitation. The analogous case of p-type semiconductors might fit the glow peaks obtained in semiconducting diamonds. In this case, measurements of conductivity as a function of temperature show that the concentration of free carriers (free positive holes) rises exponentially with temperature [29, 30], namely, $n_c = a \exp(-E/kT)$, where the factor a is directly connected with the concentration of holes in acceptor levels. Therefore, from Equation 7

$$I = -dm/dt = a \cdot A_m m \exp(-E/kT) \qquad (14)$$

This is the Randall–Wilkins equation with the frequency factor s replaced by $a \cdot A_m$.

Another possibility is when the transition is within one localized centre [13, 28]. In other words, traps and recombination centres form associated pairs, and thermal excitation raises the

trapped electrons to an excited level from which they may either be retrapped or emit luminescence by falling down to the ground level of the centre. The kinetics in this case are formulated by the following equations

$$I = -\mathrm{d}m/\mathrm{d}t = Pn_e$$

$$-\mathrm{d}n/\mathrm{d}t = s\exp(-E/kT)n - sn_e$$

$$m = n + n_e \qquad (15)$$

where $P(\mathrm{sec}^{-1})$ is the probability for recombination of an excited electron and n_e is the concentration of excited electrons. We again assume $n_e \ll n$ and hence $n = m$. From Equations 15 we now have $n_e = s\exp(-E/kT)n/(P + s)$, and inserting this expression into the first of Equations 15 we obtain

$$I = -\mathrm{d}m/\mathrm{d}t = [Ps/(P + s)]\,m\exp(-E/kT). \quad (16)$$

This is again the Randall—Wilkins equation, but with $\bar{s} = Ps/(P + s)$ replacing s. It is obvious that for very high recombination probabilities $(P \gg s)$, $\bar{s}$ reduces to s. On the other hand, for relatively low recombination rate $(s \gg P)$, $\bar{s}$ reduces to P. This can explain the appearance of the relatively low effective frequency factor s.

Coming back to the solution of Equations 7—9, these have been numerically solved without Conditions 10; Kelly et al. [31] used the Runge—Kutta—Gill fourth order process and by properly choosing the step size, obtained the exact solutions for given sets of parameters. The validity of the approximations given in Conditions 10 were found by Kelly et al. to depend critically on N, the number of active traps. For $N < 10^{15}$ cm^{-3} they found that the conventional approximations are inadequate. Shenker and Chen [27] used a change of variable by which the high sensitivity of the solution to small numerical errors is overcome; another version of the Runge—Kutta method has been employed. The symmetry parameters of the calculated peaks were used to calculate the activation energy of the peak. Although a method derived from an approximate empirical model (Equation 5) is used for an exact solution peak, the results of E (see Section 2.2) were found to be correct within 5% of the given activation energy.

It is to be mentioned here that as a by-product of either the approximate or the exact solution, one obtains the values of n_c as a function of T. This enables the calculation of the corresponding TSC peak by $\sigma(T) = e\mu n_c$ provided that $\mu(T)$ is

known (see Section 3). This mobility is usually known from separate measurements and is somewhat temperature dependent, like $T^{-\alpha}$, α being typically between 1.5 and 3.

Kelly et al. [25, 31] claim that dealing with the general three equations model, one cannot extract any information other than the value of E from TL and TSC data (and simultaneous measurement of both) unless one knows at least the luminous efficiency and the mobility. As is shown in Section 3.2, we can evaluate another important parameter, the recombination probability (and the recombination cross-section therefrom) knowing only the mobility, which, as mentioned above, can be found separately.

It is relevant at this point to mention the main difficulties in analysing a glow curve; some of these difficulties occur in the other thermally stimulated processes as well. A crystal usually has several kinds of defects and impurities and, therefore, it may possess various traps and centres. This usually produces a number of glow peaks; as long as these peaks are far apart, each of them can be considered to be a single peak. The situation becomes more difficult when two or more peaks overlap. This can be partly improved by thermal cleaning of a peak, heating the sample up to a certain temperature so as to thermally bleach all the components except for one, then cool the sample and reheat it in order to examine the remaining clean (or, at least, partially clean) peak. Another possible method to distinguish between neighbouring peaks is to take spectrally separated emitted light in cases where different recombination centres are involved. Another problem is that in addition to the possibility of several peaks resulting from several electron traps and recombination centres, other peaks may occur in the same temperature range resulting from holes released from hole traps and subsequently recombining into electron centres. These two cases can be discerned by the TSEE effect (see Section 4). The possible case of a TL peak resulting from thermal elevation into an excited state which is not a band, then recombining into a centre in the close vicinity, can be perceived by the lack of both TSC and TSEE peaks.

Recent work by Wintle [32, 33] should be mentioned here. Wintle introduces the possibility of a recombination probability which depends, in a certain temperature range, exponentially on the temperature, $A_m \propto \exp(W/kT)$, where W is an

energy depth characterizing a non-radiative process. Under these special circumstances, the glow intensity for the first order kinetics would be given by altering Equation 2 to give

$$I = Ksn_0 \exp\left[(W-E)/kT\right]$$
$$\exp\left[-(s/\beta)\int_{T_0}^{T} \exp(-E/kT')dT'\right]. \quad (17)$$

The activation energies calculated by certain methods (see Section 2.2) would yield the value E whereas by other methods the value $E-W$ will be found.

2.2. Methods for evaluating the activation energy

The various methods for evaluating the activation energies will be mentioned here only briefly, reference is made to the review article by Shalgaonkar and Narlikar [19, 20]. The methods to be mentioned in this section can be classified as follows: (1) Methods based on the temperature at the maximum. (2) the initial rise method. (3) Methods employing the shape parameters of the peak. (4) Numerical curve fitting. (5) Various heating rates. (6) Isothermal decay.

The first method for calculating activation energies by TL curves was given by Urbach [34] who found empirically that a reasonable estimate for the trap energy, E, in eV is given by $E = T_m/500$ where T_m is the temperature of the glow maximum in K. Garlick and Gibson [2] suggested the method, usually considered to be more general than others, known as the initial rise method. Studying Equation 5 (which includes as special cases Equations 1 and 3 for $b = 1$ and $b = 2$ respectively), we can see that at the beginning of the glow peak n changes only slightly with temperature and, therefore, $I \propto \exp(-E/kT)$. Thus, plotting $\ln I$ as a function of $1/T$ should yield a straight line in this region, the slope of which is $-E/k$. The method has further been developed by Gobrecht and Hofmann [35] who used subsequent heating and cooling cycles to obtain the "spectroscopy of the traps". Another improvement, by Halperin et al. [36, 37] suggests the plotting of $\ln(I/n^b)$ versus $1/T$ where the kinetic order b is known, thus obtaining a broader range in which the curve is a straight line. When the kinetic order is not known, several lines are drawn with various values of b (1, 2 and intermediate values) and the best straight line is chosen. Thus,
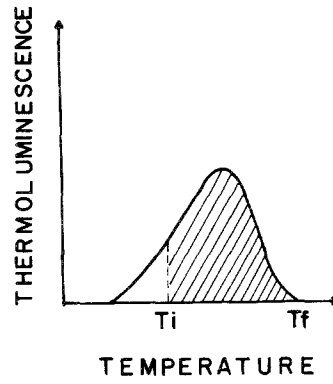

Figure 2 An isolated glow peak. The shaded area is proportional to the concentration of carriers in the trap at the temperature T_i.

the best value for E is found as well as an evaluation of the kinetic order b. The value of n is estimated by the area of the glow peak from a given point T_i in the initial rise region to the end of the peak as shown in Fig. 2. One should have from $I = -dn/dt$

$$n = \int_{t_i}^{t_f} I \, dt = (1/\beta)\int_{T_i}^{T_f} I \, dT \quad (18)$$

where T_f is the end of the glow peak (theoretically $T_f = \infty$).

The initial rise method is expected to be valid beyond the limitations of Equation 5. Considering the set of Equations 7 to 9, one should note that in the initial rise range, n_c should behave like $\exp(-E/kT)$ (therefore, the method can be used for TSC and TSEE as well). Equation 7 guarantees that as long as $m \approx m_0$, which occurs in the initial rise range, $I \propto \exp(-E/kT)$.

Some theoretical [38, 39] as well as experimental [40] reasons limit the use of the initial rise method. Thus, Bräunlich [39] showed that if a trap is filled to saturation, too small values of the activation energy will be found. One should also note that in Wintle's case [32, 33], the initial rise method should yield $E-W$ rather than E (Equation 17). In cases where the pre-exponential factor is temperature dependent as T^a [38] the initial rise range would behave like $I \propto T^a \exp(-E/kT)$. The initial rise method would mean finding

$$E_{i.r.} = -k \, d(\ln I)/d(1/T) \quad (19)$$

which in the present case is

$$E_{i.r.} = E + akT \rightarrow E = E_{i.r.} - akT. \quad (20)$$

This may amount to a few percent correction in the value of E.

TABLE I Coefficients appearing in Equation 24 for the various methods of calculating activation energies

c	First order			Second order		
	τ	δ	ω	τ	δ	ω
c_α	1.51	0.976	2.52	1.81	1.71	3.54
b_α	1.58 + (a/2)	a/2	1 + (a/2)	2 + (a/2)	a/2	1 + (a/2)

Another method, based on the Randall–Wilkins [1] solution involves the measuring of T_m. Differentiating Equation 2 and equating to zero one gets

$$\beta E/kT_m^2 = s \exp(-E/kT_m). \quad (21)$$

If one assumes a certain value for s, this transcendental equation can serve for calculating E. An interesting feature, unique to the first order case results from Equation 19; the initial concentration n_0 does not appear in this equation, therefore, the first order peak is not expected to shift with various doses of excitation. An explicit expression for the evaluation of E was found by numerical calculations [26, 41] as follows

$$E(\text{eV}) = [T_m - T_0(\beta/s)]/K(s/\beta) \quad (22)$$

where T_0 and K are numerical factors given in tables as a function of (β/s). This equation, which is an improvement of Urbach's method, still has the disadvantage that one has to assume the value of the frequency factors beforehand.

A number of methods have been developed which do not require an *a priori* assumption on the pre-expenential factor. Grossweiner [42] gave the following approximate equation for the first order case

$$E = 1.51 \, kT_m T_1/\tau \quad (23)$$

where T_1 is the lower half intensity temperature and $\tau = T_m - T_1$. The numerical factor 1.51 has been replaced by 1.41 [15] following a more detailed numerical study.

Lushchik [43] suggested methods based on the measurement of $\delta = T_2 - T_m$ for the first and second order cases, where T_2 is the higher half intensity temperature. Halperin and Braner [12] suggested a method based on the measurement of τ for both the first and second order cases. They also introduced the symmetry factor $\mu_g = \delta/\omega$, where $\omega = T_2 - T_1$. Chen [15] presented a method based on the measurement of T_m and ω and suggested numerical corrections to the method of Lushchik and Halperin and Braner. It is to be noted here that once we find the value of E by any

method, its substitution in Equation 21 would yield the frequency factor s.

The τ, δ and ω methods can be summed up in the following formula

$$E_\alpha = c_\alpha(kT_m^2/\alpha) - b_\alpha(2kT_m) \quad (24)$$

where α is τ, δ or ω. The values of c_α and b_α for the three methods and for the first and second order processes are given in Table I. The factor a appearing in b_α is related to the possible dependence of the pre-exponential factor on temperature, like T^a. The addition of $a/2$ is equivalent to the subtraction of akT from the otherwise calculated value of E_α. This is the equivalent to the subtraction of akT under the same condition while using the initial rise method (Equation 20).

Chen [15] has also discussed the comparative merits of the three kinds of methods (τ, δ, ω) for various cases and also showed that for a first order peak $\mu_g = 0.42$ whereas a second order peak is characterized by $\mu_g = 0.52$. In another paper, Chen [4] showed that when one has a "general order" case (Equations 5 and 6), one can evaluate the kinetic order by the value of μ_g. A calculated graph of μ_g, ranging from 0.36 to 0.55 for values of b between 0.7 and 2.5 is given, which can be used for the evaluation of b from a measured μ_g. The coefficients c_α and b_α in Equation 24 are calculated by interpolation as follows

$$c_\tau = 1.51 + 3.0 \, (\mu_g - 0.42);$$

$$b_\tau = 1.58 + 4.2 \, (\mu_g - 0.42) + (a/2) \quad (25)$$

$$c_\delta = 0.976 + 7.3 \, (\mu_g - 0.42); \quad b_\delta = a/2 \quad (26)$$

$$c_\omega = 2.52 + 10.2 \, (\mu_g - 0.42); \quad b_\omega = 1 + (a/2) \quad (27)$$

These methods were applied to calculated general order peaks and yielded activation energies deviating only by a few percent from the known ones.

To conclude the discussion about the general order kinetics, it seems fit to write explicitly the solution of Equation 5 in this general case [4]

$$I = s'n_0^b \exp(-E/kT) \cdot \left\{ [(b-1)s'n_0^{(b-1)}/\beta] \right.$$
$$\left. \int_{T_0}^{T} \exp(-E/kT')\mathrm{d}T' + 1 \right\}^{-b/(b-1)} . \quad (28)$$

This, certainly, includes the better known second order case ($b = 2$) given in Equation 4. $s'n_0^{b-1}$ has the units of $\sec^{-1}$ and in this sense it is similar to s in the first order case. If one writes s instead of $s'n_0^{b-1}$, one has

$$I = sn_0 \exp(-E/kT) \cdot \left\{ [(b-1)s/\beta] \right.$$
$$\left. \int_{T_0}^{T} \exp(-E/kT')\mathrm{d}T' + 1 \right\}^{-b/(b-1)} . \quad (29)$$

Although Equation 29 is not valid for the case $b = 1$, it can easily be shown that it reduces to Equation 2 when $b \to 1$.

The condition for maximum is found by equating the derivative of Equation 29 to zero

$$[(b-1)s/\beta] \int_{T_0}^{T_\mathrm{m}} \exp(-E/kT)\mathrm{d}T + 1 =$$
$$(sbkT_\mathrm{m}^2/\beta E) \exp(-E/kT_\mathrm{m}). \quad (30)$$

Owing to the dependence of s on n_0 for $b \neq 1$, and through it, on the excitation dose, one should expect T_m, as found from Equation 30 to be dose dependent. For the case of $b = 2$ this dependence has further been investigated [2, 44]. Once the activation energy E is calculated and the kinetic order b is evaluated, Equation 30 can be used for finding $s = s'n_0^{b-1}$. The constant s' can be found only if information on n_0 is available independently.

Another class of methods is the numerical curve fitting, which was shown to be more accurate (although somewhat tedious) than previous methods. Curve fitting was used for the initial rise region [45] and for the entire curve. First order [46, 47], second order [48] and general order [21] cases were studied. In the latter, the activation energy, pre-exponential factor and the kinetic order could thus be evaluated. The use of these methods was facilitated by employing a computer.

Another group of important methods is that of various heating rates. Bohun [50] and Parfianovitch [51] suggested that if a sample is heated at two different linear heating rates, β_1 and β_2, the peak temperature T_m will be different. Equation 21 can, therefore, be written once for β_1 and once for

β_2 with their corresponding $T_{\mathrm{m}1}$ and $T_{\mathrm{m}2}$. Dividing these equations one by the other, one gets an explicit equation for the calculation of E:

$$E = [kT_{\mathrm{m}1}T_{\mathrm{m}2}/(T_{\mathrm{m}1} - T_{\mathrm{m}2})]$$
$$\ln [(\beta_1/\beta_2)(T_{\mathrm{m}2}/T_{\mathrm{m}1})^2] . \quad (31)$$

Hoogenstraaten [52] suggested the use of several (linear) heating rates; plotting $\ln(T_\mathrm{m}^2/\beta)$ versus $1/T_\mathrm{m}$ should yield, according to Equation 21, a straight line from whose slope E/k, E is found. It is to be noted that even in Wintle's case [32, 33] mentioned above, using this method would yield E rather than $E-W$ which is found by the initial rise method. This is so, since the equation corresponding to Equation 21 in this case is

$$\beta(E-W)/kT_\mathrm{m}^2 = s \exp(-E/kT_\mathrm{m}). \quad (32)$$

Thus, by finding E by one method and $E-W$ by another, a good estimate of W can be found. Osada [53] proved that Equation 21 is true for an exponential heating function, $T = T_\infty - (T_\infty - T_0) \exp(-\alpha t)$ where $\alpha(\sec^{-1})$ is a constant. The linear heating rate β should be replaced here by the instantaneous heating rate β_m at T_m. Haering and Adams [54] have shown that for first order TSC peaks the maximum intensity is proportional to $\exp(-E/kT_\mathrm{m})$ (which is also true for first order TL peaks). Thus, plotting $\ln(\sigma_\mathrm{m})$ (or $\ln(I_\mathrm{m})$) as a function of $1/T_\mathrm{m}$ should give a straight line with a slope of $-E/k$. Another *approximate* method using various linear heating rates [22, 55] suggests the plotting of $\ln(1/\beta)$ versus $1/T_\mathrm{m}$ which should yield a straight line whose slope is E/k.

Chen and Winer [44] proved that Equation 21 is correct for *any* heating rate where β_m, again replaces β. This leads directly to the validity of Equation 31 for this general case as well as to the method of Hoogenstraaten. They also showed that for the general order case, one can plot $\ln[I_\mathrm{m}^{b-1}(T_\mathrm{m}^2/\beta)^b]$ versus $1/T_\mathrm{m}$ and get a straight line with a slope of $1/T_\mathrm{m}$. Moreover, they showed that even for cases other than first order (including $b = 2$) and for non-linear heating rates, plotting $\ln I_\mathrm{m}$ or $\ln(\beta_\mathrm{m}/T_\mathrm{m}^2)$ versus $1/T_\mathrm{m}$ would yield a straight line having a slope of $-E/k$ to a very good approximation.

A number of other methods are briefly to be mentioned here (see also Shalgaonkar and Narlikar's review article [19, 20]). Another method based on the measurement of T_1, T_m and

T_2 is that of Keating [14]. Land [13] suggested a method which uses, in addition to T_m, the two inflection points in the TL curve rather than the half intensity temperatures T_1 and T_2. Maxia et al. [56] suggested a somewhat complicated method for evaluating the activation energy and frequency factor. They deal with a multiple peak glow curve and assume that the various peaks result from the evaluation of electrons from a single trap and their recombination into various recombination centres. Onnis and Rucci [57] discussed an alternative explanation of obtaining several glow peaks, namely, having several traps and a single recombination centre. A shortcoming of this method is the assumption that the electrons can be retrapped only in the levels from which they have been released. Moreover, the possible general case of a series of peaks resulting from several traps as well as various recombination centres (in the same sample), has not been considered. Under these assumptions, they could find, in addition to E and s, the ratio between the probabilities for recombination and retrapping.

Last to be mentioned is the method of isothermal decay [58] which is not exactly a TL method but enables, however, the measurement of E and s in the first order case. If one holds a sample at a constant temperature in a range where TL appears during heating, one can measure the isothermal decay (phosphorescence) which is given as the solution of Equation 1 for the $T = $ const. case as follows

$$I(t) = ns \exp(-E/kT) \exp\left[-st \exp(-E/kT)\right]. \tag{33}$$

Plotting $\ln[I(t)]$ as a function of t would give a straight line (the occurrence of a straight line ensures the first order property) the slope of which is

$$M = s \exp(-E/kT). \tag{34}$$

Repeating the measurement at various temperatures, one gets various values of M. Plotting $\ln(M)$ as a function of $1/T$ should give a straight line with the slope $-E/k$, thus enabling the evaluation of E, and by substituting into Equation 34, the value of s. As mentioned by Wintle [32, 33], this method should yield the value of E (rather than $E-W$) in the case of exponentially temperature dependent recombination probability (see above).

Tables of experimental values obtained by applying some of these methods to TL curves in KCl and KBr can be found, for example in the papers by Ratnam and Gartia [59]. Similar tables for ITC curves appear in [153].

2.3. The integrals appearing in TL theory

The problem of evaluating the integrals appearing in the theory of glow curves will be discussed in this section. The solutions of, for example, Equations 1, 3 and 5 involves the integral

$$J = \int_{t_0}^{t} \exp(-E/kT)\,d\theta \tag{35}$$

when one deals with temperature independent pre-exponential factor. A number of authors [60–63] suggested the use of hyperbolic heating functions to facilitate the evaluation of J in Equation 35. The hyperbolic heating function defined by $T_0^{-1} - T^{-1} \propto t$ is characterized by $dT/dt \propto T^2$ which transforms Equation 35 into

$$J = \int_{T_0}^{T} (\gamma/T'^2) \exp(-E/dT')\,dT' \tag{36}$$

where γ is a constant. This is an elementary integral giving

$$J = (\gamma k/E)\left[\exp(-E/kT) - \exp(-E/kT_0)\right]. \tag{37}$$

When the more frequently used linear heating rate $T = T_0 + \beta t$ is taken, one gets

$$J = (1/\beta) \int_{T_0}^{T} \exp(-E/kT')\,dT'. \tag{38}$$

The integral in Equation 38 can be written as

$$\int_{T_0}^{T} \exp(-E/kT')\,dT' = F(T, E) - F(T_0, E) \tag{39}$$

where $F(T, E)$ is defined as

$$F(T, E) = \int_{0}^{T} \exp(-E/kT')\,dT'. \tag{40}$$

Since $F(T, E)$ is a very strongly increasing function of T, it is conventional to neglect $F(T_0, E)$ in comparison to $F(T, E)$. In the theory of thermally stimulated processes, E/kT is practically always of the order of 10 or more; for this range of values, a very useful method for evaluating $F(T, E)$ is by the asymptotic series found by successive integrations by parts [40, 42, 64]

$$F(T, E) = T \exp(-E/kT)$$

$$\sum_{n=1} (kT/E)^n (-1)^{n-1} n! \tag{41}$$

The series on the right hand side of Equation is divergent, but may give a good approximation for the value of the integral as follows. If one takes N terms in this asymptotic series,

$$S_N = \sum_{n=1}^{N} (kT/E)^n (-1)^{n-1} n!, \quad (42)$$

the absolute value of the maximal error $|R_N|$ would not exceed the absolute value of the $(N+1)$th term, a_{N+1}, thus

$$|R_N| = |a_{N+1}| = (kT/E)^{N+1} (N+1)! \quad (43)$$

Chen [64] showed that an optimal value of $F(T, E)$ is found when one takes the terms in the series down to the smallest one (in which $(kT/E)N \simeq 1$) and adding one half of the following term. Following Dingle [65], Chen [66] showed that the adding of one half of the next term, reduces the possible error to $(1/100)|a_{N+1}|$, namely

$$(1/100)(kT/E)^{N+1}(N+1)!.$$

It has also been shown [64, 66] that a convenient expression for the relative possible error is

$$|R_N/F(T, E)| \approx (1/100)\sqrt{[2\pi(E/kT)^3]}$$
$$\exp(-E/kT). \quad (44)$$

For $E/kT = 10$ one can thus calculate $F(T, E)$ to a relative error of $\sim 3 \times 10^{-5}$ [67]; for $E/kT = 15$ the relative possible error would be 4×10^{-7}. As seen from Equation 44, the bigger E/kT, the smaller the relative error.

Alternative methods for the evaluation of $F(T, E)$ were given by Squire [68] and Paterson [69]. Sullivan [70] extended the method to the case of non-linear heating rates. Another extension was given [71] for the cases of temperature dependent pre-exponential factors, $s = s''T^a$, where s'' is a constant. Here

$$F(T, E, a) = \int_0^T T'^a \exp(-E/kT') \, dT' \quad (45)$$

is evaluated using the asymptotic series

$$F(T, E, a) = (kT^{a+2}/E) \exp(-E/kT) \cdot$$
$$\left\{ 1 - [1/\Gamma(a+2)] \sum_{n+2} (kT/E)^{n-1}(-1)^{n-1}\Gamma(a+n+1) \right\}$$
$$(46)$$

where $\Gamma(x)$ is the gamma function. Again, one takes the terms down to the smallest one in which $N \approx E/kT - a$ and adds one half of the following term.

The possible relative error in this case is

$$|R_N/F(T, E, a)| = (1/100)\sqrt{(2\pi)}(E/kT)^{a+3/2}$$
$$\exp(-E/kT)/\Gamma(a+2). \quad (47)$$

3. Thermally stimulated conductivity (TSC)
3.1. Analysis of TSC measurements

A TSC curve is observed when a sample having two electrical contacts is excited by any of the ways described in the TL case (nuclear radiation, X-rays, etc) at a certain "low" temperature and subsequently heated when a constant voltage is applied between the terminals. In certain temperature ranges, changes in the conductivity occur in the form of "electrical glow curves". The conductivity σ is directly related to n_c, the concentration of electrons in the conduction band (or holes in the valence band) through the equation

$$\sigma = e\mu n_c \quad (48)$$

where e is the electronic charge and μ the mobility. Since μ is usually only slightly temperature dependent (the possible dependence on temperature will be separately discussed in Section 3.2) this means that σ is almost exactly proportional to n_c.

Several investigators [14, 46, 54, 72–79] assumed a constant lifetime τ; in our notation this would mean that m in Equation 7 is practically constant. The meaning of τ in this case is $(1/mA_m)$. Making this assumption, one gets TSC curves which are exactly the same as the TL curves discussed above. Most of these authors measured TSC peaks that looked like first order curves and used the various methods known from TL theory for the evaluation of s and E for the TSC curves. These include the initial rise method, the various shape methods and the methods based on various heating rates.

Haering and Adams [54] investigated two extreme cases, slow retrapping and fast retrapping. Slow retrapping is characterized by $(N_i - n_i)$ $Sv \ll \tau^{-1}$ where N_i is the concentration of trapping states, n_i the concentration of electrons in traps, S the cross-section for trapping an electron and v the thermal velocity of electrons in the conduction band. Under these conditions and assuming a linear heating rate $T = T_0 + \beta t$, one gets

$$\sigma(T) = N_c Sve\mu\tau n_0 \exp(-E/kT)$$
$$\exp\left[-(N_c Sv/\beta) \int_{T_0}^T \exp(-E/kT') dT' \right]$$
$$(49)$$

where N_c^a is the density of thermally available states in the conduction band. The product $N_c S v$, which has the dimensions of $\sec^{-1}$, replaces here the frequency factor s in the TL case. Otherwise this is a simple first order function that can be treated as any first order TL peak. The other case is fast trapping in which $(N_i - n_i) S v \gg \tau^{-1}$. The conductivity curve is given here as

$$\sigma(T) = (N_c/N_i)\,\mu e n_0 \exp(-E/kT)$$
$$\exp\left\{- [N_c/(N_i\beta\tau)] \int_{T_0}^{T} \exp(-E/kT')\mathrm{d}T'\right\}$$
$$(50)$$

In this equation $N_c/(N_i\tau)$ replaces the frequency factor, the curve being still of the first order kind. Both $N_c S v$ in Equation 49 and $N_c/(N_i\tau)$ in Equation 50 may be slightly temperature dependent and, therefore, should not be taken out of the integrals as constants. This dependence is expected, however, to behave like T^a and, therefore, the same treatment as in the TL temperature dependent frequency factor, can be given. This case for $a = 2$ was discussed by Buehler [76].

Nicholas and Woods [72] examined first and second order TSC curves and used many of the methods previously developed for TL glow curves, for the TSC peaks. Among other things, they evaluated the cross-section for retrapping from the effective frequency factors found for several peaks in CdS. A recent paper by Rabie and Rumin [80] discussed first order TSC peaks assuming a constant lifetime for a given sample. In their samples of Zn compensated Si, however, the lifetime τ depended strongly on the concentration of negatively charged Zn ions. Thus they got a series of samples having the same activation energy E, but various values of τ. Assuming fast retrapping, a condition for the maximum, similar to Equation 21 would be in this case

$$\exp(E/kT_m) = N_c k T_m^2 /N_i\beta\tau E) \qquad (51)$$

and thus, the maximum temperature would depend on τ. This effect cannot be seen in the slow retrapping case. Equation 51 can be written as

$$1/T_m = (k/E) \ln (T_m^2/\tau) + A. \qquad (52)$$

In a way somewhat similar to the various heating rates method, one can plot $\ln(T_m^2/\tau)$ versus $(1/T_m)$ and get a straight line, the slope of which yields the value of E. The various values of τ are separ-

ately determined from steady state photocurrent measurements. In a series of papers, Simmons et al. [81–86] investigated various aspects of TSC, in particular in metal–insulator–semiconductor (MIS) systems. For evaluating the activation energy they used an approximate equation by which E is found.

$$E = T_m [1.92 \times 10^{-4} \log_{10} (s/\beta)$$
$$+ 0.32 \times 10^{-3}] - 0.0155\,\mathrm{eV}. \quad (53)$$

Here too, one has to have a priori a good estimate on the value of s for obtaining accurate values of E.

Taylor [73] discussed the case of a general kinetic order assuming a constant life time τ, and found orders of $b = 1; 1.3;$ and 1.6 in different TSC peaks in KBr. The assumption that τ remains always constant has been questioned by Saunders [87] who claimed that since $\tau = 1/(A_m m)$, it should increase with temperature as m decreases. For the second order case, (which includes the assumption $n = m$), he obtained the expression for the conductivity,

$$\sigma = e\mu\tau I = (s_1/s)\mu e N_c \exp(-E/kT) \cdot$$
$$\left[1 + (s_1/\beta) \int_{T_0}^{T} \exp(-E/kT')\mathrm{d}T'\right]^{-1} (54)$$

where s is the regular frequency factor, $s_1 = n_0 s/N$, n_0 and N were defined in Section 1. Chen [88] further investigated this expression and showed that it is characterized by very slow fall-off at the high temperature region, namely, that characteristic values of $\mu_g = \delta/\omega$ are in this case about 0.8. Manchanda and Mathur [89] studied this case when the hyperbolic heating function is used. The simplification, as mentioned before for other cases, is due to the simple expression for the integral in Equation 54.

A similar treatment was given [90] (see also [25]) to a TSC peak corresponding in a similar manner, to a first order TL peak. The TSC peak was found to appear at a lower temperature than its TL counterpart (see Section 3.2). The expression for σ in this case is

$$\sigma(T) = (s/A_m) \exp(-E/kT)/$$
$$\left\{1 + \alpha \exp\left[(s/\beta) \int_{T_0}^{T} \exp(-E/kT')\mathrm{d}T'\right]\right\}$$
$$(55)$$

where $\alpha = c/n_0$ and where c is the number of trapped electrons in traps deeper than the one emitting electrons thermally at the range of appear-

ance of the peak. This means that in this range $n + c = m$. For very high values of α, Equation 55 reduces to the simple first order case, but it differs from it for $\alpha \ll 1$. In these cases one gets very low values of μ_g; for $\alpha = 10^{-4}$, for example, a value of $\mu_g = 0.267$ was found. An approximate method for finding the activation energy was found empirically

$$E = 2.8 \, kT_m^2/\theta \qquad (56)$$

where $\theta = \tau\mu_g = \tau\omega/\delta$. Quite surprisingly, it has been found [91] that this equation gives a reasonable, although rough, estimate (within an accuracy of 15%) for the activation energy in all the above-mentioned cases. These include the Saunders TSC case given in Equation 54, the first order, second order and general order TL cases. It is to be noted here that the initial rise method is also applicable for the cases in Equations 54 and 55.

3.2. Simultaneous measurements of TSC and TL

As mentioned above, while calculating theoretically a TL peak for a given set of parameters 22–25, 27, 31, 92], the TSC peak (or more exactly the function $n_c(T)$) is found as well. In all these cases, the calculated TSC peak lagged, to some extent, behind its TL counterpart as shown in Fig. 3. A similar feature was found, theoretically, in the cases mentioned in Section 3.1 [87–90]. Several investigators [93–102] performed simultaneous measurements of TL and TSC (some included simultaneous measurements of thermally stimulated electron emission, TSEE, see Section 4), and found in many cases a shift between a TL peak and the corresponding TSC peak. Usually, but not
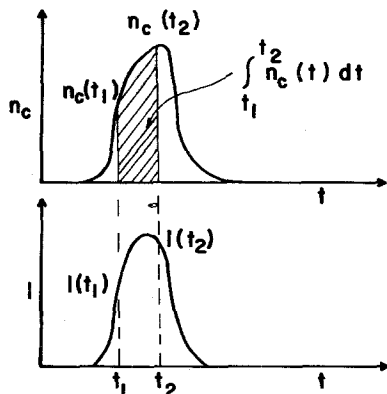
always, this shift was in the "right" direction, namely, that the TL maximum preceded that of the TSC. Chen [103] investigated the relation between the TL curve $I(T)$ and the curve of concentration of free carriers $n_c(T)$ which can be found from the experimental conductivity curve using Equation 48, $n_c(T) = \sigma(T)/[e\mu(T)]$.

In this section we will denote the recombination probability by A. One can immediately see that Equation 7, $I = -\, dm/dt = Amn_c$, has much more general meaning than just describing the situation (together with Equations 8 and 9) when only one trap and one centre are involved. As long as only transitions into one recombination centre are *measured*, one does not mind whether there are transitions into other centres. Such transitions may change the number of electrons in the conduction band, but Equation 7 holds true for the net concentration n_c. Moreover, no information about the traps contributing to n_c is needed as long as $n_c = n_c(t)$ can be measured by conductivity measurements. Assuming that $n_c(t)$ is known and that A is temperature independent, the solution of Equation 7 is

$$I = Am_0 n_c(t) \exp\left[-A \int_0^t n_c(t')\, dt'\right]; \quad (57)$$

no specific heating scheme $T = T(t)$ has to be assumed in this treatment. Writing Equation 57 for two arbitrary points t_1 and t_2 and dividing one by the other, we have

$$I(t_2)/I(t_1) = [n_c(t_2)/n_c(t_1)] \exp\left[-A \int_{t_1}^{t_2} n_c(t)dt\right].$$

$$(58)$$

All the quantities in this equation except for A are measurable and thus A can be evaluated. Fig. 3 shows schematically a peak of $n_c = n_c(t)$ its counterpart $I = I(t)$ and the quantities $I(t_1)$, $I(t_2)$, $n_c(t_1)$, $n_c(t_2)$ and $\int_{t_1}^{t_2} n_c(t)dt$. It is to be noted that only relative values of $I(t)$ are needed whereas absolute values of $n_c(t)$ are necessary. Since the recombination probability A is known [12] to be the product of the thermal velocity v and the cross-section for recombination σ_m, one can easily evaluate the latter by the values of A and v. Such evaluations have been given by Chen [103] for insulating and semiconducting diamonds.

By equating the derivative of Equation 57 to zero, one gets

$$(dn_c/dt)_{max} = A\,[n_c(t_{max})]^2 \qquad (59)$$

Figure 3 Quantities measured to find the recombination probability A_m (see Equation 58).

where the subscript "max" indicates that values are taken at the maximum of the *luminescence* peak. The right hand side of Equation 59 is always positive, and, therefore, the left hand side should also be positive. This means that when the TL peak reaches the maximum point, the curve of $n_c(t)$ is still increasing or in other words, that $n_c(t)$ maximizes later (at a higher temperature) than $I(t)$. Since the dependence of the mobility on temperature is weak, the TL peak will usually also (but not always) precede the TSC maximum. The same conclusion was arrived at by Fields and Moran [104] using a slightly different line of thought. It has also been shown [103] that even if recombinations into more than one centre are involved, the appearance of the TL peak at a lower temperature than the corresponding TSC one, still prevails.

The possible dependence of the recombination probability A on temperature has been studied [105] using the results of Lax [16] and Bemski [17] who showed that the cross-section for recombination varies with temperature like T^α where $-4 \leqslant \alpha \leqslant 0$. Since the thermal velocity depends on $T^{1/2}$, we have $A = AT^a$ with $-7/2 \leqslant a \leqslant \frac{1}{2}$. It has been shown [105] that the $\sigma(T)$ curve can precede the TL peak if the condition

$$A_m T_m n_{cm} < a\beta_m \qquad (60)$$

is fulfilled. Here T_m is the temperature of TL maximum, β_m the heating rate at T_m, n_{cm} the value of n_c at T_m and A_m is the recombination probability at T_m. Equation 60 holds true under certain circumstances, provided $a > 0$ (i.e. if $a = \frac{1}{2}$ in this case).

If we now wish to compare peak temperatures of TL and TSC (rather than $\sigma(T)$), we have to take into account the temperature dependence of the carrier mobility. According to Lax [16] this is given by

$$\mu = \mu' T^b \qquad (61)$$

where μ' is a constant and b assumes usually a value of $-\frac{3}{2}$ (sometimes -2.3). Chen and Fleming [105] have shown that the condition for the appearance of a TSC peak before the TL is

$$\bar{A}_m T_m \sigma_{max} < c\beta_m \qquad (62)$$

where $\bar{A}_m = (A'/\mu'c)T_m^c$ and where $c = a - b$ and σ_{max} is the conductivity at T_m. We now have $-2 \leqslant c \leqslant 2$ and the inversion or the order of appearance may occur more easily, for $0 \leqslant c \leqslant 2$.

As for the possibility of an exponentially temperature dependent recombination probability [32, 33], $A = K \exp(W/kT)$, we can use the general condition [105] related to $n_c(T_m)$ which is

$$(dn_c/dt)_m = A_m n_{cm}^2 - \beta_m n_{cm} (d \ln A/dT)_m. \qquad (63)$$

Inserting the function $A(T)$ we get

$$(dn_c/dt)_m = K \exp(W/kT_m)n_{cm}^2 + \beta_m n_{cm} W/kT_m^2. \qquad (64)$$

The right-hand side is always positive, which again means that the TL peak occurs at a temperature lower than the $n_c(T)$ peak.

4. Thermally stimulated electron emission (TSEE)

The effect of thermally stimulated electron emission (TSEE) can be described as follows. A sample, usually an insulator or semiconductor, is connected to an electrode in a vacuum tube, another electrode is also present in the tube at a certain distance from the sample. A given potential difference is maintained between the two electrodes. The sample is excited in any of the ways described in the TL and TSC cases during which time, electrons are being trapped in trapping levels. The sample is heated, and when the electrons are thermally stimulated from the traps, they can be entirely emitted from the sample and accelerated to the other electrode. Peaks of current as a function of temperature may thus be recorded, the shapes of the peaks and their other properties revealing information on the trapping states. Experimentally speaking, this effect differs from the TSC case by the fact that single particles can be detected. Thus, open point counters, Geiger–Müller counters as well as mulitipliers may be used instead of the collecting electrode. It is worthwhile mentioning that TSEE is used, in a way similar to TL [106] and TSC, for dosimetry purposes. In all these pehnomena, the intensity of the effect is directly related to the amount of radiation which excited the sample prior to the warm-up.

An important feature of TSEE as compared to TSC is that, evidently, only electrons can be released from the sample whereas holes cannot. Thus, one can easily distinguish between electron and hole TSC peaks by performing a simultaneous TSEE measurement; only the electron peaks would appear in the latter. Another advantage of the

TSEE is that the mobility of the sample does not have any role in this phenomenon and, therefore, its temperature dependence should not influence the results.

One complication in interpreting the TSEE is that while TL and usually TSC as well are mainly bulk phenomena, in many cases TSEE is related to surface phenomena and is, therefore, not necessarily directly related to TL and TSC. It has also been shown [107, 108] that in order to get the emitted current density from the concentration of electrons in the conduction band, one has to take into account the effective work function of the sample ϕ. One gets

$$J = n_c(T) \, [kT/(2\pi m)]^{1/2} e^{-\phi/kT} \qquad (65)$$

where m is the effective mass of a conduction electron. If we ignore the slight additional $T^{1/2}$ dependence, we get a case which is similar to Wintle's case [32, 33] mentioned above. If, for example, $n_c(T)$ has a regular order shape [109], the additional factor $e^{-\phi/kT}$ gives an equation similar to Equation 17 with $-\phi$ replacing W. Thus, the initial rise method would yield a value of $E + \phi$ for the activation energy, whereas the various heating-rate methods give a value of E. As for the temperature of appearance, the multiplication of $n_c(T)$ by the increasing function $T^{1/2} e^{-\phi/kT}$ should cause the TSEE to appear at higher temperature than the $n_c(T)$ peak. Finally, a small correction of $-\frac{1}{2}kT$ can be made (Equation 20) while evaluating the activation energy, if one takes into account the $T^{1/2}$ dependence in Equation 65.

TSEE was first found by Kramer [110]. Many other investigators have dealt with this phenomenon since then, some of the more recent references are to be mentioned. Seidl [111] and Schlenk and Huster [112] have studied the first order TSEE peaks and evaluated the activation energy from the experimental curves by the shift of the maximum temperature at various heating rates. De Muer et al. [113] have used methods based on the shape of the TSEE curve of ZnO powder. Laitano and Martinelli [114] investigated both TL and TSEE in $CaSO_4$ and $Li_2B_4O_7$. Bohun [115] has measured TSEE and TL in NaCl and other materials. The work of the following groups who dealt with various aspects of TSEE are also to be mentioned: Scharmann et al. [116–119], Becker et al. [120–122], Holzapfel et al. [107, 123] and Huzimura and Matsumura [124].

5. Ionic thermoconductivity (ITC)

Bucci et al. [125, 126] introduced in 1964 the experimental technique of ionic thermoconductivity (ITC). As described by them the experimental procedure is briefly as follows.

(1) A sample is polarized in a static field E_p, for a time t, at a temperature T_p; the temperature should be high enough to allow the orientation of dipoles in the sample, but not too high so that the space charge contribution will be avoided.

(2) The solid is cooled to a temperature $T_0 \ll T_p$, where any ionic motion is hindered, then the external field is removed.

(3) The solid is warmed up, usually at a constant heating rate β, and the discharge current is recorded as a function of temperature. ITC "electrical glow" peaks may thus be observed, generally similar to TL, TSC and TSEE peaks.

The simple explanation for the appearance of an ITC single peak was also given by Bucci et al. [126]. The relaxation time of a dipole, τ, at a given temperature is assumed to be $\tau(T) = \tau_0 \exp (E/kT)$ where τ_0 is a constant. Let us consider an ideal dielectric containing only one type of non-interacting dipoles of moment P and relaxation time τ. In the absence of an electric field the dipoles are oriented randomly, but if an electric field E_p is applied at the temperature T_p for a period of time $t_p \gg \tau(T_p)$. The dipoles will be polarized and an exponential current decay will be observed. The dielectric is now cooled to a temperature T_0 so that the relaxation time $\tau(T_0)$ is of the order of several hours or more. The field is now removed, and the dipoles remain oriented at the configuration obtained at T_p. The dielectric is now warmed up; if this is done at a linear heating rate, with $\beta = dT/dt$, a depolarization current is obtained which behaves as

$$i(T) = N_{dip} P^2 \alpha E_p / (kT_p \tau_0) \exp(-E/kT)$$
$$\left[\exp \, -(1/\beta\tau_0) \int_{T_0}^{T} \exp(-E/kT') dT' \right] \qquad (66)$$

where α is a geometrical factor depending on the possible dipolar orientation (for free rotating dipoles $\alpha = 1/3$) and N_{dip} is the concentration of dipoles. Equation 66 is exactly the same as Equation 2 where s is replaced by $1/\tau_0$ and the numerical factor in front of the exponential functions has another meaning. The simple ITC peak is thus a first order peak and all the methods developed for finding E and s in first order TL peaks can

automatically be used here for evaluating E and τ_0. These include the initial rise method, the shape methods and the various heating rates methods.

The same experimental procedure has been followed by several investigators sometimes with minor differences in their details. The resulting effects were given various names and, as will be explained below, these include mainly two processes. One is the current due to the polarization of dipoles as described by Bucci *et al.* and the other is the effect usually called thermally stimulated capacitor discharge (TSCD) [127–129]. This effect is much closer to thermally stimulated conductivity (TSC) and one author [130, 131] even calls it TSC. The two electrodes, one of which is a semiconducting film and the other ohmic, on the sample are considered to be a capacitor. The capacitor is charged at a high temperature to a certain battery voltage V, then cooled under equilibrium conditions to a sufficiently low temperature T_0; electrons fill at random the traps present in the sample (usually a semiconductor [127]. Now, the capacitor electrodes are short circuited and after a partial discharge of the capacitor, the semiconductor contains only those electrons which are captured by the traps. Subsequent heating of the semiconductor alters the free electron density because of the thermal liberation of carriers from the traps and their motion to the metal electrode, which acts as a recombination channel. As mentioned above, this is similar to the expected TSC peaks in the same sample. As opposed to the ITC dipole depolarization case, the peaks in this case are not necessarily simple first order curves. The advantage of the present technique, as opposed to the TSC measurements, is in cases where the dark current, which is the background current in TSC measurements, is high. In the present technique, this is practically eliminated. Müller *et al.* [132–134] have investigated various aspects of TSCD which they, as well as other investigators, name thermally stimulated depolarization (TSD), and ITC. In these papers they have advocated the use of hyperbolic heating rates for these cases. In another paper, Müller [135] discusses the relationship between TSD and TSC. Perlman *et al.* [136–141] have investigated ITC and TSCD, which they also called thermal currents, in various organic materials such as carnauba wax and mylar. Hickmott [142, 143] studied TSCD, which he called thermally stimulated ionic conductivity (TSIC), in SiO_2, mainly

by the use of hyperbolic heating rates. Other names used were depolarization thermocurrents (DTC) [144], dielectric relaxation current (DRC) [145] or stimulated dielectric current (SDRC) [146]. In this measurement, a voltage V_d was applied to the sample at a high temperature. The sample was then cooled to low temperature and at this low temperature, the voltage bias was changed to another value $V_i \neq V_d$; The temperature was not raised uniformly and the sample current was measured. A technique slightly different in detail, though very similar in nature, was described by Podgoršak and Moran [147, 148] who called it radiation induced thermally activated depolarization (RITAD). In this effect, investigated in LiF, a sample was irradiated at low temperature in relatively high externally applied electric fields ($\sim 10^3\,V\,mm^{-1}$). The subsequent heating of the crystals with the electrodes shorted through an electrometer, produced a series of depolarization current minima and maxima.

All the above-mentioned authors, excluding Podgoršak and Moran, reported first order ITC and TSCD peaks. Other than the possibility of having two or more overlapping peaks, the analysis of the observed curves is as simple as that of first order TL peaks. Moran *et al.* [147, 148] found a nearly symmetrical peak in CaF_2 and suggested a second order process

$$J(t) = -\,d\sigma/dt = \gamma(T)\sigma^2 \qquad (67)$$

where σ is the polarization of the electret, $J(t)$ the discharge current and $\gamma(T) = \gamma_0 \exp(-E/kT)$ where γ_0 is the pre-exponential factor. A solution similar to Equation 4 immediately follows and so does the analysis of second order TL peaks. Peaks that are of neither first nor second order kinetics have also been found experimentally by some investigators [149–152] most of whom adopted the "general order kinetics" method for analysis. They assumed an equation analogous to Equation 5 and thus could use the analysis related to Equation 5. Kristianpoller and Kirsh [153] have applied this analysis to ITC peaks in SrF_2:Tb and found values of 1.5 and 1.6 for the kinetic order b for peaks at 365 and 278 K, respectively.

Tiller *et al.* [154] mention the possibility of a pre-exponential factor in ITC which is inversely proportional to temperature. While evaluating the activation energy in this case, one should use the correction given in Equation 20 and in Table I with $a = -1$. A few recent papers [155–159] on

ITC as well as a recent book [160] dealing with thermally stimulated discharge of polymer electrets are also to be mentioned here.

6. Thermal annealing

When a solid sample is irradiated by X-rays or nuclear irradiation, defects may be produced. These are to be differentiated from the traps due to existing impurities or defects in the sample which can be filled by the irradiation. The energy stored (due to the production of new defects) can be released during the heating of the sample. This can sometimes be detected as TL as seen in Section 2; in other cases, this thermal annealing of the defects can be measured using a calorimetric method. In this method [161–163] the rate of release of stored energy is directly measured as a function of temperature. This rate of release is analogous to the intensity of emitted TL. The general equation governing the process was given by Damask and Dienes [164] as

$$- \mathrm{d}n/\mathrm{d}t = F(n)K_0 \exp(-E/kT) \qquad (68)$$

where n is the concentration of defects, $F(n)$ a continuous function of n, and K_0 the preexponential factor. Cruz-Vidal et al. [162] claimed that it is not only simplest but also most realistic to assume either a first or a second order kinetics, namely, $F(n) \propto n$ and $F(n) \propto n^2$ respectively. Once such a behaviour is established, by using the form factor of the peak μ_g, for example, one can utilize all the above-mentioned TL methods for analysing these peaks. For example, Cruz-Vidal et al. [163] calculated the activation energy by *assuming* a certain frequency factor for KCl samples after 4.6 K reactor irradiation. A better approach would be using one of the methods mentioned in Section 2.2 to evaluate E, thereafter calculating the frequency factor. So, for example, for their peak at 34.5 K this would result in a lower value for E and a correspondingly lower value for the frequency factor f_0.

Itoh et al. [165, 166] assumed that $F(n) \propto n^x$ where x is not necessarily 1 or 2. This brings us back to an equation equivalent to Equation 5 and to the treatment of general order kinetics. Saidoh and Itoh [66] discussed the annealing curve measured in an alternative way. When the defects are present in a transparent sample, the optical density can be measured which gives information on the concentration of the defects. During the heating of the sample, the absorption changes

and thus $n = n(T)$ can be evaluated. The derivation of this curve with respect to temperature gives an annealing curve analogous to the glow curve. This has been mentioned by Balarin and Zetsche [167] who dealt with first and second orders only.

Assuming that $F(n)$ is a well-behaved function, Damask and Dienes [164] and other investigators [168, 169] showed that Equation 31 gives a good approximation for the activation energy. The novelty here is that this is the case for all well-behaved functions including $F(n) \propto n^x$, but it is definitely not limited to this case. This fact can be used for the other thermally stimulated phenomena as well.

7. Partial thermoremanent magnetization (PTRM)

The ITC mentioned above is a result of freezing the electrical polarization whilst cooling a sample under an electric field. In a similar way, magnetization can be frozen in a magnetic specimen whilst it is cooled in a magnetic field. This thermoremanent magnetization (TRM) can be measured as a function of temperature whilst the sample is heated. Whereas in the electrical case, the ITC measured is directly proportional to the derivative of the polarization, one has to find the derivative curve, which is called partial thermoremanence magnetization (PTRM), from the TRM curve, in order to obtain the analogue of the ITC curve. Such measurements for synthetic and natural ilmenite-haematites gave been performed by Westcott-Lewis and Parry [170–173]. The theory of TRM and PTRM has previously been established by Néel [174] and Stacey [175]. According to Stacey, the magnetic behaviour is governed by the differential equation.

$$- \mathrm{d}M/\mathrm{d}t = CM \exp(-E/kT) \qquad (69)$$

where M is the magnetization and C the frequency factor. As pointed out by Chen and Westcott-Lewis [176], this is analogous to the Randall–Wilkins TL eqaution (Equation 1) and, therefore, the methods of analysis known for the latter are applicable to the former. According to Stacey [175], C is proportional to T. Here, too, one can use the appropriate corrections developed for TL curves. For example, if one uses the τ, δ or ω methods (Equation 24) with the parameters given in Table I, a value of $a = 1$ should be employed. Thus, for example, the activation energy can be

found from the total width of the PTRM curve by

$$E = 2.52kT_m^2/\omega - 3kTm. \qquad (70)$$

8. Thermal desorption and evolved gas analysis (EGA)

The phenomenon of thermal desorption, sometimes called flash desorption (a somewhat different version of which is referred to as evolved gas analysis (EGA) [177]) was described by Redhead [178] as follows. A sample, usually a metal is rigorously cleaned in vacuum, a known gas is then introduced and allowed to adsorb on the sample. The gas is then desorbed by heating the sample while the pressure in the system is recorded; the resulting pressure–time curve is called the "desorption spectrum". If the temperature–time relation for sample heating is suitably controlled, the desorption spectra can be analysed, usually employing linear or hyperbolic heating rates. The closely related evolved gas analysis (EGA) is the technique of determining the nature and amount of any volatile products formed during thermal analysis. The analysis of the curves can yield information on the number of various desorption phases, the population of the individual phases, the activation energies of desorption, the pre-exponential factors and the order of the desorption kinetics.

Redhead as well as other investigators [179–189] have written an equation analogous to our Equation 5 which gives the rate of desorption as follows

$$-d\theta/dt = A\theta^n \exp(-E/RT) \qquad (71)$$

where θ is the surface coverage, A the pre-exponential factor, E the activation energy, and n the order of the kinetics. It is customary to give the activation energy in the thermal desorption case, as well as in the thermogravimetry (TG) and differential thermal analysis (DTA) (see below) in kcal mol^{-1} rather than in eV. This is the reason why R, in kcal mol^{-1} K^{-1}, replaces k in Equation 71, and in the following discussion, the ratios E/kT and E/RT are the same. The units in modern use are kJ mol^{-1} for E, and kJ mol^{-1} K^{-1} for R. Some researchers dealt only with the cases of first and second order kinetics, namely, $n = 1$ and 2, whereas others assumed "general order" kinetics with values of n ranging up to 3 [190]. This can explain the occurrence of a peak with symmetry (measured by

μ_g) different from that characteristic to the first and second orders. Equation 71 is an alternative to the assumption [191] that the activation energy is coverage dependent as $E = E_0 - x\theta(t)/\theta(0)$ where both E_0 and x are constants and $x \geqslant 0$. As mentioned by Chen [189], one can apply the methods developed for general order kinetics TL for the thermal desorption curves, assuming that Equation 71 represents the situation. This seems to be the case according to the works mentioned above [178–188]. For example, the method of various heating rates has been reported to be applicable for thermal desorption when *linear* heating rates were used [185, 186]. As we know from TL theory, this can be done for any increasing heating function provided that the value of the heating rate at the maximum, β_m, replaces β in the plot of $\ln(T_m^2/\beta)$ versus $1/T_m$. McCarroll [191] has shown that the mass spectrometer signal intensity, which is the same as thermal desorption, is given by

$$I(t) = -g\theta(t)T(t)^{-1/2}. \qquad (72)$$

This is equivalent to the pre-exponential factor which depends on temperature like T^a with $a = -\frac{1}{2}$. The evaluated activation energies should, therefore, be amended by subtracting a value of $\frac{1}{2}RT_m$ (analogous to $\frac{1}{2}kT_m$) from the otherwise calculated energies. Finally, special attention should be paid to two recent review papers [186, 187] dealing with various aspects of thermal desorption.

9. Derivative thermogravimetry (DTG)

Another important member of the group of phenomena entitled "thermal analysis" is thermogravimetry [192–197]. In this technique, the weight of a substance, in an environment heated at a controlled rate, is recorded as a function of time or temperature. The record of the weight as a function of t or T is the thermogravimetric (TG) curve. Derivative thermogravimetry (DTG) is the technique yielding the first derivative of the thermogravimetric curve with respect to either time or temperature. Thus TG is analogous to the curve of n, the concentration of carriers in trapping states in TL, whereas its derivative the DTG, is analogous to the TL intensity. Since it is conventional [195] to plot weight losses downwards, a typical DTG curve looks like an upside-down TL curve. In processes such as oxidation, weight gains are involved and the curves resemble the TL peaks.

As agreed by many investigators [198–201] the equation governing the TG and DTG curves is

$$-dW/dt = A \exp(-E/RT)W^n \qquad (73)$$

where W is the fractional residue weight of the sample. This, again, is exactly analogous to our Equation 5. Certain non-integer values of the kinetic order n, such as $\frac{1}{2}$, $\frac{2}{3}$ [202], 0.4, 0.6, 0.7 and 1.6 [203] have been mentioned for certain materials. As stated before [204], the methods developed for the analysis of TL curves, can be used to extract the activation energy, the kinetic order and the pre-exponential factor from the DTG curve. According to Zsakó [205], the pre-exponential factor may be temperature dependent, behaving like T^m. The corrections mentioned above, for the calculated activation energy when a temperature dependent pre-exponential factor is involved, should be applied. An important review paper on the general treatment of the thermo-gravimetry of polymers by Flynn and Wall [206] should be mentioned here. These authors discuss the use of the initial rise method and the various heating rates method for linear as well as non-linear heating rates. They also consider the dependence of the pre-exponential factor on temperature and suggest alternative numerical evaluations of the integral appearing in Equation 35 to that given in Section 2.3.

It is to be noted that cases more complicated than those described by Equation 73 have also been considered for more complicated thermo-gravimetric results. Šatava [207] and Zsakó [205] wrote instead of Equation 73 the general equation

$$-dW/dt = Af(W) \exp(-E/RT) \qquad (74)$$

where $f(W)$ can be $W^m(1-W)^n$ or even more complex functions of W. Ozawa [208] suggested two activation energies which are active at the same temperature range, namely, an equation of the form

$$dc/dt = A_1 \exp(-E_1/RT)(1-c)$$
$$+ A_2 \exp(E_2/RT)(1-c) \qquad (75)$$

and investigated the changes in the resulting curve under various heating rates.

10. Differential thermal analysis (DTA) and differential scanning calorimetry (DSC)

Differential thermal analysis (DTA) [192–197] is the thermal technique in which the temperature of a sample compared with the temperature of a thermally inert material is recorded as a function of the sample as it is heated (or cooled) usually at a uniform rate. Temperature changes in the sample are due to endothermic or exothermic transitions or reactions such as those caused by phase changes, fusion, crystalline structure inversions, boiling, sublimation, dissociation reactions, destruction of crystalline structure and other chemical reactions. The temperature changes occurring during these chemical or physical changes are detected by a differential method.

A very closely related technique is differential scanning calorimetry (DSC), which consists of the recording of the energy necessary to establish zero temperature difference between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate [195].

Kissinger [209, 210] wrote the following equation governing the process

$$dx/dt = A(1-\alpha)^n \exp(-E/RT) \qquad (76)$$

where α is the fraction reacted. If we write y for $1-\alpha$ we obtain

$$-dy/dt = Ay^n \exp(-E/RT) \qquad (77)$$

which is exactly the same as Equation 5 and has, therefore, the same implications regarding the possible uses of the various mentioned methods. For example, Kissinger [210] has developed the method of various heating rates for this case and proved that $d[\ln(\beta/T_m^2)]/d(1/T_m) = -E/R$ not only for the first order case but for the general order kinetics as well. The possibility of using a non-linear heating function [44] has not been mentioned.

The validity of the Kissinger method has been challenged by Reed et al. [211] who showed that the maximum rate of reaction does not necessarily occur at the peak of the DTA curve and that Kissinger's method may lead to large errors in the values obtained for the activation energy and pre-exponential factor. Other investigators still tend to believe that Kissinger's method is applicable in certain cases, for example in the differential scanning calorimetry (DSC) of the crystalization process in As_2Se_3 [212].

Various methods of analysis of DTA curves were discussed by Sharp [213]. These include the important work of Borchart and Daniels [214] which is applicable to reactions in solution.

Under specific conditions, Equation 77 was arrived at and a method of trial and error based on the initial rise method was suggested for evaluating the activation energy, the pre-exponential factor and the reaction order. A refinement of this method was given by Weber and Greer [215] and an alternative method was suggested by Tateno [216].

The main experimental problem in DTA measurement (which actually occurs, to some extent, in the other thermally stimulated processes as well) is to maintain a uniform temperature throughout the sample. The existence of a temperature gradient in the sample can invalidate the methods mentioned of evaluating the reaction parameters in solids. It has also been pointed out that Equation 7 is merely a mathematically convenient expression rather than one that expresses accurately a physical reality [217]. This point seems to be similar to the convenience of using Equation 5 as opposed to the difficulties arising in dealing with the accurate set of Equations 7 to 9 in TL theory.

The theory of Borchardt and Daniels has been modified to include diffusion-controlled reactions [217, 218]. The diffusion equations can be written in the general form

$$d\alpha/dt = kf(\alpha) \qquad (78)$$

where $f(\alpha)$ depends on the particular process. For the oxidation of many metals, one has the "parabolic law" in which $f(\alpha) = 1/(2\alpha)$. For the equation of Gistling and Braunshtein [219] one has $f(\alpha) = 3/2 [(1 - \alpha)^{1/3} - 1]$.

11. Conclusion

Methods developed independently for each of the processes discussed here are shown to be applicable, under the appropriate conditions, to the analysis of the other thermally stimulated processes. Some of the methods were developed in parallel, since the investigators in one field were not aware of the advances in the other related fields. In other cases, certain methods reached a high degree of sophistication, which can now, by analogy, be almost automatically applied to the other phenomena as well. The stress in this work on the theory of TL is due, to some extent, to personal tendencies.

Acknowledgement

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