On the Calculation of Activation Energies and Frequency Factors from Glow Curves

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A new method for calculating activation energies and frequency factors from thermoluminescence and thermally stimulated current peaks is described. The validity of this method, as well as of most of the other known ones, is examined for a broad range of energies and frequency factors by the use of a computer. A combination of theoretical and empirical-computational analysis is used to give corrected formulas for some of the previous methods, while only empirical corrections are given for some others. Apart from the maximum temperature, T_m, the new method uses the total half width $\omega = T_2 - T_1$, where T_1 and T_2 are the half-intensity temperatures on the low- and high-temperature side of the peak, respectively. For a first-order peak with a frequency factor independent of temperature, the activation energy is given by $E = 2kT_m(1.26 \, T_m/\omega - 1)$ where k is Boltzmann's constant. The frequency factor is found for this case to be $s = [2\beta(1.26 \, T_m/\omega - 1)/(e^2 T_m)] \exp(2.52 T_m/\omega)$ where β is the (linear) heating rate and e is 2.718. For the case where pre-exponential factors depend on temperature as some power function and for second-order glow peaks, similar formulas are developed for the calculation of activation energies. The relative advantages of the various methods are discussed both from the theoretical and experimental points of view. The method for distinguishing between first- and second-order peaks is also discussed.

1. INTRODUCTION

An important and convenient method for investigating trapping levels in crystals is the thermal-glow method, including thermoluminescence (TL), thermally stimulated current (TSC) and thermally stimulated electron emission (TSE) measurements. The first method for calculating activation energies by TL curves was given by Urbach,[1] who found empirically that a reasonable estimate for the trap energy, E in electron volts, is given by $E = T_m/500$ where T_m is the temperature of the glow-curve maximum in °K. The first theoretical treatment for a well isolated TL peak was given by Randall and Wilkins,[2] who assumed no retrapping and a TL intensity proportional to the rate of change of the concentration of trapped electrons. The equation given by them was

$$I = -c(dn/dt) = cs \exp(-E/kT)n, \qquad (1.1)$$

where I is the TL intensity, s is a constant (having dimension of $\sec^{-1}$) called the "escape-frequency factor" or sometimes just the "pre-exponential factor," n is the concentration of trapped electrons (cm^{-3}), T is the absolute temperature, k is Boltzmann's constant, and c is a proportionality factor which can be set equal to unity without any loss in generality. The solution of the differential equation in (1.1) is

$$n = n_0 \exp\left(-(s/\beta) \int_{T_0}^{T} \exp(-E/kT') dT'\right), \qquad (1.2)$$

where n_0 is the initial concentration. This gives (assuming $c = 1$), for the TL intensity

$$I = n_0 s \exp(-E/kT)$$
$$\times \exp\left(-(s/\beta) \int_{T_0}^{T} \exp(-E/kT') dT'\right). \qquad (1.3)$$

By differentiating and equating to zero, one finds the condition for the maximum

$$\beta E/(kT_m^2) = s \exp(-E/kT_m), \qquad (1.4)$$

where T_m is the temperature at the maximum. If one has some estimate for the value of s, this could serve as a transcendental equation to be solved numerically for E.

Another approximation, more suitable for some of the glow peaks, was given by Garlick and Gibson,[3] and is represented by the following equation

$$I = -dn/dt = s'n^2 \exp(-E/kT), \qquad (1.5)$$

where s' is a constant with dimensions of $\text{cm}^3 \, \sec^{-1}$. This case is usually referred to as "second-order kinetics," whereas the previous case is "first-order kinetics." According to Garlick and Gibson, the second-order approximation applies when retrapping and recombination probabilities are equal. The solution of (1.5) is

$$I = n_0^2 s' \exp(-E/kT)$$
$$\times \left(1 + (n_0 s'/\beta) \int_{T_0}^{T} \exp(-E/kT') dT'\right)^{-2}. \qquad (1.6)$$

The term in brackets in (1.6), as well as the righthand exponential term in (1.3), varies only slightly at temperatures low in comparison to T_m. Therefore I is proportional in this region to $\exp(-E/kT)$. This provides a simple means for calculating the activation energy from the slope derived from a plot of $\ln(I)$ vs $1/T$ in the "initial rise" region.[3,4] The initial rise method is expected to be valid for intermediate order kinetics as well.[5] However, some theoretical[6,7] as well as experimental[8] reasons limit its use.

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One does not yet have any general operational method for calculating activation energies, which is based on the shape of the glow peak. The first- and second-order approximations are, however, fairly good ones for most of the experimentally found peaks, and all the methods given in the literature are based on one of these assumptions.

A number of methods for calculating activation energies are based on measurement of T_m, the temperature at the maximum, and T_1 and T_2, the first- and second-half-intensity temperatures. The formulas for finding the energies by these methods usually contain one of the following factors: (a) $\tau = T_m - T_1$, the halfwidth at the low-temperature side of the peak, (b) $\delta = T_2 - T_m$, the halfwidth towards the falloff of the glow peak, or (c) $\omega = T_2 - T_1$, the total halfwidth.

By assuming that the area of the half peak toward the falloff is equal to the area of a triangle having the same height and halfwidth, Lushchik[9] showed that the activation energy can be given by

$$E = kT_m^2/\delta. \qquad (1.7)$$

Once E is calculated by any method, insertion into Eq. (1.4) gives the value of the pre-exponential factor. Using the value of E in the more general form (1.7), one has by insertion into (1.4)

$$s = (\beta/\delta)\exp(T_m/\delta), \qquad (1.8)$$

which gives s directly. For second-order kinetics, Lushchik found by the same assumption

$$E = 2kT_m^2/\delta. \qquad (1.9)$$

Halperin and Braner[5] found two general equations for evaluating the activation energy, one for carriers raised into a level within the forbidden gap,

$$E = (q/\delta)kT_m^2, \qquad (1.10)$$

and another for excitation into the band

$$E = (q/\delta)kT_m^2(1-\Delta), \qquad (1.11)$$

where $\Delta = 2kT_m/E$ is a correction factor, usually of the order of magnitude of 0.1. The value of q depends on the order of the process, and can be found accurately only for strict first- or second-order kinetics. For first order, Halperin and Braner gave $q_1 = 1.72\mu_g(1 - 1.58\Delta)/(1-\mu_g)$, and for second order, $q_2 = 2\mu_g(1 - 2\Delta)/(1-\mu_g)$, where μ_g is defined as n_m/n_0 and n_m is the concentration of trapped carriers at T_m. The value of μ_g was used by Halperin et al.[10] for evaluating the order of the process. Values of μ_g around $(1+\Delta)/e$ indicate first-order kinetics ($e = 2.718\cdots$), and values around $(1+\Delta)/2$ indicate second order. As an approximation for μ_g, the value of $\mu_g' = \delta/\omega$ has been taken. Halperin and Braner[5] have also shown that

because of experimental considerations, a method based on the value of τ is expected to be more accurate in many cases. Advancing the previous method and assuming $\mu_g = \mu_g'$, they found for first-order kinetics when excitation is not into a band,

$$E = 1.72(kT_m^2/\tau)(1-1.58\Delta). \qquad (1.12)$$

They gave similar equations for excitation to a band and for second-order kinetics. The value of E is calculated from these equations iteratively. A first approximation is found by assuming $\Delta = 0$, and the subsequent ones are found by inserting the calculated E into Δ and thus correcting the E value.

Another method using the value of τ was given by Grosswiener[11] who found

$$E = 1.51kT_mT_1/\tau, \qquad (1.13)$$

which, he claims to be accurate to better than $\pm5\%$, provided that $s/\beta > 10^7 \deg^{-1}$ (where β is the heating rate) and $E/kT_m > 20$. Again, by inserting (1.13) into (1.4) one has

$$s = 1.51\beta T_1/(\tau T_m)\cdot\exp[1.51(T_1/\tau)]. \qquad (1.14)$$

Dussel and Bube[12] showed that Grosswiener's method for E is out by about 7% and gave some other similar formulas for E using T_m, T_2, and δ, or T_1, T_2, and ω instead of T_1, T_m, and τ. Keating,[13] following other investigators,[14,15] introduced the possibility of temperature-dependent frequency factors, $s = s''T^a$, where $-2 \leq a \leq 2$. For all values of a, Keating gave the following formulas for first-order peaks

$$kT_m/E = (1.2\gamma - 0.54)\omega/T_m + 0.0055 - [\tfrac{1}{2}(\gamma - 0.75)]^2,$$
$$(1.15)$$

from which E can be calculated. In this formula $\gamma = \delta/\tau$. The formula is reported to hold true for $0.75 < \gamma < 0.9$ and $10 < E/kT_m < 35$. It is worthwhile to mention here that Halperin and Braner's case of excitation into a band corresponds to $a = 2$, namely, $s \propto T^2$. According to Lax[14] and Bemsky,[15] the most common values of a are -2, 0, 1, and 2.

It is important to note that the validity of the first- and second-order approximations is much larger than that described by Randall and Wilkins[2] and Garlick and Gibson.[3] First-order cases appear for TL in semiconducting crystals,[16] for TL when traps and luminescence centers are geometrically adjacent,[17] and for various conditions in TSC measurements.[18] Second-order peaks might occur, not only when retrapping and

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recombination are equally probable, but also when the probability for retrapping is much larger than that for recombination.[19,20]

Two other articles should be mentioned here. Nicholas and Woods[21] reviewed most of the above mentioned methods and used them for experimental results of glow peaks observed in CdS crystals. Typical first- and second-order calculated curves can also be found in this work. Kelly and Laubitz[22] analyzed some of the methods by using computer calculations. The results of their work will be discussed in the last paragraph in comparison with those of the present one.

The scope of this paper is to: (1) introduce a new method for calculating trap parameters by the total halfwidth (ω) of a first- or second-order peak, (2) examine and correct some of the other methods using the temperature of the maximum and half intensity, and (3) to discuss the relative advantages of these methods for various concrete cases. This investigation has been done for a broad range of activation energies ($0.1 \leq E \leq 2.0$ eV) and pre-exponential factors ($10^5 \leq s \leq 10^{13}$ sec^{-1}) in order to cover all the values found thus far in various experiments. The calculations were carried out by computation of T_1, T_m, and T_2 for each set of E and s, using the IBM 360 computer.

2. METHODS BASED ON THE TOTAL HALFWIDTH OF A PEAK

A new method for calculating glow parameters by the use of the halfwidth ω and the maximum temperature for first- and second-order peaks, and for the possible dependence of the pre-exponential factor on temperature is developed here.

A. First-Order Kinetics, s Independent of T

By Eq. (1.3), the intensity at the maximum is

$$I_m = s n_0 \exp(-E/kT_m)$$
$$\times \exp\left(-(s/\beta)\int_{T_0}^{T_m} \exp(-E/kT)dT\right). \quad (2.1)$$

The integral on the right-hand side can be approximated[8,23] by the asymptotic expansion

$$\int_{T_0}^{T} \exp(-E/kT')dT'$$
$$= T \exp(-E/kT) \sum_{n=1}^{\infty} (kT/E)^n (-1)^{n-1} n!. \quad (2.2)$$

Since kT/E is usually small (about 0.05), a reasonable

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approximation is given by

$$\int_{T_0}^{T_m} \exp(-E/kT)dT \approx (kT_m^2/E)$$
$$\times \exp(-E/kT_m)(1-\Delta), \quad (2.3)$$

where $\Delta = 2kT_m/E$.

Using Eq. (2.1) and the maximum condition (1.4), one has

$$I_m = (En_0\beta/kT_m^2) \exp[-(1-\Delta)] = (En_0\beta/ekT_m^2)e^{\Delta}. \quad (2.4)$$

The assumption of Lushchik[3] about the equality of the area of the second half of the peak to that of a triangle having the same height and halfwidth can be written as $n_m = \delta_t I_m$, where n_m is the concentration of trapped carriers at T_m, and δ_t is the halfwidth of the second half of the peak in time units. Since $\delta_t = \delta/\beta$, the relation can be expressed by $\delta I_m/\beta n_m = 1$. A similar assumption about the relation between the total-glow area and a triangle can be written as $\omega I_m/\beta n_0 = 1$. This assumption can be regarded as two separate assumptions: (a) $\omega I_m/\beta n_0$ is a constant, i.e.,

$$C_\omega = \omega I_m/\beta n_0, \quad (2.5)$$

and (b) C_ω is equal to unity. The validity of these two assumptions was examined, and the results show (see Appendix) that the first one is good to quite a high precision, whereas the value of C_ω usually differs from 1.0 appreciably. Inserting βn_0 from Eq. (2.5) into Eq. (2.4) one finds now

$$E e^{\Delta} = eC_\omega kT_m^2/\omega. \quad (2.6)$$

Since Δ is always quite small, writing $e^{\Delta} \approx 1 + \Delta$ is quite a good approximation, and thus one has

$$E(1 + 2kT_m/E) = eC_\omega kT_m^2/\omega. \quad (2.7)$$

This can be written as

$$E_\omega = eC_\omega kT_m^2/\omega - 2kT_m = 2kT_m[(eC_\omega/2)T_m/\omega - 1]. \quad (2.8)$$

By insertion into (1.4) one has for the frequency factor

$$s = (2\beta/e^2 T_m)[(eC_\omega/2)(T_m/\omega) - 1] \exp(eC_\omega T_m/\omega). \quad (2.9)$$

C_ω was found to be 0.92 for this case (see Appendix), which changes Eq. (2.8) to

$$E_\omega = 2kT_m(1.25 T_m/\omega - 1). \quad (2.10)$$

Two small systematic errors have been introduced by taking only the first two terms in the asymptotic series for the integral and in the series for e^{Δ}. Further calculations (see below) show that these can be compensated for by changing the constant in the parentheses from 1.25 to 1.26. A method which is a little less accurate, but easier to use, can be derived by dropping

the unity in the parentheses and reducing the value of the other constant for compensation. It was found that quite a good approximation is given by

$$E_Q = 2.29 k T_m^2 / \omega. \tag{2.11}$$

Again by insertion into (1.4) one now has

$$s_Q = (2.29\beta/\omega) \exp(2.29 T_m/\omega). \tag{2.12}$$

Since 2.29 is close to ln10, one can write

$$s_{Q2} = (2.67\beta/\omega) 10^{T_m/\omega}. \tag{2.13}$$

Here again the constant multiplying β/ω has been slightly changed (from 2.29 to 2.67) in order to compensate partially for the additional inaccuracies. Equation (2.13) can be considered as an "express" method for evaluating the pre-exponential factor.

B. Second-Order Kinetics, s' Independent of T

For second-order kinetics, the intensity at the maximum is given according to (1.6) by

$$I_m = n_0^2 s' \exp(-E/kT_m)$$

$$\times \left(1 + (n_0 s'/\beta) \int_{T_0}^{T_m} \exp(-E/kT) dT \right)^{-2}. \tag{2.14}$$

By differentiating Eq. (1.6) and equating the derivative to zero, the condition for the maximum is found to be

$$(n_0 s'/\beta) \int_{T_0}^{T_m} \exp(-E/kT) dT$$

$$+1 = (2kT_m^2 n_0 s'/\beta E) \exp(-E/kT_m). \tag{2.15}$$

By inserting (2.15) into (2.14) we have

$$I_m = (\beta E/2kT_m^2)^2 \exp(E/kT_m)/s'. \tag{2.16}$$

Using the two first terms in the series expansion (2.2) in (2.15) and rearranging, one now has

$$(\beta E/s'kT_m^2) \exp(E/kT_m) = n_0(1+\Delta). \tag{2.17}$$

Using this in (2.16) and taking again the expression (2.5), we now find

$$E(1+\Delta) = 4C_\omega kT_m^2/\omega, \tag{2.18}$$

which in a similar way to the previous case can be written

$$E = 2kT_m(2C_\omega T_m/\omega - 1). \tag{2.19}$$

Since C_ω was found to be 0.878 (Appendix) for this case, the constant $2 C_\omega$ is now 1.756. In a way similar to the first-order case, it can be shown that a slightly higher constant is preferable in order to account for the dropping of terms of the order of Δ^2 in the series, and thus a constant of 1.77 was found to be useful here.

C. Temperature-Dependent s Values

As has been said before, the possible dependence of s on temperature is $s = s'' T^a$. The equation governing

these cases for first-order kinetics is

$$I = -dn/dt = s'' T^a \exp(-E/kT) n. \tag{2.20}$$

The solution of this is

$$I = s'' n_0 T^a \exp(-E/kT)$$

$$\times \exp\left(-(s''/\beta) \int_{T_0}^{T} T'^a \exp(-E/kT) dT'\right). \tag{2.21}$$

Keating[13] has shown that for these cases one can use

$$\int_{T_0}^{T} T'^a \exp(-E/kT') dT'$$

$$= (kT_m^{a+2}/E) \exp(-E/kT_m)(1-\Delta_1), \tag{2.22}$$

where $\Delta_1 = (a+2)kT_m/E = (1+\frac{1}{2}a)\Delta.$ The maximum condition is found to be here

$$s'' T_m^{a+2} \exp(-E/kT_m) = (\beta E/k)(1+\frac{1}{2}a\Delta). \tag{2.23}$$

By writing T_m instead of T in (2.21), I_m can be found. By inserting Eq. (2.22) into this expression for I_m and using (2.23), we now find

$$I_m = (n_0\beta E/kT_m^2)(1+\frac{1}{2}a\Delta)$$

$$\times \exp\{-(1+\frac{1}{2}a\Delta)[1-(1+\frac{1}{2}a)\Delta]\}. \tag{2.24}$$

Neglecting second-order Δ terms, and taking $(1+\Delta)$ for e^Δ, we now have

$$I_m = (n_0\beta E/ekT_m^2)[1+(1+\frac{1}{2}a)\Delta]. \tag{2.25}$$

Using as before, Eq. (2.5), one now has

$$E[1+(1+\frac{1}{2}a)\Delta] = C_\omega ekT_m^2/\omega, \tag{2.26}$$

and this gives as before

$$E = 2kT_m[\frac{1}{2}C_\omega eT_m/\omega - (1+\frac{1}{2}a)]. \tag{2.27}$$

To account for the omission of terms of the order of Δ^2, the constant given by $\frac{1}{2}eC_\omega$ can be slightly changed. The value of C_ω could, in principle, depend on the power a. However, it is shown (see Appendix) that this dependence is very weak. Equation (2.27) can therefore be written in general as with (1.26) replacing $\frac{1}{2}C_\omega e$. Equation (2.19) is a special case of Eq. (2.27) for $a=0$. The two extreme (and most common) cases, namely, $a=2$ and $a=-2$ give for $1+\frac{1}{2}a$ values of 2 and 0 respectively. Thus for $a=-2$ one has the simplest formula, which could be expected beforehand, since the integral in (2.22) can be calculated easily and analytically in this case.

Similar reasoning could be given for second-order kinetics when $s' = s'' T^a$. Without going into details, the result can be found to be

$$E = 2kT_m[2C_\omega T_m/\omega - (1+\frac{1}{2}a)]. \tag{2.28}$$

3. METHODS BASED ON THE HIGH-TEMPERATURE-SIDE HALF PEAK

The aim of this paragraph is to show that the method of Lushchik[9] has to be slightly modified so as to give

more accurate values. The assumption of Lushchik, $\delta I_m/\beta n_m = 1$, is to be changed to

$$\delta I_m/\beta n_m = C_\delta. \qquad (3.1)$$

The value of C_δ and its small variation with E and s are discussed in the Appendix. For first-order kinetics with s independent of T we have from Eq. (1.1) (with $c=1$)

$$I_m/n_m = s \exp(-E/kT_m). \qquad (3.2)$$

By the maximum condition (1.4), and using Eq. (3.1),

$$I_m/n_m = s'n_0\beta \exp(-E/kT_m) \Big/ \left(1 + (s'n_0/\beta) \int_{T_0}^{T_m} \exp(-E/kT)dT\right). \qquad (3.4)$$

Using the maximum condition (2.15) we have

$$I_m/n_m = \beta E/(2kT_m^2), \qquad (3.5)$$

which when combined with (3.1) leads directly to

$$E = C_\delta(2kT_m^2/\delta). \qquad (3.6)$$

C_δ was found to be 0.853 (variations of $\pm 1.4\%$) for this case, so that the correction seems to be essential here.

A similar treatment can be used for the cases of pre-exponential factors dependent on temperature. The method for first-order kinetics with $s=s''T^2$ is shown here, for example. The intensity in this case is given by Eq. (2.20) with $a=2$ from which we can write for T_m

$$I_m/n_m = s''T_m^2 \exp(-E/kT_m). \qquad (3.7)$$

The maximum condition (2.23) can be written here as

$$(s''T_m^2/\beta) \exp(-E/kT_m) = E/(kT_m^2) + 2/T_m. \qquad (3.8)$$

Inserting (3.8) into (3.7) gives

$$I_m/n_m = 2\beta/T_m + \beta E/(kT_m^2). \qquad (3.9)$$

By using (3.1) we now have

$$E = C_\delta kT_m^2/\delta - 2kT_m. \qquad (3.10)$$

This equation has been given before[5] in the form (1.11) with $q=1$ which, because of the closeness of C_δ to unity, $C_\delta = 0.983$ (variations of 0.6%, see Appendix) in this case, gives about the same results (but has to be solved iteratively). It is easy to show that for $s=s''T^a$ the result would be similar to (3.10), when akT_m replaces $2kT_m$. As for the second-order kinetics, in a way quite similar to that for $a=0$, it can be shown that

$$E = C_\delta(2kT_m^2/\delta) - akT_m. \qquad (3.11)$$

Similarly to C_ω, the value of C_δ was found (Appendix) to be only weakly dependent on a, and thus $C_\delta \approx 0.85$ represents an appreciable deviation from the original equation (for $a=2$).

we get right away

$$E = C_\delta kT_m^2/\delta. \qquad (3.3)$$

This is the equation of Lushchik[9] multiplied by the correction factors C_δ which was calculated to be 0.976 with variations of $\pm 0.4\%$ (Appendix). Since this is quite close to unity, the correction given here is rather small.

For the case of a second-order peak where s' is independent of T, let us take the solution of (1.5) for n, and using (1.6) one can see that

4. METHODS BASED ON THE LOW-TEMPERATURE-SIDE HALF PEAK

Activation energies calculated by the method of Halperin and Braner[5] were usually found to be too high by 10% or more. The method included two inaccuracies: (a) Lushchik's assumption given by $C_\delta = 1$, and (b) approximation of $\mu_g = n_m/n_0$ by $\mu_g' = \delta/\omega$. The necessary correction to this method is represented by introducing

$$\tau I_m/[\beta(n_0 - n_m)] = C_\tau, \qquad (4.1)$$

which means that the ratio between the first half of the peak and a triangle having the same height and half-width is a constant. The constancy is checked, again, in the Appendix. Dividing the expression for C_δ [see Eq. (3.3)] by Eq. (4.1) and rearranging, one gets

$$n_m/(n_0 - n_m) = \delta C_\tau/(\tau C_\delta). \qquad (4.2)$$

The lefthand side is equal to $\mu_g/(1 - \mu_g)$ appearing in all the expressions for q in (1.10).[5] From the equation for first-order kinetics, for example, we get for excitation into a level not in a band,

$$E = 1.72C_\delta[\mu_g/(1-\mu_g)](kT_m^2/\delta)(1-1.58\Delta), \qquad (4.3)$$

where the factor C_δ has to be introduced as in the previous case (Sec. 3). By using (4.2) we get

$$E = 1.72C_\delta \cdot (\delta C_\tau/\tau C_\delta)(kT_m^2/\delta)(1-1.58\Delta)$$
$$= 1.72C_\tau(kT_m^2/\tau)(1-1.58\Delta), \qquad (4.4)$$

and similar equations for the other three cases. C_τ was found to be between 0.88 and 0.91 for the various cases. These equations could be derived, however, from first principles and Eq. (4.1) without going into the somewhat complicated calculations of Halperin and Braner, and with the advantage of getting the corresponding noniterative formulas as follows:

A. First-Order Kinetics, Constant s Value

The expression (4.1) for C_τ can be written as

$$n_0/n_m - 1 = [\tau/(\beta C_\tau)]I_m/n_m. \qquad (4.5)$$

From (1.2) we have

$$n_0/n_m = \exp\left((s/\beta) \int_{T_0}^{T_m} \exp(-E/kT)dT\right). \quad (4.6)$$

By using the approximation for the integral (2.3) and inserting the maximum condition (1.4) we have

$$n_0/n_m = \exp(1-\Delta) \approx (1-\Delta)e. \quad (4.7)$$

By inserting (3.2) and (4.7) into (4.5) we have

$$(1-\Delta)e-1 = (\tau/\beta C_\tau)(\beta E/kT_m^2) = \tau E/C_\tau kT_m^2, \quad (4.8)$$

which gives

$$E = C_\tau(e-1)(kT_m^2/\tau)\{1-[e/(e-1)]\Delta\}. \quad (4.9)$$

This is identical to Eq. (4.4). With the value of C_τ found empirically, this becomes

$$E = 1.52(kT_m^2/\tau)(1-1.58\Delta). \quad (4.10)$$

An approximation for $n_0/n_m = \exp(1-\Delta)$, which is about as valid as (4.7), is $n_0/n_m = e/(1+\Delta)$, which gives directly the criterion of Halperin and Braner[5] for first-order kinetics, i.e.,

$$\mu_g = n_m/n_0 = (1+\Delta)/e. \quad (4.11)$$

Using this, Eq. (4.8) becomes now

$$e/(1+\Delta) - 1 = \tau E/(C_\tau kT_m^2). \quad (4.12)$$

This can be written as

$$1.72(1-0.58\Delta) = \tau E(1+\Delta)/(C_\delta kT_m^2). \quad (4.13)$$

Because of the smallness of 0.58Δ we can write

$$1.72 = \tau E(1+1.58\Delta)/(C_\tau kT_m^2), \quad (4.14)$$

or

$$E[1+1.58(2kT_m/E)] = 1.72C_\tau kT_m^2/\tau. \quad (4.15)$$

This can now be written as

$$E = 1.52kT_m^2/\tau - 1.58(2kT_m). \quad (4.16)$$

The difference in accuracy between Eqs. (4.10) and (4.16) is very slight. However, this last equation is more useful, since no iterations are necessary.

B. Second-Order Kinetics, Constant Pre-exponential Factor

By solving (1.5) directly, one has

$$n_m = n_0\left(1 + (n_0 s'/\beta) \int_{T_0}^{T_m} \exp(-E/kT)dT\right)^{-1}. \quad (4.17)$$

Using the maximum condition (2.15), one finds

$$n_m = [\beta E/(2kT_m^2 s')] \exp(E/kT_m), \quad (4.18)$$

and using (2.17), we find

$$n_0/n_m = 2/(1+\Delta). \quad (4.19)$$

Using Eq. (4.5) again and inserting n_0/n_m from (4.19) and I_m/n_m from (3.5), one has now

$$2/(1+\Delta) - 1 = \tau E/(2C_\tau kT_m^2). \quad (4.20)$$

Use of the approximation $2/(1+\Delta) \approx 2(1-\Delta)$ gives directly the formula of Halperin and Braner[5] corrected by C_τ which, with the known value of C_τ (Appendix), is written

$$E = 1.813(kT_m^2/\tau)(1-2\Delta). \quad (4.21)$$

By an argument similar to the previous case, a more convenient formula which is as accurate as (4.21) can be written by

$$E = 1.813kT_m^2/\tau - 2(2kT_m). \quad (4.22)$$

Directly from Eq. (4.19) we see that

$$\mu_g = n_m/n_0 = (1+\Delta)/2, \quad (4.23)$$

which is the criterion of Halperin and Braner[5] for second-order kinetic peaks.

C. Cases of Temperature-Dependent s Values

For temperature-dependent pre-exponential factors let us take again the case of first-order kinetics and $s = s''T^2$. The equation governing this process is (2.20) with $a = 2$. The solution of this was given by Eq. (2.21). Solving for n and inserting T_m, one has for the maximum

$$n_m = n_0 \exp\left(-(s''/\beta) \int_{T_0}^{T_m} T^2 \exp(-E/kT)dT\right). \quad (4.24)$$

By using the approximation of Keating in Eq. (2.22) for $a = 2$, we have

$$n_m/n_0 = \exp[-(s''kT_m^4/\beta E)(1-2\Delta)], \quad (4.25)$$

and by the maximum condition (3.18) we find

$$n_m/n_0 = \exp\{[kT_m^2/(\beta E)][2\beta/T_m + \beta E/(kT_m^2)](1-2\Delta)\}. \quad (4.26)$$

This becomes

$$n_m/n_0 = \exp[-(1+\Delta)(1-2\Delta)] \approx \exp[-(1-\Delta)] \approx (1+\Delta)/e. \quad (4.27)$$

This is again the μ_g value indicating first-order kinetics. By inserting (4.27) and (3.9) into (4.5) one has

$$e/(1+\Delta) - 1 = [\tau E/(C_\tau kT_m^2)](1+\Delta). \quad (4.28)$$

The corrected Halperin and Braner formula is found by dividing by $(1+\Delta)$ and writing $1/(1+\Delta)^2 \approx 1-2\Delta$ and $1/(1+\Delta) \approx 1-\Delta$. With the calculated value of C_τ for this case, one finds now

$$E = 1.515(kT_m^2/\tau)(1-2.58\Delta). \quad (4.29)$$

TABLE I. Calculated values of activation energies and preexponential factors by several methods, first-order kinetics and s independent of temperature.

E (eV)	s (sec^{-1})	E_G (eV)	E_{Gc} (eV)	s_{Gc}/s	E_K (eV)	γ	E_L (eV)	E_{Lc} (eV)	s_{Lc}/s	E_ω (eV)	$E_{\omega c}$ (eV)	$s_{\omega c}/s$	E_τ (eV)	E_Q (eV)	s_Q/s
0.1	10^5	0.109	0.101	1.48	0.107	0.770	0.103	0.101	1.08	0.097	0.098	0.741	0.098	0.102	1.79
0.2	10^5	0.217	0.203	1.45	0.215	0.767	0.205	0.201	1.06	0.195	0.197	0.757	0.196	0.204	1.72
0.4	10^5	0.433	0.404	1.40	0.432	0.762	0.411	0.402	1.08	0.391	0.395	0.773	0.390	0.407	1.67
0.8	10^5	0.864	0.807	1.36	0.867	0.759	0.821	0.802	1.08	0.784	0.791	0.788	0.783	0.811	1.60
1.6	10^5	1.726	1.611	1.33	1.738	0.756	1.641	1.603	1.07	1.571	1.585	0.803	1.578	1.618	1.55
0.1	10^7	0.108	0.100	1.27	0.109	0.750	0.102	0.100	1.02	0.099	0.100	0.840	0.100	0.100	1.40
0.2	10^7	0.215	0.200	1.23	0.218	0.747	0.205	0.200	1.03	0.196	0.199	0.856	0.199	0.200	1.35
0.4	10^7	0.429	0.400	1.19	0.438	0.744	0.410	0.400	1.05	0.396	0.399	0.871	0.398	0.400	1.31
0.8	10^7	0.857	0.799	1.15	0.877	0.742	0.819	0.800	1.04	0.792	0.799	0.887	0.797	0.799	1.25
1.6	10^7	1.712	1.597	1.12	1.757	0.740	1.638	1.600	1.04	1.586	1.599	0.902	1.596	1.595	1.21
0.1	10^9	0.107	0.100	1.05	0.110	0.735	0.102	0.100	1.01	0.099	0.100	0.943	0.100	0.099	1.10
0.2	10^9	0.214	0.199	1.04	0.218	0.735	0.204	0.199	0.98	0.199	0.201	0.759	0.201	0.198	1.05
0.4	10^9	0.426	0.397	0.99	0.440	0.732	0.409	0.399	1.02	0.398	0.402	0.975	0.401	0.396	1.02
0.8	10^9	0.852	0.795	0.96	0.880	0.730	0.818	0.799	1.01	0.797	0.804	0.991	0.804	0.790	0.99
1.6	10^9	1.702	1.590	0.94	1.759	0.729	1.636	1.598	1.01	1.595	1.609	1.01	1.606	1.579	0.95
0.1	10^{11}	0.106	0.099	0.93	0.108	0.729	0.102	0.100	0.91	0.100	0.101	1.04	0.100	0.098	0.85
0.2	10^{11}	0.212	0.198	0.85	0.219	0.724	0.204	0.199	0.99	0.200	0.202	1.07	0.201	0.197	0.83
0.4	10^{11}	0.424	0.396	0.84	0.437	0.724	0.408	0.398	0.97	0.400	0.403	1.09	0.403	0.393	0.80
0.8	10^{11}	0.848	0.793	0.81	0.877	0.722	0.817	0.798	0.98	0.800	0.807	1.10	0.812	0.784	0.76
1.6	10^{11}	1.696	1.582	0.79	1.751	0.721	1.634	1.596	0.98	1.601	1.615	1.12	1.616	1.567	1.73
0.1	10^{13}	0.106	0.099	0.79	0.107	0.723	0.102	0.100	0.90	0.100	0.101	1.17	0.101	0.098	0.67
0.2	10^{13}	0.209	0.199	0.71	0.218	0.717	0.204	0.199	0.97	0.201	0.202	1.19	0.202	0.195	0.64
0.4	10^{13}	0.422	0.397	0.70	0.434	0.717	0.408	0.398	0.94	0.401	0.405	1.21	0.405	0.390	0.61
0.8	10^{13}	0.844	0.791	0.68	0.870	0.716	0.816	0.797	0.97	0.803	0.809	1.22	0.811	0.780	0.59
1.6	10^{13}	1.693	1.578	0.65	1.737	0.715	1.633	1.595	0.96	1.606	1.620	1.24	1.622	1.559	0.57

Again the easier form of this equation is given by

$$E = 1.515 k T_m^2/\tau - 2.58(2kT_m). \qquad (4.30)$$

For other power factors $(s = s''T^a)$ it is easy to show that a good approximation is given by replacing 2.58 by $\frac{1}{2}a + 1.58$.

In this case also, we shall not give the details of calculations for the second-order peak with a temperature-dependent preexponential factor $(s' = s''T^a)$, but only give the results

$$E = 2C_r k T_m^2/\tau [1 - (2 + \tfrac{1}{2}a)\Delta]. \qquad (4.31)$$

For $a = 2$, this is the corrected Halperin and Braner formula, where $2C_r$ was calculated to be about 1.81. The noniterative corresponding equation is thus

$$E = 1.81 k T_m^2/\tau - (2 + \tfrac{1}{2}a)(2kT_m). \qquad (4.32)$$

5. CALCULATIONS OF ACTIVATION ENERGIES AND FREQUENCY FACTORS

In this chapter, computed values of T_1, T_m, T_2, τ, δ, and ω for various given E and s values are used to calculate the activation energies and the preexponential factors by several methods. The method for calculating these temperatures is described in the Appendix. The comparison between the results of the activation energies and frequency factors and the given parameters serves as a check for the accuracy of a method. In some cases it is possible and useful to change empirically some of the constants in the formulas using the results found in this way in order to reduce systematic errors.

A. First-Order Kinetics, Constant s

Table I represents some of the results found by the formulas for first-order kinetics. Column 1 gives representative given energy values (E) ranging from 0.1 eV to 1.6 eV. Column 2 shows the given s values changing from 10^5 to 10^{13} sec^{-1}. Column 3 gives the values of calculated energies (E_G) according to Grosswiener's[11] Eq. (1.13) which are seen to be too high on the average by about 7%. (This agrees well with the results of Dussel and Bube.[12]) Column 4 gives the values for a corrected Grosswiener formula (E_{Gc}) with 1.41 replacing 1.51 in Eq. (1.13). The results are now within $\pm 1.5\%$ throughout the broad E and s ranges. Column 5 shows the calculated frequency factors (s_{Gc}) by the suitably corrected Eq. (1.14), namely, taking 1.41 instead of 1.51 both in front of, and in the exponent. The values given in this column and in the other columns giving s values are the calculated values divided by the given s values. It is self-evident that small inaccuracies in the calculated E value correspond to rather high ones in the s values and thus results accurate to a factor of 1.5 seem to be fairly good. Column 6 gives the values calculated by the method of Keating[13] (E_K). The results are seen to be on the average too high by about 8%. This can be corrected

by introducing a correction factor of about 0.92. It has not been done, however, because of the relatively complicated form of his formula. Moreover, the condition given by Keating $(\gamma > 0.75$ when $\gamma = \delta/\tau)$ is not fulfilled in many of the chosen cases (which seem to be most of the real physical cases found experimentally) as seen in column 7. Calculated activation energies by the method of Lushchik (E_L) are given in column 8, whereas values calculated by the corrected formula (3.3) with $C_\delta = 0.976$ (see below) are given in column 9 (E_{Lc}). These are found to be very accurate. The values of the frequency factors (s_{Lc}) found by the corrected Eq. (1.8) are given in column 10 and found to be accurate to within 10%, which is very good for a preexponential factor. Column 11 gives the value of E_ω calculated by the full-width method according to (2.10), and column 12 gives the values $(E_{\omega c})$ calculated with the same equation when the constant 1.25 is replaced by 1.26 (see above). Column 13 shows the $s_{\omega c}$ values calculated by the correspondingly corrected (2.10) equation. The results are within 25% error. Column 14 gives the activation energies (E_r) found in the new version (4.16) of Halperin and Braner's[5,10] formula. Column 15 gives the energy values (E_Q) calculated by the less accurate, but more convenient, full-width method (2.11). The errors are not larger than 2.5%. Column 16 gives the s_{Q2} values calculated by (2.13). The results are good up to a factor of 2.

B. First-Order Kinetics, $s = s''T^2$

The results for this case are given in Table II. The calculated values of s'' are not given in the table for the sake of brevity, but they can be found by Eq. (2.23). It is expected, as in the previous case, that the s'' errors will be much higher (in percentage) than the corresponding E values, and that the more accurate methods for finding activation energies will be more precise for finding s'' as well.

Column 3 gives the energy found by the corrected method of Grosswiener (1.13). The results are seen to be high by about $2kT_m$ (given in column 4). This shows (without proof) that the correction proved to be necessary for this case in the other methods (paragraphs 2, 3, 4), namely, that $2kT_m$ has to be subtracted to give the correct result, is to be used here also. Column 5 gives the corrected Grosswiener $(E_G - 2kT_m)$ results. Column 6 shows the results found by the method of Keating (E_K) in Eq. (1.15). Though this method is meant to be useful for all cases of $s = s''T^a$, it seems that apart from multiplying by some correction factor in a way similar to the case with $a = 0$ (about 0.92), one has to subtract akT_m to have the correct E value (see also below for $a = -2$). Most of the values of γ (in column 7) do not fulfill the condition $\gamma > 0.75$, which could partly explain the inaccuracy in this method. Column 8 gives the values of E_{Lc} calculated by the corrected Lushchik method (3.10); again with

TABLE II. Calculated activation energies by several methods for first-order kinetics and $s \propto T^2$.

E (eV)	s'' (sec^{-1} °K^{-2})	E_G (eV)	$2kT_m$ (eV)	$E_G - 2kT_m$ (eV)	E_K (eV)	γ	$E_{Lc} - 2kT_m$ (eV)	E_ω (eV)	E_{rc} (eV)
0.1	10^1	0.115	0.015	0.100	0.120	0.768	0.099	0.098	0.098
0.2	10^1	0.225	0.026	0.199	0.247	0.750	0.200	0.197	0.196
0.4	10^1	0.446	0.047	0.399	0.493	0.742	0.402	0.397	0.396
0.8	10^1	0.881	0.086	0.795	0.979	0.731	0.803	0.798	0.790
1.6	10^1	1.744	0.157	1.587	1.944	0.732	1.604	1.601	1.587
0.1	10^3	0.111	0.012	0.099	0.123	0.741	0.100	0.099	0.098
0.2	10^3	0.220	0.021	0.199	0.244	0.736	0.200	0.199	0.197
0.4	10^3	0.435	0.039	0.396	0.485	0.731	0.401	0.400	0.396
0.8	10^3	0.863	0.071	0.792	0.963	0.727	0.801	0.804	0.797
1.6	10^3	1.713	0.132	1.581	1.912	0.724	1.600	1.611	1.599
0.1	10^5	0.109	0.009	0.100	0.122	0.727	0.101	0.100	0.100
0.2	10^5	0.215	0.018	0.197	0.242	0.725	0.201	0.201	0.199
0.4	10^5	0.427	0.032	0.395	0.478	0.723	0.401	0.403	0.402
0.8	10^5	0.850	0.061	0.789	0.948	0.720	0.800	0.808	0.802
1.6	10^5	1.690	0.113	1.577	1.881	0.717	1.601	1.617	1.608
0.1	10^7	0.107	0.008	0.099	0.119	0.722	0.100	0.101	0.099
0.2	10^7	0.213	0.015	0.198	0.236	0.720	0.200	0.202	0.200
0.4	10^7	0.422	0.028	0.394	0.469	0.717	0.400	0.404	0.402
0.8	10^7	0.840	0.052	0.788	0.931	0.715	0.801	0.811	0.808
1.6	10^7	1.670	0.099	1.571	1.848	0.713	1.600	1.622	1.618
0.1	10^9	0.106	0.008	0.099	0.117	0.716	0.100	0.101	0.100
0.2	10^9	0.210	0.013	0.197	0.233	0.714	0.200	0.202	0.201
0.4	10^9	0.418	0.024	0.394	0.461	0.712	0.400	0.405	0.405
0.8	10^9	0.832	0.046	0.786	0.915	0.710	0.801	0.812	0.810
1.6	10^9	1.656	0.088	1.568	1.816	0.709	1.599	1.626	1.621

very good results. Column 9 shows the results (E_ω) by the new full-width method (2.27), and column 10 represents the results (E_{rc}) by the changed Halperin and Braner method (4.32).

C. First-Order Kinetics, $s = s''T^{-2}$

Table III gives the results for this case. Column 3 gives the energy results (E_G) by the corrected Gross-wiener method (1.13), corrected by the addition of $2kT_m$. The reasonable values shown here enhance the feeling that akT_m has to be subtracted from E_G for the general case $s = s''T^a$. Column 4 gives the results found by the method of Keating. The results here are better than in the two previous cases, but still are not as good as those found by the other methods. The condition $\gamma > 0.75$ is fulfilled only for some of the values and these are *not* those for which the results are relatively good. Again better results are found by multiplying E_K by 0.92 and *adding* $2KT_m$. Column 6 gives the results (E_{Lc}) for the corrected Lushchik method according to Eq. (3.11). In column 7, the E_ω values calculated by Eq. (2.27) are given. The results are within $\pm 2\%$.

Column 8 shows the results by the corrected Halperin and Braner formula (4.32).

D. Second-Order Kinetics, s' Independent of T

Table IV gives some calculated energy values of the various methods for given E and $s'n_0$ values. Column 3 shows the values (E_L) found by the corrected Lushchik method (3.6). Column 4 represents the results (E_r) by the corrected Halperin-Braner method (4.22) when the constant $2C_\tau = 1.813$ was slightly changed to 1.83 for reasons discussed previously. Column 5 gives the values (E_ω) found by the new whole-width method (2.28). As can be expected, because of the small variations in the C_ω value for second-order kinetics (see Appendix), the ω method is the most accurate in this case. Column 6 gives the results of a method analogous to that of Grosswiener [see also Ref. (12)], namely

$$E = 1.68kT_1T_m/\tau. \qquad (5.1)$$

The value of 1.68 was chosen "empirically" in order to

TABLE III. Calculated activation energies by several methods for first-order kinetics and $s \propto T^{-2}$.

E (eV)	s'' (sec^{-1} °K^2)	E_G+2kT_m (eV)	E_K (eV)	γ	E_{Lc} (eV)	E_ω (eV)	E_τ (eV)
0.1	10^9	0.103	0.090	0.787	0.100	0.099	0.099
0.2	10^9	0.206	0.178	0.794	0.200	0.198	0.199
0.4	10^9	0.414	0.349	0.801	0.400	0.394	0.395
0.8	10^9	0.830	0.684	0.810	0.800	0.786	0.798
1.6	10^9	1.669	1.338	0.819	1.602	1.567	1.570
0.1	10^{11}	0.103	0.097	0.755	0.100	0.100	0.099
0.2	10^{11}	0.206	0.192	0.760	0.199	0.199	0.198
0.4	10^{11}	0.413	0.381	0.764	0.399	0.397	0.398
0.8	10^{11}	0.829	0.754	0.768	0.798	0.793	0.793
1.6	10^{11}	1.663	1.492	0.773	1.596	1.582	1.580
0.1	10^{13}	0.100	0.101	0.736	0.099	0.101	0.101
0.2	10^{13}	0.200	0.200	0.741	0.199	0.201	0.203
0.4	10^{13}	0.402	0.397	0.743	0.398	0.402	0.404
0.8	10^{13}	0.804	0.790	0.746	0.796	0.804	0.809
1.6	10^{13}	1.611	1.572	0.749	1.691	1.606	1.616
0.1	10^{15}	0.099	0.103	0.725	0.099	0.101	0.102
0.2	10^{15}	0.200	0.203	0.729	0.200	0.202	0.204
0.4	10^{15}	0.399	0.405	0.730	0.399	0.404	0.408
0.8	10^{15}	0.798	0.808	0.732	0.797	0.808	0.814
1.6	10^{15}	1.598	1.613	0.734	1.593	1.615	1.626
0.1	10^{17}	0.099	0.102	0.719	0.099	0.102	0.103
0.2	10^{17}	0.198	0.205	0.720	0.199	0.203	0.205
0.4	10^{17}	0.396	0.408	0.722	0.398	0.406	0.410
0.8	10^{17}	0.794	0.816	0.723	0.795	0.811	0.817
1.6	10^{17}	1.589	1.630	0.724	1.590	1.621	1.635

give a good estimation to the known values. The errors are within ±2%.

E. Second-Order Kinetics, $s' = s''T^2$

The results for this case are given in Table V. Columns 3, 4, and 5 give the E_L, E_τ, and E_ω results according to (3.11), (4.32), and (2.28), respectively. These are the same equations as in the previous case when $2kT_m$ is subtracted. Column 6 gives the results of the energies calculated by

$$E = 1.68kT_1T_m/\tau - 2kT_m, \quad (5.2)$$

which is Eq. (5.1) with the suitable correction. As in case D, here also the most accurate method seems to be the new ω method. Corrections of the same sort are expected to hold true for any possible a in $s' = s''T^a$, namely, subtracting akT_m from the expression on the right of Eq. (5.1)

6. DISCUSSION

Table VI sums up the calculated values of the "constants" C_τ, C_δ, and C_ω for first- and second-order peaks, and for some values of the power factor a. The ranges of deviations of individual calculated values from the given average values are given in percents. The ratio C_ω/C_δ and its range of deviation is also given. The detailed calculations and results are given in the Appendix.

The result $C_\delta = 0.976$ is in quite good agreement with the results of Kelly and Laubitz[22], who have shown that for the case $E/(kT_m) \to \infty$, the ratio of the triangle area to the half-peak area is 0.985, and it is smaller for finite values of $E/(kT_m)$. Thus, the error in assuming this ratio to be unity is relatively small. However, for second-order kinetics, the ratio of the areas is about 0.85 and the formula for the activation energy has to be changed substantially. Kelly and Laubitz calculated the values of C_δ and the correction factor for Gross-

TABLE IV. Calculated activation energies by several methods for second-order kinetics and s' independent of temperature.

E (eV)	$s'n_0$ (sec^{-1})	E_L (eV)	E_τ (eV)	E_ω (eV)	E_{Q2} (eV)
0.1	10^6	0.101	0.098	0.099	0.102
0.2	10^6	0.202	0.197	0.199	0.203
0.4	10^6	0.405	0.398	0.398	0.406
0.8	10^6	0.807	0.794	0.797	0.810
1.6	10^6	1.613	1.589	1.595	1.617
0.1	10^8	0.100	0.098	0.100	0.101
0.2	10^8	0.200	0.199	0.200	0.201
0.4	10^8	0.401	0.400	0.399	0.401
0.8	10^8	0.801	0.802	0.799	0.800
1.6	10^8	1.601	1.602	1.599	1.598
0.1	10^{11}	0.099	0.099	0.100	0.099
0.2	10^{11}	0.199	0.200	0.200	0.198
0.4	10^{11}	0.398	0.404	0.400	0.396
0.8	10^{11}	0.795	0.808	0.801	0.790
1.6	10^{11}	1.598	1.610	1.602	1.580
0.1	10^{15}	0.099	0.101	0.100	0.098
0.2	10^{15}	0.197	0.201	0.200	0.197
0.4	10^{15}	0.395	0.405	0.400	0.391
0.8	10^{15}	0.790	0.814	0.802	0.784
1.6	10^{15}	1.580	1.629	1.604	1.568

wiener's method for values of E between 0.1 and 3.0 eV, and values of T_m between 100°K and 800°K. Taking T_m as an independent variable is somewhat misleading, because most of the cases investigated in this way are very far from those met in experiment. Writing the condition for the maximum for a first-order peak as

$$s/\beta = [E/(kT_m^2)] \exp(E/kT_m), \qquad (1.4')$$

the values of s/β corresponding to the E and T_m values given by Kelly and Laubitz are between 10^{-2} °K^{-1} and 10^{26} °K^{-1}, whereas the values found in experiments are within the range 10^4–10^{13} °K^{-1}. This is the reason why the correction factors for the cases discussed by them vary a great deal where the parameters are changed; whereas, in this work, it is shown that the assumption of having a constant correction factor is a good one for all the experimentally possible cases. Thus, Lushchik's method is reported by Laubitz and Kelly to be out by as much as 15% in certain cases, while in this work it has been shown that the error does not exceed 3% for *experimentally possible* values of E and s. Moreover, as has already been shown above, the calculated E values are always higher than the correct ones, and thus by multiplying by the correction factor, which is in this case 0.976, the errors are reduced to less than ±0.4%.

The conclusions of Kelly and Laubitz therefore have to be modified, not only as a result of taking T_m as the independent variable, but also because they do not mention the fact that the errors are systematic and thus can be corrected easily as shown above. The accuracy of one of the discussed methods is thus dependent now on the values of ΔC_δ, ΔC_τ, and ΔC_ω (see Table VI), rather than on the deviations of C_δ, C_τ, and C_ω from unity. The influence of factors other than the "triangle area" assumption have also been checked by the computational calculation of the value of E in the various methods (Sec. 5). The additional systematic errors (usually small), due to inaccuracies in developing the formulas, can be partly corrected empirically (as far as computational results can be considered to be "empirical"), as shown in Sec. 5. As shown in Table VI, the theoretical possible error for first order would be the largest in the τ method, and the smallest in the δ method, whereas the ω-method accuracy would be intermediate. For second order, however, the ω method provides the smallest possible theoretical error. It should be noted that the values of C_δ, C_τ, and C_ω are only slightly dependent on the power factor, a, in $s = s''T^a$, but are strongly dependent on the order of the process.

TABLE V. Calculated activation energies by several methods for second order kinetics and $s' \propto T^2$.

E (eV)	$s'n_0$ (sec^{-1} °K^{-2})	E_L (eV)	E_τ (eV)	E_ω (eV)	E_{Q2} (eV)
0.1	10^3	0.101	0.099	0.100	0.102
0.2	10^3	0.202	0.197	0.201	0.202
0.4	10^3	0.402	0.396	0.398	0.401
0.8	10^3	0.803	0.796	0.797	0.801
1.6	10^3	1.602	1.598	1.596	1.596
0.1	10^5	0.101	0.100	0.100	0.101
0.2	10^5	0.201	0.200	0.200	0.200
0.4	10^5	0.400	0.400	0.400	0.399
0.8	10^5	0.800	0.803	0.799	0.796
1.6	10^5	1.597	1.608	1.599	1.587
0.1	10^9	0.100	0.100	0.100	0.099
0.2	10^9	0.199	0.201	0.200	0.198
0.4	10^9	0.398	0.404	0.401	0.395
0.8	10^9	0.795	0.809	0.801	0.789
1.6	10^9	1.588	1.618	1.602	1.574
0.1	10^{12}	0.100	0.099	0.099	0.098
0.2	10^{12}	0.199	0.199	0.199	0.196
0.4	10^{12}	0.397	0.400	0.398	0.393
0.8	10^{12}	0.792	0.802	0.798	0.785
1.6	10^{12}	1.584	1.608	1.597	1.658

TABLE VI. Calculated values of the geometrical factors C_τ, C_δ, C_ω, and C_ω/C_δ and their variation ranges.

Order	a	C_τ	ΔC_τ (%)	C_δ	ΔC_δ (%)	C_ω	ΔC_ω (%)	C_ω/C_δ	$\Delta(C_\omega/C_\delta)$ (%)
1	0	0.883	±1.4	0.976	±0.4	0.920	±0.8	0.943	±1.1
1	2	0.881	±1.4	0.983	±0.6	0.924	±1.3	0.938	±1.9
1	−2	0.892	±2.2	0.973	±0.7	0.925	±1.1	0.950	±1.8
2	0	0.907	±1.0	0.853	±1.4	0.878	±0.4	1.026	±1.8
2	2	0.902	±0.8	0.858	±1.0	0.879	±0.3	1.024	±1.2

The above mentioned analysis can give, naturally, information only about the various theoretical inaccuracies introduced in some of the methods without considering the possible experimental errors. Taking only this into account, one should prefer, for example, for the first order case, to always use Lushchik's corrected formula, and thus get values of E correct to within ±0.4%. This would be recommended, however, only in cases when the values of T_m and T_2 are known accurately, because the small difference, $\delta = T_2 - T_m$ entering the calculations, is subject to relatively large errors if considerable inaccuracies are involved in measuring the temperatures. The main factor in the possible error, $\Delta\delta = \Delta T_2 + \Delta T_m$, is ΔT_m, since the possible inaccuracy in determining the temperature is much higher at a point where the derivative is zero (T_m), than in points of high (absolute) value of the derivative (T_1 and T_2). Thus $\Delta\delta$ and $\Delta\tau = \Delta T_1 + \Delta T_m$ are much larger than $\Delta\omega = \Delta T_1 + \Delta T_2$. Moreover, since ω is bigger than τ and δ, the relative errors $\Delta\tau/\tau$ and $\Delta\delta/\delta$ are even larger in comparison to $\Delta\omega/\omega$. The additional T_m appearing in all the equations for the activation energies contributes only a small additional inaccuracy, since $\Delta T_m/T_m$ is usually relatively small because of the high value of T_m (compared to τ, δ, and ω). From this point of view, the method using the value of ω is the best one.

Another experimental fact that should be taken into account is that in many cases a glow peak is not completely clean, but rather includes sometimes additional "satellites". If this satellite appears at the low-temperature half it can be bleached thermally by heating the sample up to above the temperature of the satellite. If the satellite appears at the high-temperature half of the

TABLE VII. Constants of the various formulas for calculating the activation energies.

	First order			Second order		
	τ	δ	ω	τ	δ	ω
A	$e-1$	1	e	2	2	4
C_α	0.885	0.978	0.923	0.907	0.853	0.878
AC_α	1.52	0.978	2.52	1.813	1.70	3.54
b	$1.58 + \frac{1}{2}a$	$\frac{1}{2}a$	$1 + \frac{1}{2}a$	$2 + \frac{1}{2}a$	$\frac{1}{2}a$	$1 + \frac{1}{2}a$

peak, it cannot be cleaned thermally. From this point of view, the method using the value of τ is expected to be the best one, whereas the method using δ would probably give erroneous values. The accuracy with the ω method will be intermediate in this respect.

One can use, thus, the δ method as a "precision" method for first-order pure peaks. The τ method could be preserved for unclean peaks, where the influence of other peaks is appreciable. The ω method is to be used for many intermediate cases as a "general use" method which also has very low theoretical error in second order.

When an indeterminacy exists about the order of the kinetics, methods using the low-temperature half of the peak (Halperin–Braner and Grosswiener) are preferable since the value of τ is the least sensitive to the order of the process. The poorest method in this respect is that using the high-temperature half peak, since δ is very sensitive to the order of the kinetics (see Fig. 1 in Ref. 21). As for the possible dependence of the preexponential factor on temperature, one should use the formulas assuming that s is independent of temperature if no information is available for the value of a in $s = s'' T^a$. Since a can be between -2 and $+2$,[13] the errors could be up to $\pm 2kT_m$, which is usually not more than $\pm 10\%$. It is preferable, of course, to avoid this indeterminancy by getting some information about a. This is not so difficult in most cases.[10,13–15]

The fact that the factor akT_m should be subtracted from the calculated energy values was proved for the new ω method and for the corrected Lushchik and Halperin–Braner methods, and was shown to be true for some of the other ones. This has a close relation to the analysis of Aramu et al.[6] about the initial-rise method. For $a = 0$, the energy was found to be

$$E = -kd(\ln I)/d(1/T). \qquad (6.1)$$

If I is proportional to $T^a \exp(-E/kT)$, one has

$$E' = kd(\ln I)/d(1/T) = E + akT, \qquad (6.2)$$

where E' is the value found directly from the slope of the curve. Thus one has

$$E = E' - akT. \qquad (6.3)$$

In this case T is a variable which may change slightly, usually between $0.9\,T_m$ and $0.95\,T_m$ in the range of

initial rise. Thus the correction is about the same as that found in the other methods.

It has been shown by Halperin and Braner[5] that first-order kinetics is characterized by $\mu_g = n_m/n_0$ being equal to $(1+\Delta)/e$, whereas for pure second-order kinetics, $\mu_g = \frac{1}{2}(1+\Delta)$. As mentioned before, $\mu_g' = \delta/\omega$ was usually used for this purpose, assuming that $\mu_g' \approx \mu_g$. According to the definition of C_ω [Eq. (2.5)], and of C_δ [Eq. (3.1)], one has

$$\mu_g = \mu_g'(C_\omega/C_\delta). \quad (6.4)$$

The values of C_ω/C_δ are given in Table VI and these values can be used for adjusting the μ_g' values to be closer to the real μ_g. The fact that the values of μ_g' in these cases are smaller than $\frac{1}{2}(1+\Delta)$ is due to the result $C_\omega/C_\delta = 1.025$ in Table VI. On the other hand, the relation $(1+\Delta)/e < \mu_g'$ in Tables A–I and A–II is connected to the values of $C_\omega/C_\delta = 0.94$ for first-order peaks.

Apart from introducing the necessary correction (C_τ and C_δ) in the formulas of Halperin and Braner or Lushchik, the usual correction factors, which were multiples of $\Delta = 2kT_m/E$, are replaced by corrections which are multiples of $2kT_m$. This kind of correction, which is shown to be a valid approximation, is easier for use, since the final results are found directly without the iteration process. Thus, instead of having generally an equation of the form

$$E = A(kT_m^2/\alpha)(1-b\Delta), \quad (6.5)$$

where A and b are constants appearing in the methods of Halperin and Braner or Lushchik, and a stands for τ or ω, we have now

$$E = AC_\alpha(kT_m^2/\alpha) - b(2kT_m), \quad (6.6)$$

where C_α stands for C_τ or C_ω. For example, a formula of the form (6.5) is (1.12), whereas the corresponding (6.6)-type one is (4.30). Table VII sums up the constants appearing in equations (6.5) and (6.6) for the various cases.

All the calculations in this work have been done for a given heating rate $\beta = 0.5$ deg/sec. It is easy to see, however, that the parameter which is really meaningful is s/β (or s'/β) and thus changing s is equivalent to variations in β (in the opposite direction). Since the preexponential factor was varied in a very wide range, it was not necessary to change β separately.

ACKNOWLEDGMENTS

APPENDIX

Some details on the numerical calculations will be given here. The calculations were done for five cases: the first-order kinetics with values of a (in $s = s''T^a$) of -2, 0, and 2 and for second-order kinetics with values of a of 0 and 2.

A. First-Order Kinetics: No Dependence of the Pre-exponential Factor on Temperature

For given values of E, s and β, one has to find numerically the value of T_m from Eq. (1.4). This has been done by writing

$$f(T_m) = \beta E/(kT_m^2) - s \exp(-E/kT_m), \quad (A.1)$$

and reducing the value of $f(T_m)$ by the Newton-Raphson iterative process down to the point where the correction is smaller than $0.01°K$. The method of Urbach[1] was used as a rough first approximation (i.e., T_m (°K) $= 500 \times E$). The values of n_m and I_m were calculated by inserting T_m in (1.2) and (1.3), respectively, when the asymptotic series (2.2) up to 14 terms is used as an approximation to the integral. It has been shown that the relative inaccuracy in the estimate for the integral does not exceed 10^{-5}.

In order to calculate the temperature values at half intensity, one has to solve the following equation in T

$$I(T) = sn_0 \exp(-E/kT)$$
$$\times \exp\left(-(s/\beta)\int_{T_0}^{T} \exp(-E/kT')dT'\right) = I_m/2. \quad (A.2)$$

This equation is solved in a way similar to the previous one, when the series up to 14 terms is used for the integral in the first approximation and during the iterations. The first approximation is taken to be $0.95 T_m$ for T_1 and $1.05 T_m$ for T_2. The advantage in using the series as an approximation for the integral is that it is not necessary in this case to integrate numerically throughout the region, and the possible cumulative errors which are usually introduced in such a calculation are avoided. By the T_1, T_m, and T_2 values thus calculated, one can immediately find $\omega = T_2 - T_1$, $\delta = T_2 - T_m$, and $\tau = T_m - T_1$. Once these values are calculated, the values of $\mu_g' = \delta/\omega$ and $\gamma = \delta/\tau$ can be found. With the calculated values of I_m and n_m and the given values of n_0 and β, the values of C_τ, C_δ, and C_ω can be found.

These calculations have been done for values of s ranging from 10^5–10^{13} sec^{-1} (in multiples of 10) and values of E varying from 0.1 to 2.0 eV (in differences of 0.1). This covers most values found in experiments.

Table A-I gives the values of T_1, T_m, T_2, C_ω, C_δ, C_τ, $(1+\Delta)/e$, and μ_g' for $s = 10^5$, 10^7, 10^9, 10^{11}, and 10^{13} sec^{-1} and $E = 0.1$, 0.2, 0.4, 0.8, and 1.6 eV. The values of C_ω are found to be around 0.920 with variations of $\pm 0.8\%$. C_δ is found to be 0.976, varying within the region $\pm 0.4\%$. C_τ is 0.883 within $\pm 1.6\%$.

TABLE A-I. Calculated glow parameters for given energies and preexponential factors for first-order kinetics, and where s is independent of temperature.

E (eV)	s (sec^{-1})	T_1 (°K)	T_m (°K)	T_2 (°K)	C_ω	C_δ	C_τ	$(1+\Delta)/e$	μ_g'
0.1	10^5	75.5	83.0	88.7	0.9273	0.9731	0.8949	0.421	0.435
0.2	10^5	145.2	159.0	169.6	0.9265	0.9736	0.8934	0.418	0.434
0.4	10^5	279.6	305.3	324.8	0.9257	0.9739	0.8920	0.416	0.432
0.8	10^5	539.2	586.9	623.0	0.9250	0.9743	0.8907	0.414	0.431
1.6	10^5	1041.0	1130.0	1196.7	0.9243	0.9749	0.8895	0.413	0.430
0.1	10^7	59.5	64.2	67.7	0.9226	0.9757	0.8864	0.409	0.429
0.2	10^7	115.4	124.1	130.6	0.9220	0.9760	0.8854	0.407	0.428
0.4	10^7	223.8	240.1	252.3	0.9215	0.9763	0.8846	0.406	0.426
0.8	10^7	434.4	465.1	487.9	0.9209	0.9765	0.8836	0.405	0.426
1.6	10^7	843.9	901.8	944.5	0.9204	0.9768	0.9828	0.404	0.425
0.1	10^9	49.0	52.1	54.4	0.9192	0.9774	0.8807	0.401	0.424
0.2	10^9	95.4	101.3	105.7	0.9188	0.9777	0.8799	0.400	0.424
0.4	10^9	186.0	197.2	205.9	0.9184	0.9778	0.8793	0.399	0.422
0.8	10^9	362.7	383.9	399.5	0.9180	0.9780	0.8786	0.398	0.422
1.6	10^9	707.6	748.0	777.5	0.9176	0.9782	0.8780	0.398	0.422
0.1	10^{11}	41.5	43.8	45.4	0.9167	0.9787	0.8762	0.396	0.422
0.2	10^{11}	81.2	85.4	88.5	0.9163	0.9788	0.8759	0.395	0.420
0.4	10^{11}	158.8	166.9	172.8	0.9160	0.9789	0.8753	0.394	0.420
0.8	10^{11}	310.7	326.2	337.4	0.9157	0.9791	0.8749	0.394	0.419
1.6	10^{11}	608.1	637.9	659.3	0.9154	0.9792	0.8744	0.393	0.419
0.1	10^{13}	36.0	37.6	38.8	0.9147	0.9796	0.8729	0.392	0.419
0.2	10^{13}	70.5	73.7	76.0	0.9144	0.9796	0.8728	0.391	0.418
0.4	10^{13}	138.3	144.5	148.9	0.9142	0.9797	0.8723	0.391	0.418
0.8	10^{13}	271.4	283.2	291.7	0.9139	0.9798	0.8720	0.390	0.417
1.6	10^{13}	532.6	555.3	571.6	0.9137	0.9799	0.8716	0.390	0.417

B. First-Order Kinetics, $s=s''T^2$

The glow intensity is given in this case by

$$I = n_0 s'' T^2 \exp(-E/kT)$$

$$\times \exp\left(-(s''/\beta) \int_{T_0}^{T} T'^2 \exp(-E/kT')dT'\right). \quad (A.3)$$

The condition for the maximum is found to be

$$T_m^2(s''/\beta) \exp(-E/kT_m) = E/(kT_m^2) + 2/T_m, \quad (A.4)$$

which is solved numerically in a way similar to the previous one. The s'' values were chosen to give values of $s = s''T_m^2$ about the same as those for the previous case. Thus, the s'' values are from 10 to 10^9, whereas E values were again from 0.1 to 2.0 eV. The integral in

(A.3) is approximated by the asymptotic series

$$\int_{T_0}^{T} T'^2 \exp(-E/kT')dT'$$

$$= T^3 \exp(-E/kT) \sum_{n=1} (kT/E)^n (-1)^{n-1}(n+2)!/3!. \quad (A.5)$$

Again, the approximation is seen to be very good when 14 terms were taken in this series. The values of T_1 and T_2 were calculated in a way similar to the previous one. From the values of T_1, T_m, T_2, n_m, and I_m found in this way, the values of τ, δ, ω, C_τ, C_δ, C_ω, μ_g', and Δ were calculated. Table A-II gives some representative results. C_ω varies between 0.911 and 0.932 with an average value of 0.924 ($\pm 1.3\%$). C_δ is found to be 0.983 ($\pm 0.6\%$), C_τ is 0.880 ($\pm 1.4\%$) and C_ω/C_δ is

TABLE A-II. Calculated glow parameters for given energies and preexponential factors for first-order kinetics and $s \propto T^2$.

E (eV)	s'' (sec^{-1} °K^{-2})	T_m (°K)	C_ω	C_δ	C_τ	$(1+\Delta)/e$	μ_j'
0.1	10^1	85.4	0.9321	0.9888	0.8928	0.422	0.434
0.2	10^1	152.4	0.9242	0.9784	0.8873	0.416	0.429
0.4	10^1	274.6	0.9215	0.9771	0.8841	0.411	0.426
0.8	10^1	498.9	0.9199	0.9773	0.8817	0.407	0.424
1.6	10^1	912.9	0.9186	0.9778	0.8797	0.404	0.423
0.1	10^3	67.2	0.9211	0.9771	0.8836	0.411	0.426
0.2	10^3	122.3	0.9196	0.9774	0.8813	0.407	0.424
0.4	10^3	224.1	0.9184	0.9779	0.8793	0.403	0.422
0.8	10^3	413.1	0.9173	0.9784	0.8775	0.401	0.421
1.6	10^3	765.5	0.9164	0.9788	0.8759	0.398	0.420
0.1	10^5	55.0	0.9182	0.9780	0.8790	0.403	0.421
0.2	10^5	102.6	0.9171	0.9785	0.8772	0.400	0.420
0.4	10^5	188.4	0.9162	0.9789	0.8756	0.398	0.419
0.8	10^5	351.1	0.9153	0.9793	0.8742	0.396	0.419
1.6	10^5	657.1	0.9146	0.9796	0.8730	0.394	0.418
0.1	10^7	46.4	0.9160	0.9790	0.8753	0.397	0.419
0.2	10^7	86.5	0.9152	0.9793	0.8739	0.395	0.418
0.4	10^7	162.0	0.9144	0.9797	0.8727	0.394	0.418
0.8	10^7	304.5	0.9137	0.9799	0.8716	0.392	0.417
1.6	10^7	574.3	0.9131	0.9802	0.8706	0.391	0.416
0.1	10^9	40.0	0.9143	0.9898	0.8725	0.393	0.417
0.2	10^9	74.2	0.9136	0.9800	0.8714	0.392	0.417
0.4	10^9	141.8	0.9130	0.9803	0.8704	0.390	0.416
0.8	10^9	268.4	0.9124	0.9805	0.8695	0.389	0.415
1.6	10^9	509.2	0.9119	0.9807	0.8687	0.388	0.415

0.938 ($\pm 1.9\%$). It should be noted that in all of these cases, the term "average" is in the sense of a middle value, the deviations from which do not exceed the values in percents given in parentheses.

C. First-Order Kinetics, $s = s''T^{-2}$

The intensity is given in this case by

$$I = n_0 s'' T^{-2} \exp(-E/kT)$$

$$\times \exp\left(-(s''/\beta) \int_{T_0}^{T} T'^{-2} \exp(-E/kT') dT'\right). \quad (A.6)$$

Since the integrand here is integrable, one can find I (neglecting, as before, the very small term depending on T_0) analytically. The maximum temperature was found by solving numerically (iteratively) the cor-

responding equation for the maximum, and by using the T_m value thus found, I_m, T_1, and T_2 were calculated. The other parameters were found from these in the way shown above. The values of s'' were now between 10^9 and 10^{17} sec^{-1} deg^2. The detailed results are not given for the sake of brevity. C_ω was found to be 0.925 ($\pm 1.1\%$), C_δ is 0.973 ($\pm 0.7\%$), C_τ is 0.832 ($\pm 2.2\%$) and C_ω/C_δ is about 0.950 ($\pm 1.8\%$).

D. Second-Order Kinetics, s' Independent of T

The equation governing this process is (1.5) whose solution is (1.6). The maximum condition is given by (2.15). This has been solved numerically by, again, using 14 terms in the series (2.2) as an approximation to the integral. I_m is found by (2.16) and then T_1 and T_2 are calculated in a way similar to the previous one,

and thus the other derived parameters are found as before. The results were calculated for values of $s'n_0$ changing from 10^6 to 10^{15} sec^{-1}. The detailed results are not shown. C_r is found to be 0.907 ($\pm 1.0\%$), C_δ is 0.853 ($\pm 1.4\%$) and C_ω is 0.878 ($\pm 0.4\%$). C_ω/C_δ is now 1.026 ($\pm 1.8\%$).

E. Second-Order Kinetics, $s' = s''T^2$

The differential equation governing this process is

$$I = -dn/dt = s''T^2 \exp(-E/kT)n^2, \qquad (A.7)$$

where s'' has dimensions of sec^{-1} cm^3 deg^{-2}. The solution

of the equation for a linear heating rate is

$$I = n_0^2 s'' T^2 \exp(-E/kT)$$
$$\times \left(1 + (n_0 s''/\beta) \int_{T_0}^{T} T'^2 \exp(-E/kT')dT'\right)^{-2}, \quad (A.8)$$

and the condition for maximum is found by equating the derivative of (A.8) to zero. The values of the parameters are calculated for $s''n_0$ (which is again the important factor) between 10^3 sec^{-1} deg^{-2} and 10^{12} sec^{-1} deg^{-2}. C_ω is now 0.879 ($\pm 0.3\%$), C_δ is 0.858 ($\pm 1.0\%$), C_r is 0.902 ($\pm 0.8\%$) and C_ω/C_δ is 1.024 ($\pm 1.2\%$).

Transient Double Injection in Trap-Free Semiconductors

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When a step voltage is applied to injecting contacts on the ends of a long trap-free semiconductor, such as p-type germanium, an electron-hole plasma forms at the minority-carrier injecting end and propagates down the length of the bar. When the recombination time (τ) is much longer than the small-pulse transit time (t_0), the leading edge of the propagating plasma arrives at the far end at $t_a = (\frac{5}{6})t_0$. The arrival is marked by a cusp in the time derivative of the current, which can be used to measure the minority-carrier mobility. After t_a, the current acquires an exponential form, with a time constant equal to the recombination time. Approximate analytic solutions and numerical results indicate that the important recombination effects are small ($<2\%$) for τ/t_0 greater than about 2. Early-transient diffusion effects are small when (applied voltage/thermal voltage)$^{1/2}$ is greater than about 40. All the prominent features can be described in terms of simple physical concepts, and the theoretical predictions are verified by experiment.

I. INTRODUCTION

When a sufficiently high voltage is applied to injecting contacts on the ends of a long bar of an extrinsic semiconductor, a large-signal electron-hole plasma builds up in the bulk. The steady-state properties of this plasma have been studied extensively by several authors.[1-6] This paper deals with the turn-on transient.

The general nature of the transient is well known.[7,8] The plasma forms at the minority-carrier injecting contact and propagates down the length of the sample in the direction of minority-carrier drift. In 1949,

Herring[8] obtained a theoretical description of the propagating front for the special case of *constant* current in a semi-infinite medium. His solution indicated that for times short compared to a recombination time the electric field varies as $x^{1/2}$ behind a sharp advancing edge.

In 1966, Baron, Marsh, and Mayer[9] conducted a theoretical and experimental study of the transient following the application of an incremental voltage step to a long bar of silicon, which was already biased in the steady-state, double-injection square-law regime. (The step had to be such that the initial and final states were *both* in the square-law regime.) They found a resulting incremental current of the form,

$$\Delta I = A + B[1 - \exp(-5/\tau)],$$

where 5 is time and τ is the recombination time.

In this paper we will show the relation between Herring's description and Baron et al. findings. Both of

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