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The Fitting of Luminescence Rises and Decays[1]

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Abstract—This review presents a number of mathematical expressions which the experimental scientist may find useful to fit to time-dependent luminescence intensity (and concentration) data for both decay and rise situations. Some of these expressions have been drawn from literature sources and are presented here in a unified form. In compiling these expressions, a number of gaps were found in the literature, and, in this review, new expressions have been derived to fill some of these gaps. The final section of the review summarizes both the existing and the new kinetic expressions and provides an explanation of how to use them. Some of the subtleties and pitfalls of using kinetic data fitting to determine reaction mechanisms are also discussed.

1. INTRODUCTION

It is intended that this review will prove useful for experimental scientists in such areas as photochemistry, photobiology, chemical kinetics, radiolytic studies, etc., where it is common experimental procedure to measure the time dependence either of the luminescence intensity or of the concentration of products. Such measurements may be made on a chemical system following the initiation of a continuous photolytic or radiolytic excitation process, or, after the cessation of a transient excitation process.

There are a number of mathematical expressions available in the chemical literature that can be fitted to time-dependent luminescence intensity or concentration data. Each of these mathematical expressions corresponds to a particular type of reaction mechanism. Unfortunately, the available expressions are widely scattered in the literature and there is no comprehensive document available to summarize them all. Furthermore, there are a number of gaps in the existing literature which we attempt to fill by deriving some new expressions.

2. CLASSICAL MODELS

2.1. First-Order Models

2.1.1. Simple First Order. Consider the simple reaction scheme:

$$A \xrightarrow{k} B. \qquad \text{(I)}$$

The fall of the concentration of species A with time will be described by the integrated first-order equation (1)

$$[A] = [A]_0 \exp(-kt), \qquad (1)$$

where [A] is the concentration of species A at time t, $[A]_0$ is the initial concentration of species A, and k is the first-order rate constant for the reaction.

The above reaction scheme can easily be extended to deal with the case of a light-emitting reaction

$$A^* \longrightarrow A + h\nu. \qquad \text{(II)}$$

Here A* has been produced by some precursor process which is no longer occurring. In this case, the intensity will be given by

$$L = \varphi[A]_0 k \exp(-kt), \qquad (2)$$

where φ is the quantum efficiency of light emission, and L is the intensity of the emitted light. Quickenden *et al.* [2–7] have previously used Eq. (2).

Now consider the following reaction scheme:

$$A + h\nu_1 \xrightarrow{\text{fast}} A^* \xrightarrow{k} A + h\nu_2. \qquad \text{(III)}$$

In the above scheme, molecules of A* are being produced by the excitation of A with electromagnetic radiation, while the excited species A* is decaying back to its ground state and emitting electromagnetic radiation of a longer wavelength. This is a classical first-order scheme for the production of fluorescence. In this case, the excitation rate (indicated by "fast" in Eq. (III)) is much higher than the rate of emission, k.

When the exciting light is first turned on, there will be a rise in the luminescence intensity. This will reach a plateau level and remain there until such time as the exciting light is turned off. After this there will be a decay in the intensity of luminescence. During the rise, the luminescence intensity will be given by [6]

$$L = \varphi_1\varphi_2 I(1 - \exp(-kt)), \qquad (3)$$

where φ_2 is the quantum efficiency for the emission process, φ_1 is the quantum efficiency for the excitation process, and I is the intensity of the exciting light.

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[1] This article was submitted by the authors in English.

The concentration of A* will reach a plateau, and this will be given by [8]

$$[\mathrm{A}^*]_{\text{plateau}} = \varphi_1 I/k. \tag{4}$$

When the exciting light is turned off, the luminescence intensity will decay according to

$$L = \varphi_2 k[\mathrm{A}^*]_{\text{plateau}}\exp(-kt) = \varphi_1\varphi_2 I\exp(-kt), \tag{5}$$

which is consistent with Eq. (2) if $[\mathrm{A}]_0$ in Eq. (2) is made equal to $[\mathrm{A}]_{\text{plateau}}$ and φ is made equal to φ_2.

As well as being used for unimolecular kinetics, the first-order model can also be used in the case of bimolecular kinetics when the concentration of one of the two reacting species is constant or almost constant. In this case, the kinetics are described as being pseudo-first-order (see Section 2.2.2 for further details on this).

2.1.2. Double First-Order Models. A variation of the simple first-order model is the double first-order model. Quickenden *et al.* [6, 7] have termed this model the biexponential model and present an example of such a mechanism. For this model, an extension of expression (3) leads to the following equation for the rise of luminescence intensity with time when the exciting light is turned on [6, 7]:

$$L = a(1-\exp(-k_a t)) + b(1-\exp(-k_b t)), \tag{6}$$

where k_a and k_b are the rate constants for the two processes, and a and b are defined as follows:

$$a = \varphi_{1a}\varphi_{2a}I \tag{7}$$

and

$$b = \varphi_{1b}\varphi_{2b}I. \tag{8}$$

In this case, I is the exciting light intensity, φ_{1a} and φ_{1b} are the quantum efficiencies for the excitation of the two species, and φ_{2a} and φ_{2b} are the quantum efficiencies for the two decay processes.

In this model, the decay of luminescence intensity with time when the exciting light is turned off is given by [6, 7]

$$L = a\exp(-k_a t) + b\exp(-k_b t), \tag{9}$$

where the symbols have all been previously defined.

Quickenden *et al.* [6, 7] have suggested that the simplest phenomenological explanation for a bimolecular modeling of the rise and fall of luminescence intensity is that two excited species, A* and B*, are decaying back to their ground states independently of one another. Note that if A* and B* can return to their ground states by a number of different mechanisms, then k_a will be the sum of the rate constants for all the processes by which A* can return to its ground state, and similarly for k_b. This is explained further later in this section.

Yguerabide and Burton [9] and, more recently, Alvarez-Pez *et al.* [10] have shown that a biexponential decay also results when the two excited species can interconvert in addition to decaying back to their ground states. For clarity, the first situation (as discussed above), where the two decays are independent, will be referred to hereafter as the *uncoupled* biexponential model, and the second situation, where the two excited species may interconvert, will be termed the *coupled* biexponential model. The latter case will now be analyzed in detail.

Consider the following reaction scheme where interconversion between species A and B can occur when they are in either their ground states or their excited states:

$$\begin{tikzcd}
\mathrm{A}^* + \mathrm{M} \arrow[r, shift left, "k'_{\mathrm{BA}}"] \arrow[d, shift right, "k_{\mathrm{A}}"'] & \mathrm{B}^* + \mathrm{N} \arrow[l, shift left, "k'_{\mathrm{AB}}"] \arrow[d, shift right, "k_{\mathrm{B}}"'] \\
\mathrm{A} + \mathrm{M} \arrow[r, shift left] \arrow[u, shift right, "h\nu"'] & \mathrm{B} + \mathrm{N}. \arrow[l, shift left] \arrow[u, shift right, "h\nu"']
\end{tikzcd} \tag{IV}$$

Yguerabide and Burton [9] examined a particular example of a system like the one above, where A is a monomer and B is its dimer. Alvarez-Pez *et al.* [10] examined a system also resembling the one above, but where A and B are conjugate acid–base pairs. We will outline the equations governing luminescence decay and also derive an expression for the rise of luminescence intensity with time.

In the above scheme, A* and B* may return to their ground states by a number of possible routes—there might be quenching (Q) by a quencher molecule, Q; there might be internal conversion (IC) or intersystem crossing (ISC); or there could be fluorescence (F). For simplicity, if k_A and k_B represent the combined rate constants for all of these processes, then [10]

$$k_{\mathrm{A}} = k_{\mathrm{FA}} + k_{\mathrm{ICA}} + k_{\mathrm{ISCA}} + k_{\mathrm{QA}}[\mathrm{Q}], \tag{10a}$$

$$k_{\mathrm{B}} = k_{\mathrm{FB}} + k_{\mathrm{ICB}} + k_{\mathrm{ISCB}} + k_{\mathrm{QB}}[\mathrm{Q}]. \tag{10b}$$

Although it is not shown in the above reaction scheme, for generality we must also consider [10] the possibility that interconversion of A (or A*) to B (or B*) might occur directly without involving M or N, according to

$$\mathrm{A}^* \underset{k_{\mathrm{AB}}}{\overset{k_{\mathrm{BA}}}{\rightleftarrows}} \mathrm{B}^* \tag{Va}$$

and

$$\mathrm{A} \rightleftarrows \mathrm{B}. \tag{Vb}$$

It has been shown [9] that if the above system is excited by a rectangular pulse of exciting light, which lasts long enough for a steady state to be obtained, then coupled differential equations of the following form will result:

$$\frac{\mathrm{d}[\mathrm{A}^*]}{\mathrm{d}t} = \alpha_1[\mathrm{B}^*] - \alpha_2[\mathrm{A}^*], \tag{11a}$$

$$\frac{\mathrm{d}[\mathrm{B}^*]}{\mathrm{d}t} = \alpha_3[\mathrm{A}^*] - \alpha_4[\mathrm{B}^*], \tag{11b}$$

where

$$\alpha_1 = k_{AB} + k'_{AB}[N], \tag{12a}$$

$$\alpha_2 = k_{BA} + k'_{BA}[M] + k_A, \tag{12b}$$

$$\alpha_3 = k_{BA} + k'_{BA}[M], \tag{12c}$$

$$\alpha_4 = k_{AB} + k'_{AB}[N] + k_B. \tag{12d}$$

Yguerabide and Burton [9] provided a method of solving these coupled differential equations, and Alvarez-Pez *et al.* [10] gave their solution as

$$[B^*] = \beta_{BS}\exp(\gamma_S t) + \beta_{BL}\exp(\gamma_L t), \tag{13a}$$

$$[A^*] = \beta_{AS}\exp(\gamma_S t) + \beta_{AL}\exp(\gamma_L t), \tag{13b}$$

where

$$\gamma_{S,L} = \frac{-(\alpha_2 + \alpha_4) \mp \sqrt{(\alpha_4 - \alpha_2)^2 - 4\alpha_1\alpha_3}}{2}. \tag{14}$$

The β_{ij} coefficients in the above solutions may be solved by considering the initial values of the concentrations and their derivatives. This gives a system of simultaneous linear equations with the β_{ij} symbols as unknowns. Their solution is [8–10]

$$\beta_{AS} = \frac{(\alpha_2 + \gamma_L)[A^*]_0 - \alpha_1[B^*]_0}{\gamma_L - \gamma_S}, \tag{15a}$$

$$\beta_{AL} = \frac{(\alpha_2 + \gamma_S)[A^*]_0 - \alpha_1[B^*]_0}{\gamma_S - \gamma_L}, \tag{15b}$$

$$\beta_{BS} = \frac{(\alpha_4 + \gamma_L)[B^*]_0 - \alpha_3[A^*]_0}{\gamma_L - \gamma_S}, \tag{15c}$$

$$\beta_{BL} = \frac{(\alpha_4 + \gamma_S)[B^*]_0 - \alpha_3[A^*]_0}{\gamma_S - \gamma_L}. \tag{15d}$$

Note that the values for β_{AS} and (or) β_{BS} might be negative, but positive concentrations will still result overall.

The observed emitted light intensity will be given by

$$L = \varphi_2 k_{FA}[A^*] + \varphi_2 k_{FB}[B^*], \tag{16}$$

where φ_2 is an instrumental factor to account for the light collection efficiency and the bandpass. Hence

$$L = a\exp(\gamma_S t) + b\exp(\gamma_L t), \tag{17}$$

where

$$a = \varphi_2(k_{FA}\beta_{AS} + k_{FB}\beta_{BS}), \tag{18a}$$

$$b = \varphi_2(k_{FA}\beta_{AL} + k_{FB}\beta_{BL}). \tag{18b}$$

Note that a will be negative if both β_{AS} and β_{BS} are negative. If they are both positive, a will also be positive. If one is positive and one is negative, a may be either positive or negative depending on the relative magnitudes of the terms in Eq. (18a). On the other hand, b must always be positive.

In [9, 10], the authors derived only decay expressions. We now present an expression for the rise of luminescence intensity with time when the exciting light is turned on.

Consider the above coupled biexponential system (in Eq. (IV)), which is being excited by radiation of intensity I. The system will now be described by the following coupled differential equations:

$$\frac{d[A^*]}{dt} = \alpha_1[B^*] - \alpha_2[A^*] + \varphi_{1A}I, \tag{19a}$$

$$\frac{d[B^*]}{dt} = \alpha_3[A^*] - \alpha_4[B^*] + \varphi_{IB}I, \tag{19b}$$

where I is the exciting light intensity, φ_{1A} is the quantum efficiency for the excitation of A molecules, φ_{1B} is the quantum efficiency for the excitation of B molecules, and the other symbols have been previously defined.

The solution of the above equations is [8]

$$[A^*] = c_1\exp(\gamma_S t) + c_2\exp(\gamma_L t) + \frac{\alpha_1\varphi_{1B}I + \alpha_4\varphi_{1A}I}{\gamma_S\gamma_L}, \tag{20a}$$

$$[B^*] = c_3\exp(\gamma_S t) + c_4\exp(\gamma_L t) + \frac{\alpha_3\varphi_{1A}I + \alpha_2\varphi_{1B}I}{\gamma_S\gamma_L}, \tag{20b}$$

where from the initial conditions we find [8]

$$c_1 = \frac{I}{\gamma_S(\gamma_S - \gamma_L)}((\gamma_S + \alpha_4)\varphi_{1A} + \alpha_1\varphi_{1B}), \tag{21a}$$

$$c_2 = \frac{I}{\gamma_L(\gamma_L - \gamma_S)}((\gamma_L + \alpha_4)\varphi_{1A} + \alpha_1\varphi_{1B}), \tag{21b}$$

$$c_3 = \frac{I}{\gamma_S(\gamma_S - \gamma_L)}((\gamma_S + \alpha_2)\varphi_{1A} + \alpha_3\varphi_{1B}), \tag{21c}$$

$$c_4 = \frac{I}{\gamma_L(\gamma_L - \gamma_S)}((\gamma_L + \alpha_2)\varphi_{1A} + \alpha_3\varphi_{1B}). \tag{21d}$$

By matching up the rise solutions (Eqs. (20a) and (20b)) with the fall solutions (Eqs. (13a) and (13b)) at the point at which the exciting radiation is turned off, we observe that $\beta_{AS} = -c_1$, $\beta_{AL} = -c_2$, $\beta_{BS} = -c_3$, and $\beta_{BL} = -c_4$. Hence, c_2 and c_4 must be negative while c_1 and c_3 may be either negative or positive. Finally, the luminescence intensity for the rise case of a coupled biexponential model will be given by

$$L = \varphi_2 k_{FA}[A^*] + \varphi_2 k_{FB}[B^*]. \tag{22}$$

By substituting in the expressions for [A*] and [B*] (Eqs. (20a) and (20b) given above) and rearranging, we have

$$\begin{aligned} L &= \varphi_2\{(-k_{\mathrm{FA}}c_1 - k_{\mathrm{FB}}c_3)(1-\exp(\gamma_{\mathrm{S}}t)) \\ &\quad + (-k_{\mathrm{FA}}c_2 - k_{\mathrm{FB}}c_4)(1-\exp(\gamma_{\mathrm{L}}t))\} \qquad (23) \\ &= a(1-\exp(\gamma_{\mathrm{S}}t)) + b(1-\exp(\gamma_{\mathrm{L}}t)), \end{aligned}$$

where the symbols have all been previously defined.

2.2. Second-Order Models

2.2.1. Equal Initial Concentrations. Consider the elementary reaction

$$\mathrm{A} + \mathrm{A} \xrightarrow{k} \mathrm{C}. \qquad \mathrm{(VI)}$$

This type of reaction is said to be bimolecular because two molecules of species A are reacting. It is well known [1] that, for this type of reaction, the concentration of species A decreases according to

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{1 + k[\mathrm{A}]_0 t}, \qquad (24)$$

where k is the second-order rate constant for the reaction and the other symbols have all been previously defined.

Now consider the possible second-order reaction scheme for a fluorescent reaction:

$$\mathrm{A} + \mathrm{A} \xrightarrow{k} \mathrm{C}^* \xrightarrow{\text{fast}} \mathrm{C} + h\nu. \qquad \mathrm{(VII)}$$

If the second step is fast compared with the first, then the luminescence intensity will decay according to

$$L = \varphi\frac{\mathrm{d}[\mathrm{C}^*]}{\mathrm{d}t} = -\varphi\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{\varphi k[\mathrm{A}]_0^2}{(1 + k[\mathrm{A}]_0 t)^2}. \qquad (25)$$

Quickenden *et al.* [2–4, 6] give the above expression as

$$L = \frac{k[\mathrm{A}]_0^2}{(1 + k[\mathrm{A}]_0 t)^2}, \qquad (26)$$

which is the same as the previous one (Eq. (25)) if it is assumed that the quantum efficiency is unity (see Sections 5.1 and 6). It should be noted that, when Eq. (25) is presented in [6], the t has been inadvertently omitted.

Let us now consider the situation where species A is being produced as well as consumed:

$$\mathrm{X} + h\nu_1 \xrightarrow{\text{fast}} \mathrm{A} + \mathrm{A} \xrightarrow{k} \mathrm{C}^* \xrightarrow{\text{fast}} \mathrm{C} + h\nu_2. \qquad \mathrm{(VIII)}$$

For the above system, it has been shown [11] that

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \varphi_1 I - k[\mathrm{A}]^2, \qquad (27)$$

where φ_1 is the quantum efficiency for the production of A molecules. It should be noted that Calvert and Pitts [11] designate A by R_1.

From Eq. (27), with the assumption that $[\mathrm{A}]_0 = 0$, it follows that [11] the rise in the concentration of species A when the exciting radiation is turned on will be described by

$$[\mathrm{A}] = (\varphi_1 I/k)^{1/2}\tanh(t(\varphi_1 Ik)^{1/2}). \qquad (28)$$

The assumption that $[\mathrm{A}]_0 = 0$ is reasonable because if A was present initially, then there would already be luminescence from the C* that would form spontaneously.

Although Calvert and Pitts consider the rise of the *concentration* of species A, they do not explicitly derive an expression for the rise of luminescence intensity with time when the exciting radiation is first turned on. We will now do this.

The rise of the luminescence intensity with time will be given by

$$L = \varphi_2\frac{\mathrm{d}[\mathrm{C}^*]}{\mathrm{d}t}, \qquad (29)$$

where φ_2 is the quantum efficiency for the production of luminescence from C*. Since the rate of production of C* is equal to the rate of consumption of A, it follows that [8]

$$L = \varphi_2 k[\mathrm{A}]^2 = \alpha\tanh^2(\beta t), \qquad (30)$$

where $\alpha = \varphi_1\varphi_2 I$ and $\beta = (\varphi_1 Ik)^{1/2}$.

2.2.2. Unequal Initial Concentrations. Consider the following bimolecular elementary process where the initial concentrations of A and B are not equal:

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \mathrm{C}. \qquad \mathrm{(IX)}$$

The above case is considered generally by Benson [1], and he has some useful discussion on this situation. However, he does not present an explicit expression for the concentration of species C at time t, which we will now do. The above system can be described by the differential equation

$$-\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = k[\mathrm{A}][\mathrm{B}]. \qquad (31)$$

It may be noted that if one concentration is much greater than the other, for example, if $[\mathrm{B}] \gg [\mathrm{A}]$, we can write $k' = k[\mathrm{B}]$ and then we have

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k'[\mathrm{A}], \qquad (32)$$

which may be treated as a first-order situation. If this happens, then we have the well-known [1] case of pseudo first-order kinetics.

Later, in Section 3.2.2, we will give the solution to Eq. (31) for the nonclassical case where $k = k_0 t^{-h}$ and give the general solution as Eq. (54). The present situation represents the classical case where $h = 0$. Setting $h = 0$ in Eq. (54) leads to

$$[\mathrm{C}] = [\mathrm{B}]_0 - \frac{[\mathrm{A}]_0 - [\mathrm{B}]_0}{\frac{[\mathrm{A}]_0}{[\mathrm{B}]_0}\exp(([\mathrm{A}]_0 - [\mathrm{B}]_0)kt) - 1}. \qquad (33)$$

Now consider the luminescence-producing reaction

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \mathrm{C}^* \xrightarrow{\text{fast}} \mathrm{C} + h\nu, \qquad \text{(X)}$$

where, as is usual, the second step is much faster than the first. As was the case in Section 2.2.1 with equal initial concentrations, the luminescence intensity decays according to

$$L = \varphi\frac{\mathrm{d}[\mathrm{C}^*]}{\mathrm{d}t}. \qquad (34)$$

As has been shown by Quickenden *et al.* [2–4, 6, 7], this gives

$$L = \frac{\varphi[\mathrm{A}]_0 R(1-R)we^{wt}}{(R-\mathrm{e}^{wt})^2}, \qquad (35)$$

where $R = [\mathrm{B}]_0/[\mathrm{A}]_0$, $w = k[\mathrm{A}]_0(1 - R)$, and the other symbols have their usual meanings. The quantum efficiency is again defined as unity as in Section 2.2.1. Note that Quickenden *et al.* [2, 4, 6] have sometimes incorrectly defined R as $[\mathrm{A}]_0/[\mathrm{B}]_0$. Also, in [6, 7] the authors have mistakenly added an extra factor of $k[\mathrm{A}]_0$ in the numerator. However, because of the arbitrary nature of φ (see Section 5.1), this will not cause major problems.

We have discussed above the decay of luminescence intensity with time for a bimolecular system with initially unequal concentrations, which has been considered by previous researchers. We will now consider how the luminescence intensity from such a system rises with time when the system is first excited with radiation. This case has not been dealt with previously and is rather more complicated than the decay situation for the following reason. When two species are present in initially unequal concentrations and proceed to react according to a bimolecular reaction mechanism, it does not matter how they were produced initially or how their concentrations became unequal. However, when we consider the rise situation, we must take into account the process(es) that produced the two species and also how the concentrations became unequal. We will consider two possible mechanisms for producing unequal concentrations.

Firstly, let us consider the following system:

$$\mathrm{X} + h\nu_1 \xrightarrow{\text{fast}} \mathrm{A} + \mathrm{B} \xrightarrow{k} \mathrm{C}^* \xrightarrow{\text{fast}} \mathrm{C} + h\nu_2, \qquad \text{(XI)}$$

where A and B are produced and consumed on a one to one basis, but before the exciting radiation ($h\nu_1$) is turned on, there are already B molecules, but no A molecules, present in the system. Writing

$$D = [\mathrm{B}] - [\mathrm{A}] = [\mathrm{B}]_0 - [\mathrm{A}]_0 \qquad (36)$$

and noting that the system is described by the differential equation

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \varphi_1 I - k[\mathrm{A}][\mathrm{B}], \qquad (37)$$

we have

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \varphi_1 I - k[\mathrm{A}](D + [\mathrm{A}]). \qquad (38)$$

This may be solved [8] to give

$$[\mathrm{A}] = \frac{p^{1/2}}{2}\tanh\left(\frac{ktp^{1/2}}{2} + \tanh^{-1}\left(\frac{D}{p^{1/2}}\right)\right) - \frac{D}{2}, \qquad (39)$$

from which it follows [8]:

$$R = \frac{[\mathrm{B}]_{\text{plateau}}}{[\mathrm{A}]_{\text{plateau}}} = \frac{D + [\mathrm{A}]_{\text{plateau}}}{[\mathrm{A}]_{\text{plateau}}} = \frac{p^{1/2} + D}{p^{1/2} - D}. \qquad (40)$$

We can now use these equations to find an expression for the rise of the luminescence intensity with time. As in the case of equal initial concentrations, the rise of the intensity of the luminescence with time will be given by

$$L = \varphi_2\frac{\mathrm{d}[\mathrm{C}^*]}{\mathrm{d}t}, \qquad (41)$$

where φ_2 is the quantum efficiency for the production of luminescence from C*. Since the rate of production of C* is equal to the rate of consumption of A,

$$L = \varphi_2 k[\mathrm{A}][\mathrm{B}] = \varphi_2 k[\mathrm{A}]([\mathrm{A}] + D). \qquad (42)$$

Combining this with Eq. (38) gives [8]

$$L = \varphi_2\left\{\varphi_1 I - \frac{pk}{4}\operatorname{sech}^2\left(\frac{ktp^{1/2}}{2} + \tanh^{-1}\left(\frac{D}{p^{1/2}}\right)\right)\right\}, \qquad (43)$$

which reduces to Eq. (30) if [A] = [B] (see Section 2.2.1).

The above expression can be simplified to [8]

$$L = \varphi_2\left(\varphi_1 I + \frac{D^2k}{4}\right) \times \left(\frac{D/p^{1/2} + \tanh(ktp^{1/2}/2)}{1 + (D/p^{1/2})\tanh(ktp^{1/2}/2)}\right)^2 - \frac{\varphi_2 D^2 k}{4}. \qquad (44)$$

As usual, we may let φ_2 be unity (see Sections 5.1 and 6).

We will now consider a second possible mechanism for producing A and B in unequal concentrations. Let us take a mechanism represented by the following steps:

$$\mathrm{X} + h\nu_1 \xrightarrow{\text{fast}} \mathrm{A}, \qquad \text{(XIIa)}$$

$$\mathrm{X} + h\nu_1 \xrightarrow{\text{fast}} \mathrm{B}, \qquad \text{(XIIb)}$$

$$\mathrm{A} + \mathrm{B} \xrightarrow{k} \mathrm{C}^* \xrightarrow{\text{fast}} \mathrm{C} + h\nu_2, \qquad \text{(XIIc)}$$

where the quantum efficiencies for processes (XIIa) and (XIIb) are not equal and are given by $\varphi_{1\mathrm{A}}$ and $\varphi_{1\mathrm{B}}$, respectively. This system will be described by the differential equations

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \varphi_{1\mathrm{A}} I - k[\mathrm{A}][\mathrm{B}] \qquad (45\text{a})$$

and

$$\frac{d[B]}{dt} = \varphi_{1B}I - k[A][B]. \tag{45b}$$

Although the above equations have no known analytical solution, it may be shown that [8], at very short times, $[A] \approx [B]$ and the rise will be similar to that for the second-order model with initially equal concentrations presented in Section 2.2.1. Also [8] at very long times, the difference between the two concentrations will become very large, and the subsequent decay will resemble that for a pseudo first-order situation.

3. FRACTAL MODELS OF KINETICS

There has been much recent interest in the area of fractal kinetics since the early publication by Ovchinnikov and Zeldovich in 1978 [12]. Fractal kinetics (sometimes called “fractal-like” kinetics) may need to be used in situations where reactants are spatially constrained on a microscopic scale by walls, force fields, or phase boundaries.

In a reaction involving fractal kinetics, the rate coefficient in the long time limit is a function of time and is given [13–16] by

$$k(t) = k_0 t^{-h}, \tag{46}$$

where $k(t)$ is the rate coefficient at time t, k_0 is a constant and corresponds to the rate constant for the reaction in a nonfractal regime, and h is related [16, 17] to the spectral or fracton dimension, $\tilde{d}$, of the system by

$$h = 1 - \tilde{d}/4. \tag{47}$$

For a discussion on the dimensions involved with fractals, the work of Rammal and Toulhouse [18] should be referred to.

3.1. Second-Order Fractal Kinetics with Equal Initial Concentrations

Consider the reaction below occurring in a fractal medium:

$$A + A \xrightarrow{k_0 t^{-h}} C^* \xrightarrow{\text{fast}} C + h\nu. \tag{XIII}$$

This situation was considered in [12–14, 19–22], and an expression for the decay of concentration with time has been reported [13, 14, 20–22]. Dissado [19] also derived an expression for the decay of luminescence intensity with time, but it is incorrect due to an error in the final differentiation step. The above system will be described by the differential equation

$$\frac{d[A]}{dt} = -k_0 t^{-h}[A]^2, \tag{48}$$

which may be solved [8, 13, 14, 20] to give

$$[A] = \frac{[A]_0}{1 + \dfrac{k_0[A]_0 t^{1-h}}{1-h}}. \tag{49}$$

The luminescence intensity will be given by

$$L = -\varphi\frac{d[A]}{dt} = \varphi k_0 t^{-h}[A]^2 = \frac{\varphi k_0 t^{-h}[A]_0^2}{\left(1 + \dfrac{k_0[A]_0 t^{1-h}}{1-h}\right)^2}. \tag{50}$$

As in the classical second-order expressions, φ, the quantum efficiency, can be made equal to unity (see Sections 5.1 and 6).

3.2. Second-Order Fractal Kinetics with Unequal Initial Concentrations

3.2.1. Introduction. In this section we will focus on reactions of the type $A + B \longrightarrow C$ occurring in a fractal medium. Species C may be inert and not react any further ($A + B \longrightarrow 0$), or it may undergo a subsequent “fast” light-emitting step, viz.,

$$A + B \xrightarrow{k(t) = k_0 t^{-h}} C^* \xrightarrow{\text{fast}} C + h\nu. \tag{XIV}$$

By fast, it is meant that the second step in the above scheme occurs on a much shorter time scale than the first.

The current literature on fractal kinetics [12–14, 19–22] normally examines the special case where A and B are initially in equal concentrations or the special case where the concentration of one species is much greater than the other. The latter is often called pseudo-unimolecular or pseudo-first-order. These situations have been discussed in the above sections of this review.

Kang and Redner [17] have considered the case of fractal kinetics with initially unequal concentrations. They have found that, in the short time limit, the concentration decays as

$$[A] = ct^{-d/4}, \tag{51}$$

where [A] is the concentration of species A, t is time, d is the spatial dimension of the system, and c is a constant. By short time limit, it is meant that $t \ll t_\xi$, where t_ξ is the characteristic time of the system. This is the time taken for a particle to diffuse across a region of linear dimension ξ, where ξ is given by [17]

$$\xi = \left((N_A[B]_0)^{1/2} - (N_A[A]_0)^{1/2}\right)^{-2/d}, \tag{52}$$

where $[B]_0$ and $[A]_0$ are the initial concentrations of B and A, respectively, and N_A is the Avogadro number.

Kang and Redner [17] derived an expression for the initially unequal concentration case, but it is not fully evaluated—there are several constants left out. In addition, they did not consider the case, where species C subsequently produces luminescence. The expressions derived in this work are in two forms, viz., an explicit expression which includes all constants and has concentration as a function of time and an expression for luminescence intensity as a function of time when the reaction being studied is chemiluminescent.

Schnörer *et al.* [23, 24] have also derived concentration versus time expressions for the case of initially unequal concentrations. However, unlike the present derivation, which is valid for the more common three-dimensional space situation, these derivations are only for one-dimensional space. They also assume that there are localized regions where there are only molecules of species A and other regions where there are only molecules of species B. In order to achieve these localized regions, a sufficiently high reaction rate is required [24].

3.2.2. Derivation. Consider the following second-order reaction scheme:

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_0 t^{-h}} \mathrm{C}. \tag{XV}$$

For second-order kinetics [13–15, 19] of the fractal type considered above,

$$-\frac{\mathrm{d[C]}}{\mathrm{d}t} = \frac{\mathrm{d[A]}}{\mathrm{d}t} = -k_0 t^{-h}[\mathrm{A}][\mathrm{B}]. \tag{53}$$

This may be solved to give [8]

$$[\mathrm{C}] = [\mathrm{B}]_0 - \frac{[\mathrm{A}]_0 - [\mathrm{B}]_0}{\frac{[\mathrm{A}]_0}{[\mathrm{B}]_0}\exp\left(\frac{([\mathrm{A}]_0 - [\mathrm{B}]_0)t^{1-h}k_0}{1-h}\right) - 1}. \tag{54}$$

If we now extend Eq. (XV) to include the luminescent reaction scheme in Eq. (XIV), we can show that [8]

$$L = \frac{\varphi R[\mathrm{A}]_0(1-R)wt^{-h}\exp\left(\frac{wt^{1-h}}{1-h}\right)}{\left(R - \exp\left(\frac{wt^{1-h}}{1-h}\right)\right)^2}, \tag{55}$$

where $w = k_0[\mathrm{A}]_0(1-R)$ and $R = [\mathrm{B}]_0/[\mathrm{A}]_0$, and φ is the quantum efficiency.

In the special case where h is equal to zero, the situation of a nonfractal bimolecular luminescent reaction between A and B occurs and Eq. (55) reduces to Eq. (35).

In the case of $R \gg 1$ or $R \ll 1$, the situation of pseudo-first-order fractal kinetics occurs, and this case is discussed in the next section.

3.3. Fractal Kinetics As Treated by Plonka

3.3.1. Luminescence Decay Kinetics. Plonka has derived a function for fitting time-dependent decay kinetics and has shown that it fits a large amount of experimental data quite satisfactorily. The derivation and subsequent fitting of data have appeared in a large number of papers by Plonka and his coworkers, of which some representative examples are [20–22]. This expression has been used by other researchers, for example, Quickenden *et al.* [5–7]. However, although it has been shown that this function frequently fits experimental data quite well, until now it has been unclear what mechanistic information this provides. This section attempts to clarify this situation.

In order to derive his expression, Plonka begins with the time-dependent rate coefficient

$$k(t) = k_0 t^{\alpha - 1}. \tag{56}$$

If we let $\alpha = 1 - h$, then this equation is equivalent to the time-dependent rate coefficient for fractal kinetics mentioned in Section 3. Plonka then goes on to show that the luminescence intensity will decay according to

$$L = \gamma\alpha\tau^{-1}\left(\frac{t}{\tau}\right)^{\alpha-1}\exp\left(-\left(\frac{t}{\tau}\right)^{\alpha}\right), \tag{57}$$

where τ is called the “effective lifetime” and γ is a proportionality constant.

Plonka and coauthors have interpreted the above expression in two ways. Firstly, they consider that the luminescence results from a number of simultaneous first-order processes. This would correspond to a generalization of the uncoupled biexponential model (see Section 2.1.2). The second interpretation made by Plonka and his coworkers is that the luminescence results from a second-order fractal process with initially unequal concentrations and with one of the concentrations being much greater than the other one. This is similar to the classical case of pseudo-first-order kinetics discussed earlier in Section 2.2.2. In this discussion, we show that the first interpretation is much more likely to be correct. Additionally, Plonka [21] attempts to explain the case of fractal kinetics with equal initial concentrations as a number of simultaneous second-order processes and, by similar reasoning, we will show that this interpretation is unlikely to be valid.

We will now consider Plonka’s derivation and show how it applies to pseudo-first-order fractal kinetics. Consider the following reaction:

$$\mathrm{A} + \mathrm{B} \xrightarrow{k(t)} \mathrm{C}^* \xrightarrow{\text{fast}} \mathrm{C} + h\nu. \tag{XVI}$$

If this reaction occurs in a fractal medium, then, at long times, we can let $k(t) = k_0^{\prime\prime} t^{-h}$. (Here we use a double prime on $k_0^{\prime\prime}$ to indicate that it is a second-order rate constant.) The above system will be described by the following differential equation:

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = -k_0^{\prime\prime} t^{-h}[\mathrm{A}][\mathrm{B}]. \tag{58}$$

Since $[\mathrm{B}] \gg [\mathrm{A}]$, we can write

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = -k_0 t^{-h}[\mathrm{A}], \tag{59}$$

where $k_0 = k_0^{\prime\prime}[\mathrm{B}]$. On integration this gives [8, 21, 22]

$$[\mathrm{A}] = [\mathrm{A}]_0 \exp\left(-\frac{k_0 t^{1-h}}{1-h}\right). \qquad (60)$$

This will apply whether or not the reaction is light-emitting.

The dependence of luminescence intensity with time for a chemiluminescent reaction, which follows the Plonka kinetics, is then given as [8]

$$L = \varphi[\mathrm{A}]_0 k_0 t^{-h} \exp\left(-\frac{k_0 t^{1-h}}{1-h}\right). \qquad (61)$$

Plonka defines the “effective lifetime” τ as

$$\tau = \left(\frac{1-h}{k_0}\right)^{1/\alpha}. \qquad (62)$$

Using $\alpha = 1 - h$, we can rearrange Eq. (61) in the form

$$L = \gamma\alpha\tau^{-1}\left(\frac{t}{\tau}\right)^{\alpha-1} \exp\left(-\left(\frac{t}{\tau}\right)^{\alpha}\right), \qquad (63)$$

which is identical to Eq. (57) (γ will equal $\varphi[\mathrm{A}]_0$).

The above treatment shows how the Plonka equation applies to a pseudo-first-order reaction occurring in a fractal medium. We will now examine Plonka’s “simultaneous reaction” interpretations of kinetics in the cases of pseudo-first-order fractal and second-order fractal with equal initial concentrations.

Plonka writes [21]

$$\begin{aligned} L &= \gamma\alpha\tau^{-1}\left(\frac{t}{\tau}\right)^{\alpha-1} \exp\left(-\left(\frac{t}{\tau}\right)^{\alpha}\right) \\ &= \int_0^{\infty} \exp(-t/\tau)\, f(\tau)\mathrm{d}\tau \end{aligned} \qquad (64a)$$

for pseudo-first-order kinetics and

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{1 + \dfrac{k_0[\mathrm{A}]_0 t^{1-h}}{1-h}} = \int_0^{\infty} \frac{[\mathrm{A}]_0}{1 + k_0[\mathrm{A}]_0 t} f(\tau)\mathrm{d}\tau \qquad (64b)$$

for second-order fractal kinetics with initially equal concentrations. Plonka then points out that $f(\tau)$ can be evaluated using an inverse Laplace transform in the first case and an inverse Mellin transform in the second case. Although there is no problem mathematically with these ideas, there is no phenomenological reason why these things must occur. In fact it is possible to write the first-order equation as a sum of second-order equations and the second-order equation as a sum of first-order equations. Furthermore, this logic can be applied to any function so that it may be written as the sum of any other arbitrary functions weighted according to some weighting factors given by $f(\tau)$. By using the appropriate transform, we can always evaluate $f(\tau)$, even if it cannot be done analytically. This is what is done, for example, in signal analysis when a square wave is written as the sum of a number of sine waves using a Fourier transform. Because this can be done mathematically, it does not mean that the square wave actually resulted from the superpositioning of a number of sine waves.

3.3.2. Kinetics of Rise in Luminescence Intensity. Despite publishing many papers, Plonka has derived only an expression for the decay of luminescence intensity with time. In this section, we will develop a method to treat data from the rise of luminescence intensity with time. As there is no analytical solution here, we must resort to a numerical treatment.

Consider the reaction scheme

$$\mathrm{X} + h\nu_2 \xrightarrow{\text{fast}} \mathrm{A} + \mathrm{B} \xrightarrow{k(t)} \mathrm{C}^* \xrightarrow{\text{fast}} \mathrm{C} + h\nu_2, \qquad (\mathrm{XVII})$$

where $k(t)$ has its usual form. This system will be described by the differential equation

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \varphi_1 I - k_0 t^{-h}[\mathrm{A}], \qquad (65)$$

where φ_1 is the quantum efficiency for the excitation step in Eq. (XVII).

Equation (65) may be solved to give [8]

$$L = \frac{y - \dfrac{\mathrm{d}L}{\mathrm{d}t}\dfrac{1}{k_0 t^{-h}}}{1 + \dfrac{h}{k_0 t^{1-h}}}, \qquad (66)$$

φ_2 is the quantum efficiency for the light-emitting step above, and y is equal to $y = \varphi_1\varphi_2 I$. Equation (66) can be used to fit to an observed set of rise data. All that is required is a numerical differentiation of the luminescence intensity data, L, to obtain $\dfrac{\mathrm{d}L}{\mathrm{d}t}$.

4. TUNNELING MECHANISM

Tachiya and Mozumder [25] have derived a kinetic expression for the decay of luminescence intensity with time when it is produced as a result of geminate-ion recombination occurring by a tunneling mechanism. They give [25] L as proportional to t^{-m}, where m is a constant.

5. PROBLEMS, PITFALLS, AND SUBTLETIES OF FITTING KINETIC DATA

5.1. The Implications of Assuming a Value of Unity for the Quantum Efficiency

When fitting second-order expressions to luminescence intensity decay data, Quickenden and coauthors have often assumed that the quantum efficiency is unity. Section 6 discusses why it is necessary to do this. Of course, experimentally, it is very unlikely that this is ever the case. Mathematically, however, we can show that it is still acceptable to do this provided we note that the parameters obtained from the fit will not be absolute and will have the quantum efficiency contained or "hidden" in them. This means that all concentrations found from the fitting of data to kinetic expressions need to be adjusted by dividing them by the quantum efficiency to obtain the "true" or absolute concentration. Furthermore, all second-order rate constants need to be adjusted by multiplying them by the quantum efficiency in order to obtain the "true" or absolute second-order rate constant. This can be shown to be true for both the rise and fall expressions for second-order kinetics, whether or not the concentrations are initially equal or unequal. For second-order fractal kinetics, k_0 needs to be multiplied by the quantum efficiency in order to obtain its "true" or absolute value.

As an example, we will now show how the above adjustments apply to the second-order decay with initially equal concentrations. The other situations can be examined in a similar way.

Consider the equation

$$L = \frac{\varphi k[\mathrm{A}]_0^2}{(1+k[\mathrm{A}]_0 t)^2}, \tag{67}$$

where k and $[\mathrm{A}]_0$ are "true" or absolute. Now let us suppose that

$$k = k_{\mathrm{fit}}\varphi \tag{68a}$$

and

$$[\mathrm{A}]_0 = \frac{([\mathrm{A}]_0)_{\mathrm{fit}}}{\varphi}, \tag{68b}$$

where the "fit" subscript denotes fitted values for k and $[\mathrm{A}]_0$. If the quantum efficiency is assumed to be unity, the following equation would be fitted to the experimental luminescence intensity decay data:

$$L = \frac{k_{\mathrm{fit}}([\mathrm{A}]_0)_{\mathrm{fit}}^2}{(1+k_{\mathrm{fit}}([\mathrm{A}]_0)_{\mathrm{fit}}t)^2}. \tag{69}$$

By substituting the above expressions for the "fit" parameters, we obtain

$$L = \frac{\frac{k}{\varphi}([\mathrm{A}]_0\varphi)^2}{\left(1+\frac{k}{\varphi}[\mathrm{A}]_0\varphi t\right)^2} = \frac{\varphi k[\mathrm{A}]_0^2}{(1+k[\mathrm{A}]_0 t)^2}, \tag{70}$$

which is the same as the original expression (Eq. (67)) with an arbitrary quantum efficiency φ. This proves that the adjustments to the concentration and rate constant are correct.

5.2. *The Apparent Mathematical Equivalence of the Biexponential and Second-Order Unequal Decays*

A complication that may arise when fitting expressions to observed luminescence intensity decay data is that more than one function may appear to fit adequately. This is a particular problem when trying to distinguish a biexponential fit from a second-order fit with unequal initial concentrations. This problem arises because, under certain limiting conditions, the two equations used for these fits are mathematically equivalent. This is discussed elsewhere [8].

5.3. *Normalization*

When examining luminescence intensity decay curves, it is quite common to collect several curves and to average them in order to improve the signal-to-noise ratio. This does not present a problem if the curves are taken under identical conditions. However, significant random error is often present, and this may result in different starting intensities for the curves. In order to overcome this problem, experimenters often normalize their decay curves to have the same starting intensity prior to averaging them. However, this is not always mathematically justifiable. For first-order fits normalization does not present a problem, but it may not be valid for second-order fits. Here we will show why this is the case for a second-order equal decay.

First, let us consider the effect of normalization on a simple exponential function. Let L_A and L_B be two first-order luminescence decay curves, where

$$L_\mathrm{A} = \varphi_\mathrm{A}[\mathrm{A}]_{0,\mathrm{A}}k\exp(-kt), \tag{71a}$$

$$L_\mathrm{B} = \varphi_\mathrm{B}[\mathrm{A}]_{0,\mathrm{B}}k\exp(-kt). \tag{71b}$$

The normalized averaged function will be

$$L = \frac{1}{2}\left(\frac{\varphi_\mathrm{A}[\mathrm{A}]_{0,\mathrm{A}}k\exp(-kt)}{\varphi_\mathrm{A}[\mathrm{A}]_{0,\mathrm{A}}k} + \frac{\varphi_\mathrm{B}[\mathrm{A}]_{0,\mathrm{B}}k\exp(-kt)}{\varphi_\mathrm{B}[\mathrm{A}]_{0,\mathrm{B}}k}\right) = \exp(-kt), \tag{72}$$

where the starting intensity for each curve has been normalized to be unity. It is clear that the form of the function is still exponential, and the rate constant k is not affected.

Now consider two second-order equal (initial concentration) decay curves

$$L_\mathrm{A} = \frac{\varphi_\mathrm{A}k[\mathrm{A}]_{0,\mathrm{A}}^2}{(1+k[\mathrm{A}]_{0,\mathrm{A}}t)^2} \tag{73a}$$

and

$$L_\mathrm{B} = \frac{\varphi_\mathrm{B}k[\mathrm{A}]_{0,\mathrm{B}}^2}{(1+k[\mathrm{A}]_{0,\mathrm{B}}t)^2}. \tag{73b}$$

Summary of practical expressions to fit to time-dependent luminescence intensity data

Model	See section	Decay expression	Rise expression (see note 6)	See note(s)
1st-Oder	2.1.1	$L = a_1 \exp(-kt)$	$L = a_1(1 - \exp(-kt))$	4
Double 1st-Oder	2.1.2	$L = a\exp(-k_a t) + b\exp(-k_b t)$	$L = a(1 - \exp(-k_a t)) + b(1 - \exp(-k_b t))$	–
2nd-Oder ($[A]_0 = [B]_0$)	2.2.1	$L = \dfrac{k[A]_0^2}{(1 + k[A]_0 t)^2}$	$L = \alpha\tanh^2(\beta t)$	7
2nd-Oder ($[A]_0 \neq [B]_0$)	1.2.2	$L = \dfrac{[A]_0 R(1 - R)we^{wt}}{(R - e^{wt})^2}$	$L = I_0 - \dfrac{pk}{4}\text{sech}^2\left(\dfrac{ktp^{1/2}}{2} + \tanh^{-1}\left(\dfrac{D}{p^{1/2}}\right)\right)$	1, 2, 3, 7
Fractal 2nd-Oder ($[A]_0 = [B]_0$)	3.1	$L = \dfrac{k_0 t^{-h}[A]_0^2}{\left(1 + \dfrac{k_0[A]_0 t^{1-h}}{1-h}\right)^2}$	–	7
Fractal 2nd-Oder ($[A]_0 \neq [B]_0$)	3.2	$L = \dfrac{R[A]_0(1-R)wt^{-h}\exp\left(\dfrac{wt^{1-h}}{1-h}\right)}{\left(R - \exp\left(\dfrac{wt^{1-h}}{1-h}\right)\right)^2}$	–	1, 7
Fractal Pseudo 1st-Oder (Plonka)	3.3	$L = \gamma\alpha\tau^{-1}\left(\dfrac{t}{\tau}\right)^{\alpha - 1}\exp\left(-\left(\dfrac{t}{\tau}\right)^{\alpha}\right)$	$L = \dfrac{y - \dfrac{dL}{dt}\dfrac{1}{k_0 t^{-h}}}{1 + \dfrac{h}{k_0 t^{1-h}}}$	–
Tunneling	4	$L = Pt^{-m}$	–	5

Notes: 1. Set $w = k[A]_0(1 - R)$ when fitting the equation.

2. Set $p = \dfrac{4I_0}{k} + D^2$ when fitting the equation.

3. $I_0 = \varphi_1 I$, i.e., the quantum efficiency must be assumed to be unity (see earlier in Section 6).

4. $a_1 = \varphi[A]_0 k$ in the rise expression and $a_1 = \varphi_1\varphi_2 I$ in the decay expression. These two definitions are consistent as shown at the end of Section 2.2.1. Again these arise because the quantum efficiencies must be assumed to be unity.

5. P is a constant of proportionality.

6. If initial data is truncated, then all rise functions must have an arbitrary constant added to them.

7. For second-order fits, the rate constants and concentrations are not "true" or absolute. It is necessary to divide concentrations by φ and to multiply rate constants by φ in order to get true values. See Section 5.1 for more details.

If we attempt to normalize both of these curves to have a starting intensity of unity and then average them, we get

$$
\begin{aligned}
L_A &= \frac{1}{2}\left(\frac{\varphi_A k[A]_{0,A}^2}{\varphi_A k[A]_{0,A}^2(1 + k[A]_{0,A}t)^2}\right. \\
&\quad \left. + \frac{\varphi_B k[A]_{0,B}^2}{\varphi_B k[A]_{0,B}^2(1 + k[A]_{0,B}t)^2}\right) \qquad (74)\\
&= \frac{1}{2}\left(\frac{1}{(1 + k[A]_{0,A}t)^2} + \frac{1}{(1 + k[A]_{0,B}t)^2}\right),
\end{aligned}
$$

which is no longer a second-order equal function unless the initial concentrations $[A]_{0,A}$ and $[A]_{0,B}$ happen to be equal. This demonstrates that we cannot always normalize and average two second-order decay curves.

5.4. Effect of Truncating Initial Data

Sometimes it is necessary to truncate the initial data in a decay or rise curve. A common reason for doing this might be that in an experiment there is a finite time taken for a shutter to open or close, which affects the initial portion of the decay or rise curve. In other cases, it is possible that there is a transient short-lived rise or decay component superimposed on a longer lived one and it is desired that this short-lived be removed component. There is no problem in removing the initial portion of a decay curve, because it is known that the curve must end on zero, and we can extrapolate the fitted function back to zero time. It should be noted, however, that this extrapolation may not match the experimentally measured starting intensity, particularly, if there is a superimposed short-lived decay.

The situation for a rising curve of luminescence intensity is a little more complicated. It is known that it will start at zero experimentally, but this does not take into account any initial short-lived rise from the shutter or from another superimposed luminescence band. Also, the final intensity will be uncertain, particularly if there is a short-lived rise at the start of the curve. As a result, an arbitrary constant needs to be added to any rise function to account for these uncertainties.

6. FITTING PROCEDURES

When an experimental set of time-dependent luminescence intensity data is obtained, it is tested by the fitting program against the appropriate equation from the table. The fitting program will also require starting values for each of the parameters in the equation that is being tested.

It is usually necessary to assume that the quantum efficiency is unity (see Section 5.1) for the following reasons. As an example, consider Eq. (25) for the decay of luminescence intensity in a second-order equal reaction mechanism. There are two possible fitted constants here, viz., $\varphi k[\mathrm{A}]_0^2 = s_1$ and $k[\mathrm{A}]_0 = s_2$. We now have only two expressions from which to derive three variables, and this is impossible to do. Accordingly, we reduce the number of variables to two by assuming φ is unity.

The program will report fitted parameters and the sum of the squared residuals (SSR). The equation of best fit will be that having the lowest SSR value as well as the least correlated residuals.

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