

Mathematical functions for the analysis of luminescence decays with underlying distributions: 2. Becquerel (compressed hyperbola) and related decay functions

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Abstract

The Becquerel (compressed hyperbola) decay law is analyzed in detail and shown to be an interesting approach for the analysis of complex luminescence decays. A decay function unifying the modified Kohlrausch and Becquerel decay laws is also introduced. It is proposed that the analysis of luminescence decays with a sum of Becquerel functions is a powerful alternative to the usual sum of exponentials. It is also shown that some complex decay laws can be written as a sum of an infinite number of exponentials and have for this reason an infinite but discrete spectrum of rate constants.

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1. Introduction

The first quantitative studies of the time evolution of luminescence (following flash excitation) were carried out by Edmond Becquerel (1820–1891) and published in 1861. The functions used by this author for the description of the experimental decays already included an exponential of time, and also a sum of two such exponentials [1]. Becquerel also noticed that for some of his experimental systems (inorganic solids), an empirical decay function of the form

$$I(t) = \frac{1}{(1 + at)^2} \quad (1)$$

gave better fits than a sum of two exponentials. Later on, he proposed a more general equation in the form $I^m(t + a) = b$ that can be rewritten as

$$I(t) = \frac{1}{(1 + at)^p} \quad (2)$$

with p taking values between 1 and 2 [1].

This function that decays faster than a hyperbola (for which $p = 1$) can be called *compressed* or *squeezed hyperbola*. But owing to Becquerel pioneering studies, and reviving a now almost forgotten denomination [2], we shall also call this function the Becquerel decay law.

The luminescence decay of phosphors is often complicated on account of the trapping and re-trapping processes. A distribution of traps with different depths originates a distribution of decay times, even when interaction of different luminescent centers and hence re-trapping is neglected. On the other hand, when the trapping probability is negligible, all luminescent centers

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interact, and the process is analogous to an elementary bimolecular reaction where both reactants (electrons and holes) are present with identical concentration, and can be described by

$$\frac{dN}{dt} = -kN^2, \quad (3)$$

where N is the number of luminescent centers (in a given volume) after δ -pulse excitation. Integration leads to a normalized decay law $I(t) = N(t)/N_0$ that is formally identical to Eq. (1).

Eq. (2) can be obtained from an interpolating rate equation of the type

$$\frac{dN}{dt} = -kN^{2-\beta}, \quad (4)$$

where $0 \leq \beta \leq 1$. The extreme values $\beta = 0$ and $\beta = 1$ correspond to second-order ($p = 1$) and first-order kinetics, respectively. Integration of Eq. (4) leads to Becquerel's decay law written in the following form:

$$I(t) = \frac{1}{\left[1 + (1 - \beta) \frac{t}{\tau_0}\right]^{1/(1-\beta)}}. \quad (5)$$

The control parameter β has a role similar to that played in the stretched exponential or Kohlrausch function that was discussed in the preceding paper of this series [3],

$$I(t) = \exp[-(t/\tau_0)^\beta]. \quad (6)$$

In fact, the Kohlrausch and Becquerel laws become both a single exponential law in the limiting case where $\beta = 1$. For phosphors, this occurs when the excitation is localized and the electron never leaves the initial luminescent center, where a single type of trap exists.

In the preceding paper of this series, we discussed the use of the Kohlrausch decay law for analyzing complex luminescence decays with underlying distributions [3]. The Kohlrausch decay law is in fact convenient as a fitting function, even in the absence of a model, given that it allows gauging in simple way deviations to the “canonical” single exponential behavior through parameter β . The same can be said about the Becquerel function, although its less direct relation to the exponential decay has limited its use up to now mainly to the luminescence of phosphors [4–6]. The few examples reported in other fields deserve citation. Wlodarczyk and Kierdaszuk [7] rediscovered the Becquerel function and showed that it provides good fits for fluorescence decays that slightly depart from the exponential behavior, implying a relatively narrow distribution of decay times around a mean value. The same authors used the Becquerel function for analyzing luminescence decays when triplet excitation transport occurs in disordered organic solids [8]. This function was also used for describing the decay of delayed fluorescence resulting from triplet–triplet annihilation in polyphenylquin-

oxalines in frozen solutions or films [9]. Another example that is not relevant to photophysics concerns the dynamics of ligand binding to myoglobin [10].

We show in the present paper that the Becquerel decay law is an interesting approach for the analysis of complex luminescence decay laws. Moreover, we introduce a decay function unifying the Kohlrausch and Becquerel decay laws.

2. Becquerel decay function

Let us consider the first-order kinetic equation

$$\frac{dN}{dt} = -k(t)N, \quad (7)$$

where k is time-dependent according to

$$k(t) = \frac{1}{\tau_0 + (1 - \beta)t}, \quad (8)$$

where $0 \leq \beta \leq 1$. The solution of Eq. (7) is the Becquerel decay function, Eq. (5).

It should be noted that values of β outside the range defined above yield unphysical results: for $\beta \leq 0$ the integrated intensity (total intensity) diverges, and for $\beta > 1$ the intensity becomes zero at a finite value of t .

Let us examine now the relationship with an underlying distribution $H(k)$ of rate constants in the fluorescence decay according to

$$I(t) = \int_0^\infty H(k)e^{-kt} dk. \quad (9)$$

The time-dependent rate coefficient is then given by

$$k(t) = \frac{\int_0^\infty kH(k)e^{-kt} dk}{\int_0^\infty H(k)e^{-kt} dk}. \quad (10)$$

The average rate constant defined as

$$\langle k \rangle = \int_0^\infty kH(k) dk = -I'(0) = k(0) \quad (11)$$

takes the following value for the Becquerel function:

$$\langle k \rangle = \frac{1}{\tau_0}. \quad (12)$$

Hence, the decay can be rewritten as

$$I(t) = \frac{1}{\left[1 + (1 - \beta)\langle k \rangle t\right]^{1/(1-\beta)}}. \quad (13)$$

As in the preceding paper, we define a time-averaged rate constant defined by

$$\bar{k} = \frac{\int_0^\infty k(t)I(t) dt}{\int_0^\infty I(t) dt} = \frac{1}{\int_0^\infty I(t) dt}. \quad (14)$$

The convention of a bar for the time average, and of brackets for the distribution (“ensemble”) average will be followed throughout.

For the Becquerel function, we have

$$\bar{k} = \frac{\beta}{\tau_0}. \quad (15)$$

Let us consider now a distribution of lifetimes $f(\tau)$ instead of rate constants so that the decay is written as

$$I(t) = \int_0^\infty f(\tau) e^{-1/\tau} d\tau. \quad (16)$$

An average time constant can then be defined as

$$\langle \tau \rangle = \int_0^\infty \tau f(\tau) d\tau = \int_0^\infty I(t) dt \quad (17)$$

and its value for the Becquerel function is

$$\langle \tau \rangle = \frac{\tau_0}{\beta}. \quad (18)$$

The average decay time defined as

$$\bar{\tau} = \frac{\int_0^\infty t I(t) dt}{\int_0^\infty I(t) dt} \quad (19)$$

is, in the present case, given by

$$\bar{\tau} = \frac{\tau_0}{2\beta - 1} \quad (20)$$

for $\beta > 1/2$. For $\beta < 1/2$ the average decay time is infinite.

For β close to 1, the decay approaches a single exponential decay with lifetime τ_0 , while for small β the decay slows down dramatically, see Fig. 1. From Eq. (13) it follows that for small β the decay becomes hyperbolic

$$I(t) = \frac{1}{1 + \langle k \rangle t} \quad (21)$$

a result exact for $\beta = 0$, and is therefore controlled by a single parameter $\langle k \rangle$, while for other values of β there are two independent parameters, β and τ_0 , or β and $\langle k \rangle$, as is always the case for the Kohlrausch function.

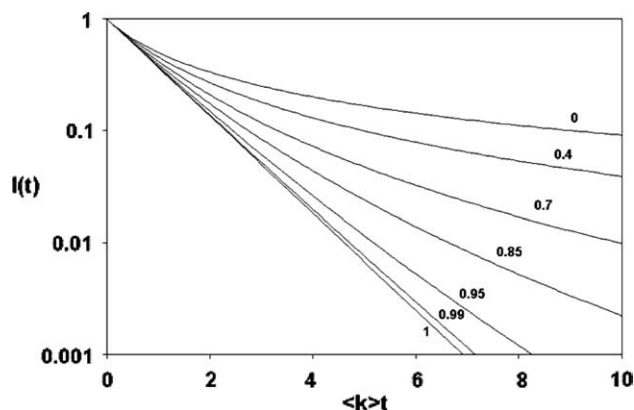


Fig. 1. Becquerel decay law, Eq. (13). Numbers next to each curve are the respective values of parameter β . The decay is hyperbolic for $\beta = 0$ and exponential for $\beta = 1$.

The Becquerel decay law has also the advantage of possessing a simple inverse Laplace transform,

$$H(k) = \frac{\left(\frac{1}{1-\beta} \frac{k}{\langle k \rangle}\right)^{\beta/(1-\beta)} \exp\left(-\frac{1}{1-\beta} \frac{k}{\langle k \rangle}\right)}{(1-\beta) \langle k \rangle \Gamma\left(\frac{1}{1-\beta}\right)}, \quad (22)$$

which is a Gamma distribution, and whose mean and standard deviation are $\langle k \rangle$ and $\langle k \rangle \sqrt{(1-\beta)}$, respectively. This distribution is shown in Fig. 2 for several values of β . For $\beta = 0$, the distribution of rate constants is exponential. On the other hand, for β sufficiently close to 1 ($\beta > 0.95$, say), the rate constant distribution becomes a relatively narrow normal (gaussian) distribution with mean and standard deviation given by the previous expressions. When $\beta \rightarrow 1$, the standard deviation goes to zero, and the distribution becomes $\delta(k - \frac{1}{\tau_0})$, as could be expected.

The Becquerel decay is initially exponential,

$$I(t) = \exp(-\langle k \rangle t) \quad (23)$$

and the initial decay rate is always finite. This short-time behavior is more realistic than that displayed by the primitive Kohlrausch function, but is shared by the modified Kohlrausch function proposed before [3].

For sufficiently long times, the Becquerel decay becomes a power law,

$$I(t) = [(1-\beta) \langle k \rangle t]^{1/(\beta-1)} \quad (24)$$

and the decay is the slower, the smaller the β parameter, see Fig. 1.

The slowing down of the decay rate can also be seen in the time-dependent rate coefficient, Eq. (8). For $\beta \neq 1$ it always decays with t^{-1} , while for the Kohlrausch function the decay of the rate coefficient is slower, with $t^{\beta-1}$ [3], and only approaches that of the Becquerel function for very small β .

It is interesting to remark that a decay law of the form [11,12]

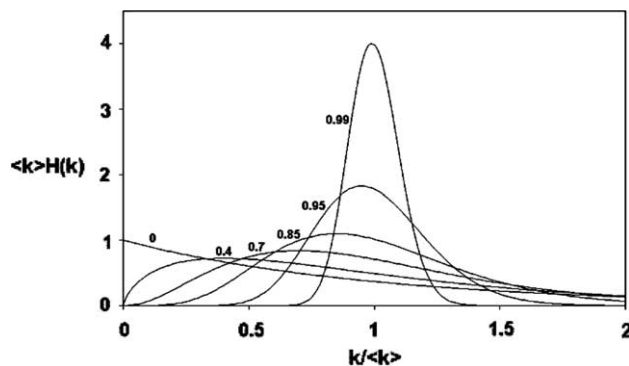


Fig. 2. Distribution of rate constants for the Becquerel decay law (Gamma density function), as a function of parameter β .

$$I(t) = \frac{1}{1 + \left(\frac{t}{\tau_0}\right)^\alpha} \quad (25)$$

with $\alpha < 1$, that has been suggested for ground-state peptide folding kinetics [12], as an alternative to a stretched exponential, and indeed also successfully fitted experimental data spanning 7 orders of magnitude [12], cannot be a fully valid luminescence decay law over the entire time range, given that $\int_0^\infty I(t) dt$ is divergent for $\alpha < 1$. Its distribution of rate constants is given in [13]. As mentioned before [3], these restrictions are lifted if the full decay contains a multiplicative exponential.

3. Mixed first- and second-order decay

It also worthwhile to compare the Becquerel decay law with a decay law that interpolates between first- and second-order kinetics in a different way. This law is the mixed first- and second-order kinetics that can be obtained from the following equation:

$$\frac{dN}{dt} = -k_1 N - k_2 N^2 \quad (26)$$

with time-independent and nonzero k_1 and k_2 . Integration yields

$$I(t) = \frac{k_1}{(k_1 + k_2 N_0) e^{k_1 t} - k_2 N_0}, \quad (27)$$

where N_0 is the initial number of excited luminophores. This equation can be rewritten as

$$I(t) = \frac{\beta}{e^{k_1 t} - 1 + \beta}, \quad (28)$$

where

$$\beta = \frac{k_1}{k_1 + k_2 N_0}, \quad (29)$$

where β is again the control parameter: For $\beta = 0$ the decay is second-order, while for $\beta = 1$ the decay is first-order.

The time-dependent rate coefficient is

$$k(t) = \frac{k_1}{1 - (1 - \beta) e^{-k_1 t}} \quad (30)$$

hence,

$$\langle k \rangle = k_1 \quad (31)$$

and

$$\langle \tau \rangle = \frac{1}{k} = \frac{\ln \beta}{(\beta - 1) k_1}. \quad (32)$$

The average decay time is

$$\bar{\tau} = -\frac{Li_2(1 - \beta)}{k_1 \ln \beta}, \quad (33)$$

where $Li_n(x)$ is the polylogarithmic function,

$$Li_n(x) = \sum_{p=1}^{\infty} \frac{x^p}{p^n}. \quad (34)$$

Eq. (28) can be rewritten as

$$I(t) = \frac{\beta e^{-k_1 t}}{1 - (1 - \beta) e^{-k_1 t}} \quad (35)$$

or, expanding

$$\begin{aligned} I(t) &= \beta e^{-k_1 t} [1 + (1 - \beta) e^{-k_1 t} + (1 - \beta)^2 e^{-2k_1 t} + \dots] \\ &= \beta \sum_{n=1}^{\infty} (1 - \beta)^{n-1} e^{-nk_1 t}. \end{aligned} \quad (36)$$

Hence, the rate constant distribution is

$$H(k) = \beta \sum_{n=1}^{\infty} (1 - \beta)^{n-1} \delta(k - nk_1) \quad (37)$$

and therefore the decay law corresponds to an infinite (but discrete) sum of exponentials with equally spaced rate constants, and of decreasing amplitude. Interestingly, the rate constants are independent of k_2 that affects only the amplitudes, and acts therefore like a perturbation. For $\beta = 1$, only the first term survives, and the decay is single exponential. For $\beta < 1$, a fixed comb-like pattern of eigenvalues exists, with decreasing weights as k increases. For $\beta = 0$, (second-order decay) the decay is

$$I(t) = \frac{1}{1 + k_2 N_0 t}. \quad (38)$$

Eq. (37) is not valid, and the distribution of rate constants is exponential,

$$H(k) = \frac{1}{\langle k \rangle} \exp\left(-\frac{k}{\langle k \rangle}\right) \quad (39)$$

with $\langle k \rangle = k_2 N_0$, cf. Eq. (22) with $\beta = 0$.

The mixed decay function given by Eq. (28) is reasonably well adjusted by the Becquerel decay function, especially for values of β close to the upper and lower limits. A fitting with a common \bar{k} gives

$$\beta_b = \beta_m (0.801 \beta_m^2 - 1.948 \beta_m + 2.151), \quad (40)$$

where β_b is the parameter of the Becquerel decay law corresponding to the β_m parameter of the mixed first- and second-order decay. Note however the different asymptotic behavior of the two functions. In fact, the mixed decay law Eq. (28) is asymptotically exponential, with rate constant k_1 .

The above decay law applies to the phosphorescence arising from triplet–triplet annihilation. However, if one considers the decay of delayed fluorescence, which is proportional to N^2 , the appropriate decay law is

$$I(t) = \left(\frac{\beta}{e^{k_1 t} - 1 + \beta} \right)^2 \quad (41)$$

that gives, upon expansion

$$I(t) = \beta^2 e^{-2k_1 t} [1 + 2(1 - \beta)e^{-k_1 t} + 3(1 - \beta)^2 e^{-2k_1 t} + \dots] \\ = \beta^2 \sum_{n=1}^{\infty} n(1 - \beta)^{n-1} e^{-(n+1)k_1 t}. \quad (42)$$

Hence, the rate constant distribution is

$$H(k) = \beta^2 \sum_{n=1}^{\infty} n(1 - \beta)^{n-1} \delta[k - (n + 1)k_1]. \quad (43)$$

For $\beta = 0$ the decay is

$$I(t) = \frac{1}{(1 + k_2 N_0 t)^2}. \quad (44)$$

Eq. (43) is not valid, and the distribution of rate constants is

$$H(k) = \frac{k}{\langle k \rangle^2} \exp\left(-\frac{k}{\langle k \rangle}\right) \quad (45)$$

with $\langle k \rangle = k_2 N_0$.

4. A decay law with extreme sub-exponential behavior

If one considers a rate coefficient that decays very fast to zero, like

$$k(t) = k_0 e^{-at} \quad (46)$$

one obtains from Eq. (7),

$$I(t) = \exp\left[-\frac{k_0}{a}(1 - e^{-at})\right]. \quad (47)$$

This decay law applies to quenching in micelles and other compartmentalized systems, see [14] and references therein.

The corresponding $H(k)$ is

$$H(k) = e^{-k_0/a} \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{k_0}{a}\right)^n \delta(k - na). \quad (48)$$

The rate coefficient for this law goes so fast to zero that the integral $\int_0^{\infty} k(u) du$ is convergent and therefore the decay at infinite time, $I(\infty)$, is larger than zero. In the absence of a multiplicative exponential, the integral $\int_0^{\infty} I(t) dt$ is clearly divergent.

5. A decay function unifying the modified Kohlrausch and Becquerel decay laws

A simple formula interpolating between the modified Kohlrausch and Becquerel decay laws is

$$I(t) = \exp[\alpha^{1-\alpha(1-\beta)}] \\ \times \exp\left\{-\left[\alpha + \frac{\ln\left[1 + (1-\alpha)(1-\beta)\frac{t}{\tau_0}\right]}{(1-\alpha)(1-\beta)}\right]^{1-\alpha(1-\beta)}\right\}, \quad (49)$$

where α is a parameter taking values between 0 (Becquerel) and 1 (modified Kohlrausch). For the recovery of the modified Kohlrausch law, one has to take the limit $\alpha \rightarrow 1$ in Eq. (49).

The rate coefficient for the unified decay law is

$$k(t) = \frac{1 - \alpha(1 - \beta)}{\left[1 + (1 - \alpha)(1 - \beta)\frac{t}{\tau_0}\right]^{\alpha(1-\beta)}} \frac{1}{\tau_0} \quad (50)$$

and therefore

$$\langle k \rangle = k(0) = \frac{1 - \alpha(1 - \beta)}{\alpha^{\alpha(1-\beta)}} \frac{1}{\tau_0} \quad (51)$$

and the decay law can be rewritten as

$$I(t) = \exp[\alpha^{1-\alpha(1-\beta)}] \\ \times \exp\left\{-\left[\alpha + \frac{\ln\left[1 + \frac{(1-\alpha)(1-\beta)}{1-\alpha(1-\beta)} \alpha^{\alpha(1-\beta)} \langle k \rangle t\right]}{(1-\alpha)(1-\beta)}\right]^{1-\alpha(1-\beta)}\right\}. \quad (52)$$

The asymptotic behavior of the unified decay law is (for $\alpha \neq 1$)

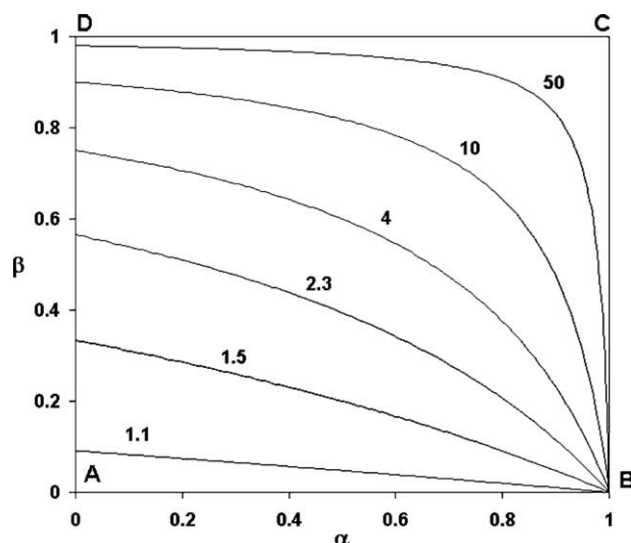


Fig. 3. Parameter space (α, β) for the unified decay law, Eq. (49). The number next to each curve is the power a of the asymptote t^{-a} . In corner A (0,0) the decay law is second-order (hyperbolic). In corner B (1,0) there is no decay. In corners C (1,1) and D (0,1), as well as along the line CD, the decay is exponential. Along line AB, the decay has asymptote t^{-1} . Along line BC, the decay law is the modified Kohlrausch law. Along line AD, the decay law is the Becquerel law.

$$I(t) \propto t^{-\frac{1-\alpha(1-\beta)}{(1-\alpha)(1-\beta)}}. \quad (53)$$

In Fig. 3 the type of decay law obtained is shown diagrammatically as a function of α and β . For $\beta = 1$, the decay is single exponential, irrespective of α . For $\beta = 0$, the decay is

$$I(t) = \exp \left[\alpha^{1-\alpha} - \left(\alpha + \frac{1}{1-\alpha} \ln \left[1 + (1-\alpha) \frac{t}{\tau_0} \right] \right)^{1-\alpha} \right] \quad (54)$$

or

$$I(t) = \exp \left[\alpha^{1-\alpha} - \left(\alpha + \frac{1}{1-\alpha} \ln [1 + \alpha^x \langle k \rangle t] \right)^{1-\alpha} \right] \quad (55)$$

and the asymptote is t^{-1} for all $\alpha < 1$, hence the integral $\int_0^\infty I(t) dt$ is divergent.

6. Analysis of complex decays with a sum of Becquerel functions

As discussed previously [3], two approaches to fit decay laws with a discrete sum of terms are the use of exponentials and hyperbolae as base functions. Since the Becquerel decay law interpolates between these two extreme cases, it seems reasonable to assume that a sum of a few Becquerel functions, appropriately weighted, will be a powerful fitting function for complex decays,

$$I(t) = \sum_i \alpha_i (1 + \gamma_i t)^{1/(\beta_i - 1)} \quad (56)$$

with

$$\sum_i \alpha_i = 1 \quad (57)$$

and

$$\gamma_i = (1 - \beta_i) \langle k_i \rangle = \frac{1 - \beta_i}{\tau_i}. \quad (58)$$

The corresponding distribution of rate constants will be a weighted sum of Gamma density functions.

The average lifetime is

$$\langle \tau \rangle = \sum_i \alpha_i \langle \tau_i \rangle = \sum_i \frac{\alpha_i \tau_i}{\beta_i} \quad (59)$$

while the average decay time is, for $\beta_i > 1/2$,

$$\bar{\tau} = \frac{\langle \tau^2 \rangle}{\langle \tau \rangle} = \frac{\sum_i \alpha_i \langle \tau_i^2 \rangle}{\sum_i \alpha_i \langle \tau_i \rangle} = \frac{\sum_i \alpha_i \tau_i \bar{\tau}_i}{\sum_i \alpha_i \langle \tau_i \rangle} = \frac{\sum_i \frac{\alpha_i \tau_i^2}{\beta_i (2\beta_i - 1)}}{\sum_i \frac{\alpha_i \tau_i}{\beta_i}} \quad (60)$$

and the average rate constant and the average rate coefficient are

$$\langle k \rangle = \sum_i \alpha_i \langle k_i \rangle = \sum_i \frac{\alpha_i \beta_i}{\tau_i}, \quad (61)$$

$$\bar{k} = \frac{1}{\langle \tau \rangle} = \frac{1}{\sum_i \frac{\alpha_i \tau_i}{\beta_i}}. \quad (62)$$

7. Conclusions

We showed in the present paper that the Becquerel decay law is an interesting approach for the analysis of complex luminescence decays. A decay function unifying the modified Kohlrausch and Becquerel decay laws was also introduced. It is proposed that the analysis of luminescence decays with a sum of Becquerel functions, Eq. (56), is a powerful alternative to the usual sum of exponentials. Finally, analysis of some known decay laws, Eqs. (28), (41) and (47), showed that they can be written as a sum of an infinite number of exponentials and have an infinite but discrete spectrum of rate constants.

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