

The propagation of radiation through a medium containing a component that absorbs the radiation and is steadily destroyed by it

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Abstract The Beer–Lambert law is inadequate to describe the absorption of radiation by a medium if the absorbing component is being simultaneously destroyed by the radiation. A replacement law is derived and solved in terms of a family of polynomials. The solution is confirmed numerically and by simulation.

Keywords Radiation absorption · Beer–Lambert law · Polynomials · Time dependence

1 Introduction

The wide range of systems to which the title of this document has potential relevance includes photochemical studies of photolabile species [1], neutron capture, water splitting [2], the dissipation of aerosol mists by sunlight, and the remediation of water by ultra-violet radiation [3]. Perhaps the simplest realization of the phenomenon is the passage of light through a solution of a dye that is bleached by the light; the discussion that follows is couched in terms of that model system.

If the dissolved dye absorbs the light and is otherwise unaffected, the physics of the absorption is described by a law that was first enunciated by Bouguer [4], but is usually attributed to Lambert [5] and Beer [6]. Although it is more often encountered in integrated form, the fundamental Beer–Lambert law is

$$\frac{d}{dX} I(X) = -\epsilon C(X) I(X), \quad (1)$$

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where C is the dye concentration (in molecules per cubic metre), and X measures distance (metres) along the light path. The empirical constant ϵ , which is specific to the nature of the absorber and the light's wavelength, goes by a variety of names, one of which is "absorptivity" (square metres per molecule). Because light absorption occurs by interaction of photons with dye molecules, it is appropriate to express the light intensity I as a photon flux (photons per square metre per second).¹ The notation in Eq. (1) recognizes that the light intensity will, and the absorber concentration may, vary from point to point along a ray of light.

However, if the dye is subject to bleaching, the absorption of light by the dye is accompanied by its transformation to a non-absorbing² product, and then the Beer–Lambert law no longer tells the whole story. The bleaching causes a decrease in dye concentration, leading to a diminution in absorption, and a consequential increase in the local light intensity. A subtle interplay develops between intensity and concentration and both become dependent not only on location, but also on time, T , an independent variable (seconds) that is absent from the Beer–Lambert law.

2 How concentration and intensity interact

Though it is then inadequate, there is no reason to believe that the Beer–Lambert law, in the form of Eq. (1), has become invalid when bleaching occurs. That equation still applies at any particular site in the solution and at each instant of time, though it should now be rewritten as

$$\frac{\partial}{\partial X} I(X, T) = -\epsilon C(X, T) I(X, T) \quad (2)$$

to recognize the importance of time.

To proceed further, a specific system geometry will be adopted. Suppose the dilute dye solution, of initially uniform concentration $C(X, 0)$, fills a cell shaped as a rectangular parallelepiped of volume AL . Separated internally by a distance³ L , two opposite faces of the cell are transparent vertical plates, one of which, starting at time $T = 0$, is perpendicularly irradiated by monochromatic light of constant and uniform intensity $I(0, T)$. In a typical experiment, the intensity, $I(L, T)$, of the light emerging horizontally from the second plate would be monitored at one or more times. Here, however, interest is in predicting both the light intensity $I(X, T)$ and the dye concentration $C(X, T)$ at *all* locations in $0 \leq X \leq L$ and at *all* time instants $T \geq 0$.

Focus attention on a narrow vertical wafer of solution, of area A and thickness dX . The Beer–Lambert law, Eq. (2), shows that the number of photons destroyed in this wafer in the time interval dT is

¹ Alternatively one might prefer to express I in Einsteins per square metre per second and C in moles per cubic metre.

² Only minor changes in the theory are needed if the product also absorbs light, but is otherwise inert.

³ The cell width L does not appear in the ensuing mathematics. Though necessarily finite in experimental practice, there is no theoretical limit to the cell width. In the simulation L is accorded the value $2.5/[\epsilon C(X, 0)]$.

$$[I(X, T) - I(X + dX, T)]AdT = \varepsilon AC(X, T)I(X, T)dXdT \quad (3)$$

It will be assumed that the absorption of light occurs by interaction between a single photon and a single molecule of dye, and leads to annihilation of the photon and simultaneous destruction of the molecule. Not every photon-molecule encounter is effective, however, and photochemists refer to the fractional success of the encounter as the “quantum yield” ϕ (molecules per photon), a constant for a given dye at a specified wavelength. Thus the number of molecules destroyed within the wafer in time dT will be ϕ times the quantity in Eq. (3). That is,

$$[C(X, T) - C(X, T + dT)] AdX = \phi \varepsilon AC(X, T)I(X, T)dXdT \quad (4)$$

or equivalently

$$\frac{\partial}{\partial T} C(X, T) = \phi \varepsilon C(X, T)I(X, T) \quad (5)$$

Compare Eqs. (2) and (5). The remarkable result

$$\frac{\partial}{\partial T} C(X, T) = \phi \frac{\partial}{\partial X} I(X, T) \quad (6)$$

emerges. In words, this equation states that, apart from the constant factor ϕ , *the dependence of the concentration on time exactly matches the dependence of intensity on distance*, an important result that was recognized previously [7]. A single bivariate function describes both dependences but, in itself, Eq. (6) provides no information as to what the function might be. The remainder of this document is devoted to elucidating this obscure bivariate function. First, however, it is opportune to adopt dimensionless variables.

The two independent variables in the system—distance and time—are replaced as follows:

$$x = \varepsilon C(X, 0)X \quad (7)$$

and

$$t = \phi \varepsilon I(0, T)T \quad (8)$$

while the replacements for the two dependent variables—dye concentration and light intensity—are

$$c(x, t) = \frac{C(X, T)}{C(X, 0)} \quad (9)$$

and

$$i(x, t) = \frac{I(X, T)}{I(0, T)} \quad (10)$$

Each of the latter pair of dimensionless variables takes a value between zero and unity. Equations (2) and (5) may now be combined and expressed in terms of the four dimensionless quantities as

$$-\frac{\partial}{\partial t}c(x, t) = c(x, t)i(x, t) = -\frac{\partial}{\partial x}i(x, t) \quad (11)$$

The goal is to solve this dual equation.

Though they are coupled, there are two distinct problems. The first of these is to determine the distribution of concentration in space and time by solving the partial differential equation given below with its attendant boundary conditions:

$$\frac{\partial}{\partial t}c(x, t) = -c(x, t)i(x, t) \quad \text{with} \quad \begin{cases} c(x, 0) = 1 \\ c(0, t) = \exp\{-t\} \\ c(x, \infty) = 0 \end{cases} \quad (12)$$

The first and third of these boundary conditions are self-evident. The second arises from noting that, at the $x = 0$ front of the cell, light intensity is invariant and so the differential equation may be recast as

$$\frac{d}{dt} \ln\{c(0, t)\} = -i(0, t) = -1, \quad (13)$$

and integrated to

$$c(0, t) = c(0, 0)\exp\{-t\} = \exp\{-t\}. \quad (14)$$

A straightforward integration would solve the differential equation in (12) if the form of the $i(x, t)$ function were known. However, the latter function is itself the solution to the second problem, which is described by the following set of equations:

$$\frac{\partial}{\partial x}i(x, t) = -i(x, t)c(x, t) \quad \text{with} \quad \begin{cases} i(0, t) = 1 \\ i(x, 0) = \exp\{-x\} \\ i(\infty, t) = 0 \end{cases} \quad (15)$$

and is likewise insoluble without knowledge of the function $c(x, t)$. A classic “chicken and egg” paradox has arisen. Standard methods [8] of solving partial differential equation appear to be inapplicable. Numerical methods [9] could be adopted, but here the rudimentary method of “undetermined coefficients” [10] is pursued. The form of the solutions to the twin problems will be guessed, the guesswork being later confirmed. First, however, a brief digression is made to establish terminology.

3 Complementarity

Consider two bivariate functions f and g , each having a value that depends on the two independent variables y and z . The functions $f(y, z)$ and $g(y, z)$ are distinct, but

on interchanging the variables in one of these functions, it becomes identical with the unchanged other; that is, $f(z, y) = g(y, z)$ and $f(y, z) = g(z, y)$. Though it has other meanings in mathematics, here we use the term “complementary functions” to describe the interrelation of f and g . For example, the functions $f(y, z) = y^2 \exp\{z\}$ and $g(y, z) = z^2 \exp\{y\}$ are complementary.

It is evident from expression (11) that the functions $\partial i/\partial x$ and $\partial c/\partial t$ are complementary in their dependences on x and t . This fact does not guarantee that i and c are themselves similarly complementary but, coupled with the complementarity evident in the boundary conditions in (12) and (15), it implies that they are.

If $f(y, z)$ and $g(y, z)$ are complementary functions, their product⁴ $f(y, z)g(y, z)$ is “self-complementary”. Self-complementary bivariate functions have the property that interchanging their independent variables leaves the function unchanged. Thus, if the function $h(y, z)$ is self-complementary, then $h(z, y) = h(y, z)$. The function $(yz)^2 \exp\{y + z\}$ provides an example.

Notice from Eq. (11) that, because the product $c(x, t)i(x, t)$ is self-complementary, so too are the derivatives $\partial c(x, t)/\partial t$ and $\partial i(x, t)/\partial x$. The existence of self-complementarity in these three terms proves invaluable in the mathematics that follows.

4 A putative series solution

With the identity of the bivariate function $F(\cdot)$, yet to be established, consider the twin expressions

$$c = \exp\{-t\} [1 + txF(t, x)] \quad (16)$$

and

$$i = \exp\{-x\} [1 + xtF(x, t)] \quad (17)$$

as candidate solutions to the two problems posed in (12) and (15). Supporting this candidacy is that the two candidate functions are complementary, and that, *irrespective of the form of the $F(\cdot)$ function*,⁵ all six of the boundary conditions in (12) and (15) are successfully satisfied by the formulas in Eqs. (16) and (17). At this stage, there is no other justification for the postulate that the solutions to the twin problems can be so represented. Nevertheless, some confidence is gleaned from the difficulty encountered in searching for alternative expressions that meet all the boundary conditions. None was found that is equally simple.

To allow a high degree of flexibility in the function $F(x, t)$, it is considered to be analytic and composed of all possible products of nonnegative integer powers of the t and x variables. That is, F is treated as expansible as the two-dimensional power series

⁴ As is their sum $f(y, z) + g(y, z)$

⁵ Provided that F remains finite for all positive values of x and t .

Table 1 Early values of the coefficients

a_{jk}	$k = 1$	$k = 2$	$k = 3$	$k = 4$	$k = 5$	$k = 6$	$k = 7$
$j = 1$	1	$-\frac{1}{2}$	$\frac{1}{6}$	$-\frac{1}{24}$	$\frac{1}{120}$	$-\frac{1}{720}$	$\frac{1}{5040}$
$j = 2$	$-\frac{1}{2}$	$\frac{5}{4}$	$-\frac{13}{12}$	$\frac{29}{48}$	$-\frac{61}{240}$	$\frac{25}{288}$	$-\frac{253}{10080}$
$j = 3$	$\frac{1}{6}$	$-\frac{13}{12}$	$\frac{73}{36}$	$-\frac{301}{144}$	$\frac{1081}{720}$	$-\frac{3613}{4320}$	
$j = 4$	$-\frac{1}{24}$	$\frac{29}{48}$	$-\frac{301}{144}$	$\frac{2069}{576}$	$-\frac{11581}{2880}$		
$j = 5$	$\frac{1}{120}$	$-\frac{61}{240}$	$\frac{1081}{720}$	$-\frac{11581}{2880}$			
$j = 6$	$-\frac{1}{720}$	$\frac{25}{288}$	$-\frac{3613}{4320}$				
$j = 7$	$\frac{1}{5040}$	$-\frac{253}{10080}$					

$$F(x, t) = \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} a_{jk} t^{j-1} x^{k-1}, \quad (18)$$

where the doubly subscripted a 's are constant numerical coefficients yet to be determined. Thus, the two dependent variables are assumed to be expansible as the series

$$c(x, t) = \exp\{-t\} \left[1 + \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} a_{jk} t^j x^k \right] \quad (19)$$

and

$$i(x, t) = \exp\{-x\} \left[1 + \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} a_{jk} x^j t^k \right]. \quad (20)$$

To evaluate the a_{jk} coefficients, series (19) and (20) were substituted into the three terms in expression (11), each of which was then expanded as a lengthy algebraic sum involving the coefficients and various combinations of powers of x and t . On collection of the terms, it became possible to identify each value of a_{jk} . In this endeavour, repeated use was made of the self-complementarity of each of the three terms, which implies that the coefficient of $x^j t^k$ must match that of $x^k t^j$. Details of this extensive operation will be omitted, but Table 1 presents some of the results. In some stages during the compilation of this table, the facilities of *Mathematica* [11] were employed to reduce both the algebraic tedium and the likelihood of arithmetic blunders.

In as much as a limitless number of coefficients is accessible, albeit tediously, by the method of undetermined coefficients, the F function is fully identified and the twin problems inherent in the bleachable dye paradox are, in principle, now solved. However, the solution is cumbersome and unappealing, motivating the following section.

5 Improving the solution

Inspection of the data in Table 1 reveals the following rules:

- (a) $a_{kj} = a_{jk}$. This reflects the self-complementarity of the F function.
- (b) The sign of a_{jk} is determined by the parities of j and k . If these indices share the same parity (both even or both odd), the coefficient is positive; otherwise the coefficient is negative.
- (c) When each a_{jk} coefficient is multiplied by $j!k!$, an odd integer results.
- (d) Immediately evident from the first row of the table is that $a_{1k} = (-1)^{k+1}/k!$, with a similar result for the columnar a_{j1} values.
- (e) For a constant j , the magnitude of a_{jk} at first increases with k and then declines, implying convergence of $\sum_{k=1}^{\infty} a_{jk}$ because the summands alternate in sign.

Inspired by rules (b) and (c), the formula for F in Eq. (18) may be reorganized into

$$F(x, t) = \frac{1}{xt} \sum_{j=1}^{\infty} \frac{(-t)^j}{j!} \sum_{k=1}^{\infty} [(-1)^j j! a_{jk}] x^k \tag{21}$$

Consider the quantity in square brackets for ever-increasing values of k . Rule (d) reveals that

$$[(-1)^j j! a_{j1}] = -1. \tag{22}$$

for $k = 1$. One observes by careful inspection of the $k = 2$ column in Table 1 that

$$[(-1)^j j! a_{j2}] = \frac{1}{2} \{-3 + 2(2^j)\} \tag{23}$$

and, less obviously from the $k = 3$ column, that

$$[(-1)^j j! a_{j3}] = \frac{-1}{6} \{7 - 12(2^j) + 6(3^j)\}. \tag{24}$$

A pattern emerges whereby the k th square-bracketed term may be expressed as a sum of k terms:

$$[(-1)^j j! a_{jk}] = \frac{(-1)^k}{k!} \{b_{k1} + b_{k2}(2^j) + \dots + b_{kk}(k^j)\} = \frac{(-1)^k}{k!} \sum_{h=1}^k b_{kh} h^j, \tag{25}$$

where the b multipliers are integers of either sign, many of which are listed in Table 2. Note that the table also includes supplementary, italicized, entries for certain kh pairs that do not arise in Eq. (25); their significance will become apparent later. Each non-italicized value of b_{kh} is divisible by h and other regularities exist.

Table 2 Early members of the b integers

b_{kh}	$h = 0$	$h = 1$	$h = 2$	$h = 3$	$h = 4$	$h = 5$	$h = 6$	$h = 7$	$h = 8$
$k = 0$	<i>1</i>	0	0	0	0	0	0	0	0
$k = 1$	<i>-1</i>	1	0	0	0	0	0	0	0
$k = 2$	<i>1</i>	-3	2	0	0	0	0	0	0
$k = 3$	<i>-1</i>	7	-12	6	0	0	0	0	0
$k = 4$	<i>1</i>	-15	50	-60	24	0	0	0	0
$k = 5$	<i>-1</i>	31	-180	390	-360	120	0	0	0
$k = 6$	<i>1</i>	-63	602	-2,100	3,360	-2,520	720	0	0
$k = 7$	<i>-1</i>	127	-1,932	10,206	-25,200	21,920	-20,160	5,040	0
$k = 8$	<i>1</i>	-255	6,050	-46,620	166,824	-257,520	272,640	-181,440	40,320

The combination of Eqs. (25) and (21) produces an expression in the form of three nested summations:

$$xtF(x, t) = \sum_{j=1}^{\infty} \frac{(-t)^j}{j!} \sum_{k=1}^{\infty} \frac{(-x)^k}{k!} \sum_{h=1}^k b_{kh} h^j. \quad (26)$$

However, the number of summations may be reduced to two by the following permutation

$$\begin{aligned} xtF(x, t) &= \sum_{k=1}^{\infty} \frac{(-x)^k}{k!} \sum_{h=1}^k b_{kh} \sum_{j=1}^{\infty} \frac{(-ht)^j}{j!} \\ &= \sum_{k=1}^{\infty} \frac{(-x)^k}{k!} \sum_{h=1}^k b_{kh} [\exp\{-ht\} - 1]. \end{aligned} \quad (27)$$

Notice from Table 2 that $\sum_{h=1}^k b_{kh} = (-1)^{k+1}$, permitting Eq. (27) to be rewritten as

$$xtF(x, t) = \left(\sum_{k=1}^{\infty} \frac{(-x)^k}{k!} \sum_{h=1}^k b_{kh} \exp\{-ht\} \right) + \exp\{x\} - 1. \quad (28)$$

If the choice is made to define $b_{k0} = (-1)^k$, as in the italicized column in Table 2, formula (28) may be contracted to

$$xtF(x, t) = \left(\sum_{k=0}^{\infty} \frac{(-x)^k}{k!} \sum_{h=0}^k b_{kh} \exp\{-ht\} \right) - 1, \quad (29)$$

and when this result is substituted into Eqs. (16) and (17), one discovers that the concentration function is

$$c = \exp\{-t\} \sum_{k=0}^{\infty} \frac{(-x)^k}{k!} \sum_{h=0}^k b_{kh} \exp\{-ht\}, \tag{30}$$

with the complementary result

$$i = \exp\{-x\} \sum_{j=0}^{\infty} \frac{(-t)^j}{j!} \sum_{h=0}^j b_{jh} \exp\{-hx\} \tag{31}$$

for the intensity.

Solutions (30) and (31) are superior to (19) and (20) inasmuch as the b_{kh} coefficients are easily calculable by the recursion formula⁶

$$b_{(k+1)h} = hb_{k(h-1)} - (h + 1)b_{kh}, \tag{32}$$

whereas each a_{jk} requires individual calculation. However, further improvement is feasible.

6 Solution in terms of polynomials

Consider a family of polynomials⁷ defined, for $k = 1, 2, 3, \dots$, by the recursion

$$B_{k+1}(z) = [z - 1] \frac{d}{dz} z B_k(z) \quad \text{with} \quad B_0(z) = 1. \tag{33}$$

Because these polynomials play a paramount role in the mathematics of the bleachable dye problem, they will be termed “bleaching polynomials”. Early family members are

$$\left. \begin{aligned} B_1(z) &= -1 + z \\ B_2(z) &= 1 - 3z + 2z^2 \\ B_3(z) &= -1 + 7z - 12z^2 + 6z^3 \\ B_4(z) &= 1 - 15z + 50z^2 - 60z^3 + 24z^4 \\ &\vdots \end{aligned} \right\}. \tag{34}$$

Notice that all the coefficients of the bleaching polynomials are to be found in Table 2, such that

$$B_k(z) = \sum_{h=0}^k b_{kh} z^h. \tag{35}$$

For $k > 0$, the special values $B_k(1) = \sum_{h=0}^k b_{kh} = 0$ and $\frac{dB_k}{dz}(1) = \sum_{h=0}^k h b_{kh} = 1$ are among the interesting properties of these polynomials. The first ensures that each polynomial is exactly divisible by $1 - z$, as is also evident from definition (33).

⁶ Applicable, after augmentation by the italicized entries in Table 2, to all positive integer values of k and h .

⁷ Not to be confused with the Bernoulli polynomials for which the same notation is in use.

In terms of bleaching polynomials, solutions (30) and (31) are expressible as

$$c = \exp\{-t\} \sum_{k=0}^{\infty} \frac{(-x)^k}{k!} B_k(\exp\{-t\}) \quad (36)$$

and

$$i = \exp\{-x\} \sum_{k=0}^{\infty} \frac{(-t)^k}{k!} B_k(\exp\{-x\}). \quad (37)$$

It is straightforward to derive from these equations that

$$-\frac{\partial c}{\partial t} = \frac{1}{\exp\{t\} - 1} \sum_{k=0}^{\infty} \frac{(-x)^k}{k!} B_{k+1}(\exp\{-t\}) \quad (38)$$

and, complementarily,

$$-\frac{\partial i}{\partial x} = \frac{1}{\exp\{x\} - 1} \sum_{k=0}^{\infty} \frac{(-t)^k}{k!} B_{k+1}(\exp\{-x\}). \quad (39)$$

Equations (36) and (37) provide a concise representation of the solution to the problem of the bleachable dye. It remains to confirm that these solutions do, indeed, satisfy expression (11).

7 Confirmation

The skills of the author proved inadequate to confirm analytically⁸ that Eq. (38) equals the product of Eqs. (36) and (37), for all positive values of x and t . Confirmation was therefore sought numerically. For a variety of values of the independent variables, Table 3 lists the approximate magnitudes of the three terms in expression (11) calculated⁹ via Eqs. (36)–(39) by *Mathematica* [11]. Discrepancies between trios of tabulated values seldom exceed 0.1%, providing a clear validation of the theory. To make assurance doubly sure, a simulation was also performed.

8 Simulation

Dye bleaching experiments were simulated using the *Excel* 2010 software [12]. A two-dimensional $(N + 1) \times (M + 1)$ array¹⁰ was created in which the vertical dimension, corresponding to the discretized x coordinate, has $(N + 1)$ evenly spaced sampling

⁸ Other than by retracing the derivation backwards through the b integers and the a coefficients.

⁹ By truncating the summations after $k = 12$ and adding one-half of the $k = 13$ term.

¹⁰ In the examples used to create the figures, the values $M = N = 499$ were employed.

Table 3 Comparison of values calculated from bleaching polynomials

x	t	c	i	$-\frac{\partial c}{\partial t}$	ci	$-\frac{\partial i}{\partial x}$
0.5	0.5	0.71763	0.71763	0.51500	0.51499	0.51500
0.5	1.0	0.48967	0.80733	0.39532	0.39533	0.39532
0.5	1.5	0.32136	0.87357	0.28073	0.28073	0.28073
1.0	0.5	0.80733	0.48967	0.39532	0.39533	0.39532
1.0	1.0	0.61270	0.61270	0.37540	0.37540	0.37540
1.0	1.5	0.43844	0.72285	0.31692	0.31693	0.31692
1.5	0.5	0.87357	0.32136	0.28108	0.28073	0.28108
1.5	1.0	0.72286	0.43844	0.31685	0.31693	0.31685
1.5	1.5	0.56279	0.56279	0.31676	0.31673	0.31676

points indexed by $n = 0, n = 1, n = 2, \dots, n = N - 1, n = N$. Likewise the horizontal dimension, corresponding to the discretized t coordinate, has $M + 1$ evenly spaced sampling points indexed by $m = 0, m = 1, m = 2, \dots, m = M - 1, m = M$. A typical point in the array corresponds to $x = n \delta x$ and $t = m \delta t$, small values being chosen for δx and δt such that $N \delta x$ and $M \delta t$ respectively represent the largest distance (the cell width L) and the longest time of interest.

Each sampling point has two associated values, namely $i(n \delta x, m \delta t)$ and $c(n \delta x, m \delta t)$. Corresponding to the $c(x, 0) = 1$ and $c(0, t) = \exp\{-t\}$ boundary conditions in (12), the c value associated with each $m = 0$ sampling point is set to unity, whereas the c value associated with each $n=0$ point is set to $\exp\{-m \delta t\}$. Similarly, one sets $i(0, m \delta t) = 1$ and $i(n \delta x, 0) = \exp\{-n \delta x\}$, as required by the boundary conditions in (15). All other $i(n \delta x, m \delta t)$ and $c(n \delta x, m \delta t)$ values are initially unassigned. Unlike many other modelling exercises, once an i or a c value is allocated, it is retained permanently.

The continuous operations described by the differential equations in (12) and (15) are discretized into the twin formulas

$$\left. \begin{aligned} i(n \delta x, m \delta t) &= i((n - 1) \delta x, m \delta t) [1 - \delta x c((n - 1) \delta x, m \delta t)] \\ c(n \delta x, m \delta t) &= c(n \delta x, (m - 1) \delta t) [1 - \delta t i(n \delta x, (m - 1) \delta t)] \end{aligned} \right\} \quad (40)$$

and applied to all the sampling points whose values had not been initialized. The assignment was made in the sequence $(n, m) = (1, 1), (1, 2), \dots, (1, M), (2, 1), (2, 2), \dots, (2, M), (3, 1), \dots, (N - 1, M), (N, 1), (N, 2), \dots, (N, M)$. After the simulation was complete, horizontal rows provide a time series of the dependent variable (i and c), whereas vertical columns reveal changes with distance at a specific time instant.

Some results of the simulations are included in Figs. 1 and 2. They provide additional confirmation of the validity of the results of this study.

9 Summary and examples

When a return is made to dimensional variables, the outcome of this study is a formula, namely

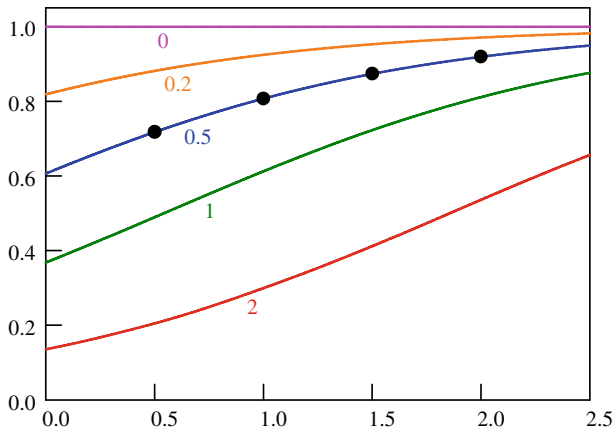


Fig. 1 The curves in this figure employ data numerically modelled by Eqs. (36 or 37). Axis labels are deliberately omitted, because the figure may be interpreted in two ways. One interpretation is that the lines are plots of c versus x , initially and at four other instants of time, $t = 0.2$, $t = 0.5$, $t = 1$ and $t = 2$. Alternatively, each curve may be regarded as a plot of i versus t at the entry plane $x = 0$ and at four other locations, $x = 0.2$, $x = 0.5$, $x = 1$ and $x = 2$. The black points on the “0.5” curve result from the simulation described in the text

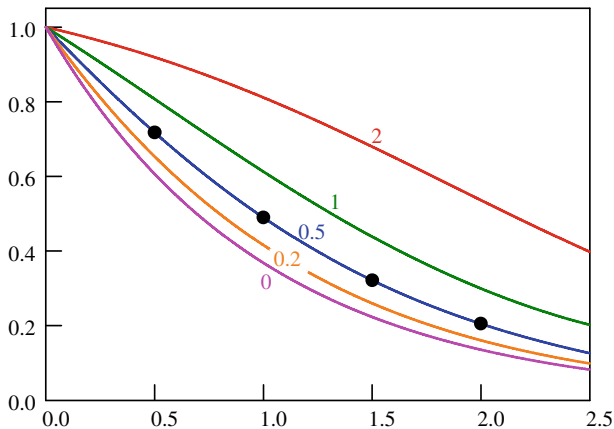


Fig. 2 Again, there are two interpretations of the curves in this figure. They represent the declining dye concentration c with time t at each of five x locations. Or they represent the extinguishing of the light intensity i as the beam progresses through the solution, at each of five different times t . As in the earlier figure, the curves arise from mathematical modelling, whereas the black points come from simulation

$$\frac{C(X, T)}{C(X, 0)} = \sum_{k=0}^{\infty} \frac{(-\varepsilon C(X, 0)X)^k}{k!} \frac{B_k(\exp\{-\phi \varepsilon I(0, T)T\})}{\exp\{\phi \varepsilon I(0, T)T\}}, \quad (41)$$

that describes how the concentration C of a radiation-absorbing photolabile component of a medium depends on distance X and time T when the medium is irradiated by a constant and uniform photon flux of intensity $I(0, T)$. The constants $C(X, 0)$ and ε are the initially uniform concentration of the absorber, and its absorptivity. The quantum

yield ϕ represents the fraction of photon-absorber encounters that lead to destruction of the absorber. The complementary formula

$$\frac{I(X, T)}{I(0, T)} = \sum_{k=0}^{\infty} \frac{(-\phi \varepsilon I(0, T)T)^k}{k!} \frac{B_k(\exp\{-\varepsilon C(X, 0)X\})}{\exp\{\varepsilon C(X, 0)X\}} \quad (42)$$

describes the attenuation of the photon flux with distance and its local increase with time. That these equations provide valid solutions to the problem has been confirmed numerically and by simulation.

Diagrams have been prepared to exemplify the predictions of Eqs. (36) and (37). Figure 1 shows profiles of the dye concentration plotted versus distance at a number of instants in time, while Fig. 2 reports how concentration evolves with time at the entry plane and four other vertical planes within the cell. Note from this second figure that whereas the concentration decays exponentially, with time, at the entry plane, $x = 0$, the initial fall-off has become linear at $x = 1$.

The complementarity of the c and i variables with respect to the independent variables x and t means that Figs. 1 and 2 serve equally well to depict the behaviour of the light intensity. Figure 2 provides five “snapshots” of how the photon flux declines with distance, whereas the plots in Fig. 1 are of i versus t at a selection of sites, increasingly distant from the entry plane.

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References

1. P. Klán, J. Wirz, *Photochemistry of Organic Compounds; From Concepts to Practice* (Wiley, Chichester, 2009)
2. W.J. Youngblood, S.-H.A. Lee, K. Maeda, T.E. Mallouk, Visible light water splitting using dye-sensitized oxide semiconductor. *Acc. Chem. Res.* **42**, 1966–73 (2009)
3. K. Rajeshwar, J. Ibanez, *Environmental Electrochemistry: Fundamentals and Applications in Pollution Abatement, chap 6* (Academic Press, San Diego, 1997)
4. P. Bouguer, *Essai d’optique sur la graduation de la lumiere* (Jombert, Paris, 1729)
5. J.H. Lambert, *Photometria sive de mensura et gradibus luminis* (Klett, colorum et umbrae, Augsburg, 1760)
6. A. Beer, Bestimmung der Adsorption des rothen Licht in farbigen Flüssigkeiten. *Annalen der physikalischer Chemie* **86**, 74–88 (1852)
7. J.M. Parnis, K.B. Oldham, Beyond the Beer–Lambert law: the dependence of absorbance on time in photochemistry. *J. Photochem. Photobiol. A Chem.* **267**, 6–10 (2013)
8. Y. Pinchover, J. Rubinstein, *Introduction to Partial Differential Equations* (Cambridge University Press, New York, 2005)
9. L. Lapidus, G.F. Pinder, *Numerical Solution of Partial Differential Equations in Science and Engineering* (Wiley, Chichester, 1982)
10. M.L. Boas, *Mathematical Methods in the Physical Sciences*, 2nd edn. (Wiley, New York, 1983), p. 365
11. S. Wolfram, *The Mathematica Book*, 4th edn. (Cambridge University Press, New York, 1999)
12. Microsoft. Excel spreadsheet software. (The Microsoft Corporation, Redmond, 2010)