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MATHEMATICS OF INTERMITTENT IRRADIATION*

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ABSTRACT

Initiation of reactions by intermittent irradiation is frequently encountered in physical, chemical, and biological systems. Mathematical expressions for transient and steady state concentrations of reactive species in these systems are useful for predicting performance and for research purposes. A general method of formulation of the intermittent irradiation problem is presented herein, and illustrative solutions are obtained for radioactive decay chains and for the rotating sector method.

MATHEMATICS OF INTERMITTENT IRRADIATION

The kinetics of reacting systems subject to intermittent irradiation is a matter of interest in a number of technological and research applications. In the nuclear field, initiation of radioactive decay chains by intermittent irradiation arises frequently. Initiation of fission product chains in liquid nuclear fuels or activation of the coolant or a liquid isotopic source occurs as the pertinent stream passes through a nuclear reactor. Decay without initiation occurs outside the reactor as the stream passes through heat exchangers or irradiators and returns to the reactor. A knowledge of the startup concentration transients and steady state concentrations of radioactive species in these systems is important for the determination of fuel processing rates for the control of fission product poisoning in liquid-fueled reactors (4), in setting requirements for shielding for the portions of the recirculating stream outside of the reactor (17), and for calculating the average power of an isotopic irradiator over a typical reactor operating cycle (16).

The decay chains initiated in these systems involve successive first order reactions. In other applications, more complex reactions are no doubt important. Thus, proposed designs for nuclear reactors for the

production of chemicals - so-called "chemonuclear" reactors - usually show a recirculating reactant stream passing between reactor and product and/or fuel recovery units (19). Also photochemical processes have been described (18) in which a recirculating reactant stream passes through an irradiator.

Intermittent irradiation is also found in a research application. It has long provided a technique for the study of mechanism and measurement of rates of intermediate steps in photochemical chain reactions (2). The technique, referred to as the rotating sector method, involves measuring the yield of stable product as a function of frequency of illumination of a reaction vessel containing a static reactant mixture. For chains which terminate by radical recombination, the yield varies strongly with frequency when the lengths of the light and dark intervals are comparable to the radical lifetime. Chain rate constants may be deduced from this variation (3,13). The technique has been used extensively since World War II, and has been applied in radiation chemistry (7,8) as well as in photochemistry. Its use in flow systems has received preliminary study (12). Intermittency of irradiation in space as well as in time has been considered, and, as a result, a method has been developed which permits the measurement of diffusion coefficients of reactive intermediates (14,15).

Finally, a very interesting field involving intermittent irradiation is that concerned with the response of living systems to variation in the natural day-night cycle, in terms of such phenomena as growth, flowering and fruiting of plants, etc. The kinetic bases for these phenomena do not as yet appear to be understood, and are the subjects of current intensive research efforts (20).

In view of the foregoing discussion it is apparent that expressions for the calculation of transient and steady state concentrations in systems subjected to intermittent irradiation are useful in design and research applications. With a wide range of expressions available for interpretation of experiments, intermittent irradiation techniques may be useful in the study of photochemical and radiation chemical reactor performance.

Methods of calculating steady state concentrations have been presented for a number of kinetic schemes, including those for which the rotating sector method is useful (3,13), and including those for recirculating nuclear reactor streams (4,5). Transient state expressions however have not been developed in a general way. In the present paper a method

of formulation of the transient state problem is presented which is of general applicability, and which, on solution, yields both concentration transients and the steady state. The method is first illustrated by treatment of a system in which a species produced by radiation disappears in a first order reaction. A solution is obtained and its characteristics are examined. These results are then generalized for a series of successive first order reactions. The effect of chemical processing is considered. Finally a reaction with second order disappearance is treated.

First Order Disappearance

The reaction to be considered involves the production of a substance A_1 as a primary product of irradiation, and its disappearance by first order decomposition:

The expression for the concentration of A_1 as a function of time after the onset of intermittent irradiation has been derived previously using an inductive method (11). Its derivation here will serve to illustrate the principles of the present method.

The rate of production of A_1 is Q_1 , a constant. Q_1 is proportional to the constant radiation flux or intensity and the concentration of A_0 . The latter is assumed to remain constant with time either because of restriction of the treatment to small burn-up or because of replenishment.

Prior to the onset of the intermittent irradiation of A_0 , no A_1 is present. The form of the final solution is somewhat simplified if the sequence of dark and light intervals is visualized as starting with a dark interval. The x -th light interval then follows the x -th dark interval. The dark and light intervals are of duration t_D and t_L , respectively. The concentration of A_1 during the x -th dark period will be denoted by $c_{1D}(x,t)$ and, during the following light period, by $c_{1L}(x,t)$.

Using this notation, the differential equations describing the unsteady state concentration of A_1 are

$$\frac{d}{dt} c_{1D}(x,t) = -k_1 c_{1D}(x,t) \quad (2)$$

during the x -th dark interval, and

$$\frac{d}{dt} c_{1L}(x,t) = Q_1 - k_1 c_{1L}(x,t) \quad (3)$$

during the following light interval.

The solution of Eqn. (2) evaluated at $t = t_D$ is

$$c_{1D}(x, t_D) = c_{1D}(x, 0)e^{-k_1 t_D} \quad (4)$$

Since $c_{1D}(x, 0)$, the concentration of A_1 at the beginning of the x -th dark interval, is equal to $c_{1L}(x-1, t_L)$, the concentration present at the end of the previous light interval, then Eqn. (4) may be written

$$c_{1D}(x, t_D) = c_{1L}(x-1, t_L)e^{-k_1 t_D} \quad (5)$$

In a similar way the terminal conditions for the x -th light interval may be related in the solution of Eqn. (3):

$$c_{1L}(x, t_L) = \frac{Q_1}{k_1}(1 - e^{-k_1 t_L}) + c_{1D}(x, t_D)e^{-k_1 t_L} \quad (6)$$

Eliminating $c_{1D}(x, t_D)$ between Eqns. (5) and (6):

$$c_{1L}(x, t_L) = \frac{Q_1}{k_1}(1 - e^{-k_1 t_L}) + c_{1L}(x-1, t_L)e^{-k_1(t_D+t_L)} \quad (7)$$

Eqn. (7) is a complete linear first order difference equation with constant coefficients in the variable x . Its solution is (9):

$$c_{1L}(x, t_L) = \frac{1 - e^{-k_1(t_D+t_L)x}}{1 - e^{-k_1(t_D+t_L)}} \cdot \frac{Q_1}{k_1}(1 - e^{-k_1 t_L}) \quad (8)$$

The steady state solution is obtained by letting $x \rightarrow \infty$ in Eqn. (8), or by letting $x-1$ and $x \rightarrow \infty$ in Eqn. (7). The result is

$$c_{1L}(\infty, t_L) = \frac{Q_1}{k_1} \frac{1 - e^{-k_1 t_L}}{1 - e^{-k_1(t_D + t_L)}} \quad (9)$$

Eqn. (8) gives the concentration of A_1 at the end of the x -th light period. The concentration history during a given pair of dark and light intervals may be found by substituting Eqn. (8) in Eqns. (5) and (6), each evaluated at a time t within the particular interval. Thus, in the dark interval,

$$c_{1D}(x, t) = \frac{1 - e^{-k_1(t_D + t_L)(x-1)}}{1 - e^{-k_1(t_D + t_L)}} \frac{Q_1}{k_1} (1 - e^{-k_1 t_L}) e^{-k_1 t}, \quad 0 \leq t \leq t_D \quad (10)$$

and, in the light interval,

$$c_{1L}(x, t) = \frac{1 - e^{-k_1(t_D + t_L)(x-1)}}{1 - e^{-k_1(t_D + t_L)}} \frac{Q_1}{k_1} (1 - e^{-k_1 t_L}) e^{-k_1(t_D + t)} + \frac{Q_1}{k_1} (1 - e^{-k_1 t}), \quad 0 \leq t \leq t_L \quad (11)$$

The concentration history given by Eqns. (10) and (11) is shown graphically in Fig. 1. The concentrations in the dark and light intervals, expressed as fractions of Q_1/k_1 , the steady state concentration obtained under steady irradiation, are plotted against x , the number of pairs of dark and light intervals. Three cases are shown in which the parameters

$\theta_D = k_1 t_D$ and $\theta_L = k_1 t_L$ each assume the values 0.1, 1, and 10. For $\theta_D = \theta_L = 10$, the steady state is closely approached in the second pair of dark and light intervals. The repetition of the transients found for the second pair which occur in the third and succeeding pairs is not shown. Steady state is closely approached for $\theta_D = \theta_L = 1$ after 4 pairs of intervals and the repetition which follows is not shown. A steady state is not achieved for $\theta_D = \theta_L = 0.1$ in the range of x shown. In general, the approach to steady state is more rapid, and the range of concentrations during a pair of dark and light intervals is greater for light and dark intervals which are long compared to the mean lifetime. For intervals which are short compared to the mean lifetime, many cycles are required for a close approach to steady state. Little decay occurs during a dark period, and little increase is found in a light interval. In the extreme case of very short light and dark intervals concentration increases occur in a continuous fashion without any apparent distinction between light and dark intervals. An expression appropriate for this situation may be obtained from Eqn. (8). For light and dark intervals which are short compared to the mean lifetime, $k_1 t_L$ and $k_1(t_D + t_L)$ are small, but $k_1(t_D + t_L)x$ is not necessarily so. Hence, using the approximation $e^{-u} = 1 - u$ when u is small, Eqn. (8) becomes

$$c_{1L}(x, t_L) = \frac{t_L}{t_L + t_D} \frac{Q_1}{k_1} [1 - e^{-k_1(t_D + t_L)x}] \quad (12)$$

Thus the expression for the concentration transient is that appropriate for steady irradiation but with the rate of initiation multiplied by the fraction of time during which the system is irradiated (11). Eqn. (12), expressed in terms of $\theta = k_1 t$, is plotted in Fig. 1 as the dotted line for the case in which $\theta_D = \theta_L = 0.1$, and it may be seen that Eqn. (12) is already a fair approximation for Eqn. (8).

Successive First Order Reactions

The preceding results for a first order reaction may be generalized for a series of successive reactions with $r+1$ members. This is the important case of a radioactive decay chain initiated by fission or by a variety of other nuclear reactions. Solutions have been available for this system heretofore only for isolated special cases (11). The reactions and the growth and decay processes associated with them are represented in Fig. 2. As before, the zeroth member of the series is subject to decomposition on irradiation, producing in this case amounts of each of the daughter species as primary products at the rate Q_i . Again Q_i is proportional to the radiation flux, the concentration of A_0 , and, in this

case, the direct yield of the i -th member. It remains constant for the reasons given in the previous section. First order decomposition of each member of the series except the zeroth is governed by the rate constant $\kappa_i = \lambda_i + \mu_i$. The rate constant λ_i governs the production of the daughter of i . By definition $\lambda_r = 0$. The rate constant μ_i is associated with the process of removal of i by absorption of radiation. It is thus proportional to the radiation flux, and is zero in the dark.

In a manner similar to that used in the preceding section, the intermittent irradiation problem may be formulated by deriving in this case a sum equation which relates the concentration of the i -th member of the series after x pairs of dark and light intervals to the concentration of i and in this case its predecessors as well after $x-1$ pairs of intervals. This is done, as before, by first solving the differential equations describing the net rate of production of the members of the series in the dark interval,

$$\left. \begin{aligned} \frac{d}{dt} c_{1D}(x,t) &= -\kappa_1 c_{1D}(x,t), \\ &\dots\dots\dots \\ \frac{d}{dt} c_{iD}(x,t) &= \lambda_{i-1} c_{i-1D}(x,t) - \kappa_i c_{iD}(x,t), \quad i = 2, 3, \dots, r \end{aligned} \right\} (13)$$

and in the light interval,

$$\left. \begin{aligned} \frac{d}{dt} c_{1L}(x,t) &= Q_1 - \kappa_1 c_{1L}(x,t), \\ &\dots\dots\dots \\ \frac{d}{dt} c_{iL}(x,t) &= Q_i + \lambda_{i-1} c_{i-1L}(x,t) - \kappa_i c_{iL}(x,t), \quad i=2,3,\dots,r \end{aligned} \right\} \quad (14)$$

Let us consider $c_{jD}(x, t_D)$, the concentration of the j -th member of the series at the end of the x -th dark interval. This concentration can be visualized as having been produced by the decay of portions of $c_{kL}(x-1, t_L)$, $k \leq j$, the concentrations of j and its predecessors present at the beginning of the dark interval. Thus, the solution of Eqns. (13) may be written (see Appendix):

$$c_{jD}(x, t_D) = \sum_{k=1}^j b_{jk}(t_D) c_{kL}(x-1, t_L), \quad (15)$$

where $b_{jk}(t)$ is defined below in Eqn. (17). Similarly the concentrations at the beginning and the end of the x -th light interval may be related using the solution (see Appendix) of Eqns. (14):

$$c_{iL}(x, t_L) = \sum_{j=1}^i [a_{ij}(t_L) Q_j + b_{ij}(t_L) c_{jD}(x, t_D)] \quad (16)$$

where

$$\left. \begin{aligned} a_{ij}(t) &= \left(\prod_{m=j}^{i-1} \lambda_m \right) \left(\sum_{m=j}^i \frac{1}{\prod_{\substack{n=j \\ n \neq m}}^i (\kappa_n - \kappa_m)} \int_0^t e^{-\kappa_m t'} dt' \right) \\ b_{ij}(t) &= \frac{d}{dt} [a_{ij}(t)] \end{aligned} \right\} \quad (17)$$

The sum equation sought is obtained by eliminating $c_{jD}(x, t_D)$ between Eqns. (15) and (16):

$$c_{iL}(x, t_L) = c_{iL}(1, t_L) + \sum_{j=1}^i b_{ij}(t_L) \sum_{k=1}^j b_{jk}(t_D) c_{kL}(x-1, t_L) \quad (18)$$

In writing Eqn. (18), it has been noted that, since no member of the series but A_0 is present prior to the onset of intermittent irradiation,

$$\sum_{j=1}^i a_{ij}(t_L) Q_j = c_{iL}(1, t_L).$$

Consideration may be given to continuous removal of products from two types of flow irradiators. Thus in Fig. 3(a) a perfectly mixed stirred

tank reactor having an intermittent light source is shown. Continuous inlet and outlet streams are provided. A reactant recovery unit is not shown. Product removal represents an additional mode of first order disappearance and is taken into account by letting $\kappa_i = \lambda_i + \mu_i + F$ where F is the rate of flow through the reactor. With this change in mind, Eqn. (18) is applicable to the system in Fig. 3(a) as it stands. The solution of Eqn. (18) gives the concentration of i at the end of the x -th pair of light and dark intervals. The concentration of i in the effluent stream varies with time. If it is assumed that the reactions are quenched immediately on leaving the reactor, the concentration of i in the effluent stream is

$$\sum_{j=1}^i b_{ij}(t) c_{jL}(x, t_L), \quad 0 \leq t \leq t_D,$$

at any instant of the $(x+1)$ -st dark period, and

$$\sum_{j=1}^i [a_{ij}(t) Q_j + b_{ij}(t) \sum_{k=1}^j b_{jk}(t_D) c_{kL}(x, t_L)], \quad 0 \leq t \leq t_L,$$

at any instant of the $(x+1)$ -st light period.

In Fig. 3(b), a recirculating flow system is shown in which products are withdrawn in a separation unit located in the dark portion of the system (5). Each member of the series is removed in an amount in

proportion to its concentration. Thus the fraction q_i of the concentration of i entering the unit is removed and $1-q_i = p_i$ remains. If the unit is located a time t_1 downstream from the reactor outlet and a time t_2 upstream from the reactor inlet with $t_1+t_2 = t_D$ (hold-up time in the separation unit is included in t_1 and/or t_2 and hence in t_D), then following arguments similar to those used in formulating Eqn. (18), the equation applicable for Fig. 3(b) is

$$c_{iL}(x, t_L) = c_{iL}(1, t_L) + \sum_{j=1}^i b_{ij}(t_L) \sum_{k=1}^j b_{jk}(t_2) p_k \sum_{m=1}^k b_{km}(t_1) c_{mL}(x-1, t_L), \quad (19)$$

and the concentration of i in the product stream, assuming that the reactions are quenched on leaving the separation unit, is

$$q_i \sum_{j=1}^i h_{ij}(t_1) c_{jL}(x, t_L)$$

during the $(x+1)$ -st pass.

Solutions.

Eqn. (18) or Eqn. (19) may be solved in step-by-step fashion, first for $i = 1$, then for $i = 2$, and so on. Thus, for example, for $i = 1$, Eqn. (19) is

$$c_{1L}(x, t_L) = c_{1L}(1, t_L) + b_{11} c_{1L}(x-1, t_L) \quad (20)$$

where $b_{11} = b_{11}(t_L)b_{11}(t_2)p_1b_{11}(t_1)$. The solution of Eqn. (20) is

$$c_{1L}(x, t_L) = \frac{1 - b_{11}^x}{1 - b_{11}} c_{1L}(1, t_L) \quad (21)$$

For $i = 2$, Eqn. (19) is

$$c_{2L}(x, t_L) = c_{2L}(1, t_L) + b_{22}c_{2L}(x-1, t_L) + b_{21}c_{1L}(x-1, t_L) \quad (22)$$

where

$$b_{22} = b_{22}(t_L)b_{22}(t_2)p_2b_{22}(t_1),$$

$$b_{21} = b_{21}(t_L)b_{11}(t_2)p_1b_{11}(t_1) + b_{22}(t_L)b_{21}(t_2)p_1b_{11}(t_1) \\ + b_{22}(t_L)b_{22}(t_2)p_2b_{21}(t_1).$$

After substituting the solution for $c_{1L}(x, t_L)$, Eqn. (21), in Eqn. (22),

the solution of the resulting equation is found to be

$$c_{2L}(x, t_L) = \frac{1 - b_{22}^x}{1 - b_{22}} c_{2L}(1, t_L) + \left[\frac{1}{(1 - b_{11})(1 - b_{22})} - \frac{b_{11}^x}{(1 - b_{11})(b_{11} - b_{22})} \right. \\ \left. + \frac{b_{22}^x}{(b_{11} - b_{22})(1 - b_{22})} \right] b_{21}c_{1L}(1, t_L). \quad (23)$$

The solutions rapidly become cumbersome and unwieldy although the method of obtaining them is simple in principle. When solved in

the way shown above the equations which arise successively are complete linear first order difference equations with constant coefficients for which standard methods of solution are available (19).

The steady state solutions are obtained by letting $x \rightarrow \infty$ in the solutions of Eqns. (18) and (19), e.g., in Eqns. (21) and (23), or, alternatively, by letting $x-1$ and $x \rightarrow \infty$ in Eqns. (18) and (19) directly. In the latter instance solution of a system of simultaneous linear algebraic equations arises.

Illustration of concentration transients as in Fig. 1 is in general complicated for successive reactions by the large number of parameters involved. Illustrative calculations were therefore not made for successive reactions. The development of approximations for small t_D and t_L similarly involves a large number of cases. For a specific case of interest the appropriate expression may be found by letting $e^{-u} = 1-u$ as in the derivation of Eqn. (12).

Second Order Disappearance

It is possible to obtain the solutions presented for first order systems because the difference equations which generate them are linear. Closed form solutions are not in general possible for fractional and higher order

reactions. Hand or machine iteration of the difference equations is then necessary. It happens, however, that an analytical solution for one such reaction can be obtained since the pertinent difference equation may be transformed into a linear one. This reaction which is the principal one important in the rotating sector method (13), involves the production of radicals on irradiation and termination of the resulting chain reaction by radical-radical combination.

The formulation of the difference equation parallels the treatment for first order systems. The differential equations describing the radical concentration are

$$\frac{d}{dt} c_{1D}(x,t) = -k_t c_{1D}^2(x,t) \quad (25)$$

in the dark, and,

$$\frac{d}{dt} c_{1L}(x,t) = Q_1 - k_t c_{1L}^2(x,t) \quad (26)$$

during the light interval.

It is convenient to introduce the dimensionless variables

$$C_{1D}(x, \theta) = \frac{c_{1D}(x, \theta)}{c_{1S}}, \quad C_{1L}(x, \theta) = \frac{c_{1L}(x, \theta)}{c_{1S}}, \quad \theta = t/\tau_1 \quad (27)$$

where

$c_{1S} = (Q_1/k_t)^{1/2}$, the steady state concentration of A_1 under steady irradiation,

$\tau_1 = (Q_1/k_t)^{-1/2}$, the mean lifetime of A_1 under steady irradiation.

In terms of these variables, Eqns. (25) and (26) are, respectively,

$$\frac{d}{d\theta} C_{1D}(x, \theta) = -C_{1D}^2(x, \theta) \quad (28)$$

and

$$\frac{d}{d\theta} C_{1L}(x, \theta) = 1 - C_{1L}^2(x, \theta) \quad (29)$$

Terminal concentrations for the x -th dark interval may be related in the solution of Eqn. (28),

$$C_{1D}(x, \theta_D) = \frac{C_{1L}(x-1, \theta_L)}{1 + \theta_D C_{1L}(x-1, \theta_L)}, \quad (30)$$

and, similarly, the solution of Eqn. (29) relates the initial and final concentration of the x -th light interval:

$$C_{1L}(x, \theta_L) = \frac{\beta_L + C_{1D}(x, \theta_D)}{1 + \beta_L C_{1D}(x, \theta_D)} \quad (31)$$

where $\beta_L = \tanh \theta_L$.

From Eqns. (30) and (31), on eliminating $C_{1D}(x, \theta_D)$, one finds

$$C_{1L}(x, \theta_L) = \frac{\beta_L + (1 + \beta_L \theta_D) C_{1L}(x-1, \theta_L)}{1 + (\beta_L + \theta_D) C_{1L}(x-1, \theta_L)} \quad (32)$$

Eqn. (32) is non-linear. It can be transformed to a linear one (1,6) by introducing the new variable $w(x)$ defined by

$$C_{1L}(x, \theta_L) + \frac{1}{\beta_L + \theta_D} = \frac{w(x+1)}{w(x)} \quad (33)$$

In terms of $w(x)$, Eqn. (32) is

$$w(x+1) - \frac{2 + \beta_L \theta_D}{\beta_L + \theta_D} w(x) + \frac{1 - \beta_L^2}{(\beta_L + \theta_D)^2} w(x-1) = 0 \quad (34)$$

Eqn. (34) is satisfied by a solution of the form

$$w(x) = Ar_1^x + Br_2^x, \quad (35)$$

where A and B are arbitrary constants, and

$$\left. \begin{aligned} r_1 &= \frac{1}{2(\beta_L + \theta_D)} \left[2 + \beta_L \theta_D - \sqrt{(2 + \beta_L \theta_D)^2 - 4(1 - \beta_L^2)} \right] \\ r_2 &= \frac{1}{2(\beta_L + \theta_D)} \left[2 + \beta_L \theta_D + \sqrt{(2 + \beta_L \theta_D)^2 - 4(1 - \beta_L^2)} \right] \end{aligned} \right\} \quad (36)$$

Using Eqn. (35) in Eqn. (33), and rearranging,

$$C_{1L}(x, \theta_L) = r_2 - \frac{1}{\beta_L + \theta_D} + \frac{r_1 - r_2}{1 + C(r_2/r_1)^x} \quad (37)$$

where $C = B/A$.

In Eqn. (31), if $C_{1D}(1, \theta_D) = 0$, then $C_{1L}(1, \theta_L) = \beta_L$. After using this initial condition to evaluate C , Eqn. (37) may be written

$$C_{1L}(x, \theta_L) = r_2 - \frac{1}{\beta_L + \theta_D} - \frac{r_2 - r_1}{1 - \frac{r_1 - \beta_L - \frac{1}{\beta_L + \theta_D}}{r_2 - \beta_L - \frac{1}{\beta_L + \theta_D}} (r_2/r_1)^{x-1}} \quad (38)$$

It can be determined from Eqns. (36) that $r_2/r_1 > 1$, and that, therefore, as $x \rightarrow \infty$, the last term in Eqn. (38) approaches zero. Hence

$$\begin{aligned} C_{1L}(\infty, \theta_L) &= r_2 - \frac{1}{\beta_L + \theta_D} \\ &= \frac{1}{2(\beta_L + \theta_D)} [\beta_L \theta_D + \sqrt{(2 + \beta_L \theta_D)^2 - 4(1 - \beta_L^2)}] \end{aligned} \quad (39)$$

The same result can be obtained by letting $x \rightarrow 1$ and $x \rightarrow \infty$ in Eqn. (32).

Eqn. (38) may be used in Eqns. (30) and (31), each evaluated at a time t within the dark or light interval, to obtain the concentration history

during the intervals. This has been done for illustrative purposes with the results shown in Fig. 4. The same general discussion applies here as was found for Fig. 1 for first order disappearance. Steady state is closely approached in two cycles for $\theta_D = \theta_L = 10$, and, in four cycles for $\theta_D = \theta_L = 1$. For $\theta_D = \theta_L = 0.1$, steady state is not closely approached for $x = 9$. The curve for the latter condition is closely approximated by

$$C_{1L}(x, \theta_L) = \left(\frac{\theta_L}{\theta_D + \theta_L} \right)^{1/2} \tanh \{ [\theta_L(\theta_L + \theta_D)]^{1/2} x \} \quad (40)$$

Rather than obtain this expression by letting θ_D and θ_L be small in Eqn. (38) as was done to derive Eqn. (12) from Eqn. (8), the following procedure, which is simpler in this case, was used.

As was stated earlier when θ_D and θ_L are sufficiently small the concentration increases in a continuous fashion with no distinction between dark and light periods being apparent. A single equation is then valid during both periods:

$$\frac{dC_{1L}(x, \theta)}{d\theta} = \frac{\theta_L}{\theta_D + \theta_L} - C_{1L}^2(x, \theta) . \quad (41)$$

This is Eqn. (29) with the source term weighted by the fraction of the time during which the system is irradiated. The solution of Eqn. (41) with θ set equal to $(\theta_D + \theta_L)x$ is given by Eqn. (40).

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Notation

$a_{ij}(t)$	= coefficient defined by Eqn. (17)
A	= a constant
A_i	= i-th substance in a series
A_0	= zeroth substance in a series
b_{ij}	= coefficient of $C_{jL}(x-1, t_L)$ in difference equation for $c_{iL}(x, t_L)$; see, for example, for $i = 2$, Eqn. (22)
$b_{ij}(t)$	= coefficient defined by Eqn. (17)
B	= a constant
$c_{iD}(x, t)$	= concentration of i-th member of a series at a time t during the x -th dark interval
$\bar{c}_{iD}(x, s)$	= Laplace transform with respect to t of $c_{iD}(x, t)$
$c_{iL}(x, t)$	= concentration of i-th member of a series at a time t during the x -th light interval
$\bar{c}_{iL}(x, s)$	= Laplace transform with respect to t of $c_{iL}(x, t)$
c_{iS}	= steady state concentration of i under steady irradiation
$C_{iD}(x, \theta)$	= dimensionless form of $c_{iD}(x, t)$ defined by Eqn. (27)
$C_{iL}(x, \theta)$	= dimensionless form of $c_{iL}(x, t)$ defined by Eqn. (27)
C	= a constant
D	= determinant defined by Eqn. (A2)

D_i	= determinant defined by Eqn. (A3)
F	= flow rate through stirred tank irradiator
k_t	= rate constant for radical-radical termination of a chain reaction
k_1	= rate constant for first order disappearance of A_1
p_i	= fraction of i entering product recovery unit which is not separated from recirculating stream
P	= reaction product
q_i	= fraction of i entering product recovery unit which is separated from system
Q_i	= rate of production of A_i as a direct product of the irradiation of A_0
r	= pertaining to the stable product at the end of a series of successive first order decompositions
r_1, r_2	= defined by Eqn. (36)
s	= Laplace transform variable
t	= time
t_D	= duration of dark interval
t_L	= duration of light interval
t_1	= time for passage from irradiator exit to product recovery unit

- t_2 = time for passage from product recovery unit to irradiator inlet
- $w(x)$ = function defined by Eqn. (33)
- x = number of dark or light interval following onset of intermittent irradiation. Sequences start with a dark interval.
- β_L = $\tanh \theta_L$
- κ_i = total rate constant for first order disappearance of A_i
- λ_i = rate constant for production of A_{i+1} from A_i
- μ_i = rate constant for decomposition of A_i upon irradiation
- θ = t/τ_1 , dimensionless time
- θ_D = t_D/τ_1
- θ_L = t_L/τ_1
- τ_1 = mean lifetime of A_1 under steady irradiation

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Appendix

Solution of Equations (13) and (14).

The Laplace transformations of Eqns. (14) are

[illegible]

where $\bar{c}_{iL}(x,s)$ is the Laplace transform of $c_{iL}(x,t)$ and the $c_{jD}(x,t_D)$, $j = 1, 2, \dots, i$, are the initial values of $c_{jL}(x,t)$. Eqns. (A1) are to be solved for $\bar{c}_{iL}(x,s)$.

The determinant of the coefficients of the left hand side is

$$D = \begin{vmatrix} s^2 + \kappa_1 s & 0 & \dots & 0 & 0 \\ -\lambda_1 s & s^2 + \kappa_2 s & \dots & 0 & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & -\lambda_{i-1} s & s^2 + \kappa_i s \end{vmatrix}$$

$$= s^i \prod_{j=1}^i (s + \kappa_j) \quad (A2)$$

The numerator of $\bar{c}_{iL}(x,s)$ is

$$D_i = \begin{vmatrix} (s^2 + \kappa_1 s) & 0 & 0 & \dots & 0 & Q_1 + sc_{1D}(x, t_D) \\ -\lambda_1 s & (s^2 + \kappa_2 s) & 0 & \dots & 0 & Q_2 + sc_{2D}(x, t_D) \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & 0 & -\lambda_{i-2} s & (s^2 + \kappa_{i-1} s) & Q_{i-1} + sc_{i-1D}(x, t_D) \\ 0 & \dots & 0 & 0 & -\lambda_{i-1} s & Q_i + sc_{iD}(x, t_D) \end{vmatrix} \quad (A3)$$

Expanding D_i by means of the elements and cofactors of the i -th row, we obtain

$$D_i = [Q_i + sc_{iD}(x, t_D)] s^{i-1} \prod_{j=1}^{i-1} (s + \kappa_j) + \lambda_{i-1} s D_{i-1} \quad (A4)$$

Equation (A4) is a complete linear first order difference equation with variable coefficients. Its solution is (10):

$$D_i = \prod_{j=1}^{i-1} (s \lambda_j) \left\{ Q_1 + sc_{1D}(x, t_D) + \sum_{j=1}^{i-1} [Q_{j+1} + sc_{j+1D}(x, t_D)] \prod_{m=1}^j \frac{s + \kappa_m}{\lambda_m} \right\} \quad (A5)$$

Hence

$$\bar{c}_{iL}(x,s) = \frac{D_i}{D} = \frac{1}{s\lambda_i} \sum_{j=1}^i [Q_j + s c_{jD}(x,t_D)] \prod_{m=j}^i \frac{\lambda_m}{s + \kappa_m} \quad (A6)$$

Inverting Eqn. (A6),

$$c_{iL}(x,t) = \sum_{j=1}^i [a_{ij}(t)Q_j + b_{ij}(t)c_{jD}(x,t_D)], \quad (A7)$$

where

$$a_{ij}(t) = \left(\prod_{m=j}^{i-1} \lambda_m \right) \left(\sum_{\substack{n=j \\ n \neq m}}^i \frac{1}{(\kappa_n - \kappa_m)} \int_0^t e^{-\kappa_m t'} dt' \right), \quad (A8)$$

$$b_{ij}(t) = \frac{d[a_{ij}(t)]}{dt} \quad (A9)$$

After comparison of Eqns. (13) and (14), the solution of Eqn. (13) may

be obtained from Eqn. (A7) on inspection:

$$c_{iD}(x,t) = \sum_{j=1}^i b_{ij}(t)c_{jL}(x-1,t_L) \quad (A10)$$

Figure Captions

- Figure 1** **Concentration transients for first order disappearance.**
- Figure 2** **Production and removal processes in successive first
order reactions.**
- Figure 3** **Schematic flow diagrams for product removal.**
- Figure 4** **Concentration transients for second order disappearance.**

FIGURE 1

FIGURE 2

(a) PERFECTLY MIXED REACTION VESSEL WITH INTERMITTENT SOURCE

(b) PLUG FLOW TUBULAR REACTOR WITH STEADY SOURCE AND RECIRCULATING FLOW

FIGURE 3

FIGURE 4