Calculation of Concentration Response to Intermittent Irradiation

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There are a number of instances of scientific or technological interest in which chemical or nuclear reactions are initiated intermittently by exposure to a succession of pulses of radiation. The radiations involved include visible light, ultraviolet light, gamma rays and other ionizing radiation, and neutrons. The fields in which such intermittent irradiations occur are therefore diverse and include photochemistry, photobiology, radiation chemistry, nuclear science, and corresponding areas of engineering application.

From a chemical engineering point of view two types of intermittent irradiators are commonly found, a continuous tubular irradiator with partial or total recycle and a batch irradiator with an intermittent source. The continuous irradiator is found frequently in the nuclear field, most often with total or nearly total recycle. The reactions initiated are those of radioactive decay chains. In the recirculating fuel stream of a liquid-fueled nuclear reactor fission product chains are initiated, and fission products decay as the fuel passes through the neutron field in the reactor. Decay without initiation occurs outside the reactor as the stream passes through heat exchangers and returns to the reactor. Intermittent initiation occurs similarly in nuclear reactor coolant streams and in circulating liquid isotopic source streams. A knowledge of the start-up concentration transients and steady state concentrations of radioactive species in these sysems is important for the determination of fuel processing rates for the control of fission product poisoning in liquid-fueled reactors (*6*), in setting requirements for shielding for the portions of the recirculating stream outside of the reactor (*19*), and for calculating the average power of an isotopic irradiator over a typical reactor operating cycle (*18*).

The continuous irradiator with recycle has been used in a photochemical process (*20*) and is included in proposed designs of nuclear reactors for the production of chemicals, so-called *chemonuclear* reactors (*22*).

Batch irradiators with intermittent sources (actually with chopped radiation beams) are found in a research application. Photochemists have long used these irradiàtors in 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 measurement of 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-radical reaction the yield varies strongly with frequency when the lengths of the dark intervals are comparable to the radical lifetime. Chain rate constants may be deduced from this variation (*5, 16*). The technique has been used extensively since World War II and has been applied in radiation chemistry (*11, 12*) as well as in photochemistry.

The batch irradiators just described involve intermittency in time, whereas the irradiators with recycle may be thought of as involving spatial intermittency. Other types of uses of spatial intermittency have been described, including a flow system variation (*15*) of the rotating sector method, and a method of measurement of the diffusion coefficients of reactive intermediates (*17, 21*). Spatial intermittency has been used to enhance the extent of isotope separation (*10*). Batch irradiators with continuous sources are used in the growth of algae cultures. A form of spatial intermittency is obtained by stirring optically dense cultures. The rate of growth is thereby affected (*4, 8*).

A very interesting field involving intermittent irradiation is that concerned with the response of living systems to variation in the natural daynight cycle, in terms of such phenomena as growth, flowering and fruiting of plants. The kinetic bases for these phenomena do not as yet appear to be understood and are the subjects of current intensive research efforts (*23*).

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 for design and research purposes. With a variety of expressions available for interpretation of experiments the use of intermittent irradiation techniques for the study of photochemical and radiation chemical reactor performance may be facilitated. Furthermore intermittent initiation techniques in general may provide an additional method for the study of the engineering aspects of chemical kinetics and the interactions of kinetics with physical rate processes. Crowell (*3*) has discussed the determination of activation energy from oscillating temperature experiments in batch and continuous systems.

In the applications of intermittent irradiation described above the reactions involved are usually complex. The concentrations which are of most interest are those of reactive intermediates. Once these are available, the concentrations of final products can frequently be calculated in a straightforward way. Methods of calculating steady state concentrations of intermediates have previously been presented for first- and second-order reactions of intermediates in batch irradiators (*5, 16*) and in continuous tubular irradiators with recycle (*6, 7*). In most instances transient state expressions have not been developed.

In the present paper methods of formulation of the transient as well as the steady state problem are given. The methods of formulation are presented through illustrations. First a system is treated in which a species produced by irradiation disappears via a first-order reaction. This system is treated in some detail for a number of irradiator types, a batch irradiator, a continuous stirred tank irradiator, and a continuous tubular reactor with recycle, and illustrative solutions are obtained. Then the treatment for the batch irradiator is applied to two other kinetic schemes including first a series of consecutive first-order reactions and finally second-order reaction of the intermediate species.

The form of the radiation pulses which has most often been of interest heretofore is that of square waves, and that form is used here throughout. Other forms which may be of interest can be used, although sometimes with difficulty. Thus in the use of the rotating sector method trapezoidal pulses can be encountered as a deviation from the ideal square pulses (*16*). Consideration of the nonideal wave form leads to nonlinear equations requiring numerical solution.

FIRST-ORDER REACTION OF INTERMEDIATES

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

$$A_0 \overset{Q_1}{\rightsquigarrow} A_1 \xrightarrow{k_1} P \tag{1}$$

The rate of production of A_1 during irradiation is Q_1. The latter is constant in space and time during an irradiation interval. Q_1 is proportional to the absorbed radiation flux or intensity and the concentration of A_0. In the initiation of fission product chains for example $Q_1 = \gamma_1 \Sigma_f \phi$. For photochemical initiation, $Q_1 = \phi_1 E_0 c_0 I$. Weak absorption of radiation is assumed so that absorption does not vary appreciably with the path length in the reactant. The concentration of A_0 is assumed to remain constant with time by restriction of the treatment to small conversions. Decomposition of A_1 to produce product P occurs both in the presence and absence of irradiation via first-order reaction with rate constant k_1. If the substance A_1 is itself subject to decomposition on irradiation, the rate constant k_1 is augmented during the irradiation interval by the rate constant for that process. For example if A_1 is a primary fission product with an appreciable neutron capture cross section, then removal of A_1 by neutron capture in a neutron field occurs via first-order reaction with rate constant $\sigma_a \phi$. The total rate constant during irradiation then is $k_1 + \sigma_a \phi$, and in the absence of irradiation it is k_1.

Batch Irradiator

The expression appropriate for the concentration of A_1 as a function of time after the onset of intermittent irradiation in a batch irradiator has been derived previously through the use of an inductive method (*14*). Its derivation here will serve to illustrate the principles of the present method.

Consider a batch irradiator in which a reactant A_0 is irradiated uniformly throughout the irradiator volume but intermittently in time. The sequence of light and dark intervals to which the reactant is exposed is thought of as starting with a light interval. The xth dark interval then follows the xth light interval. The light interval is of duration t_L, and the dark interval is of duration t_D. The concentration of A_1 during the xth light interval is denoted by $c_{1L}(x, t)$, $0 \leq t \leq t_L$, and during the following dark interval by $c_{1D}(x, t)$, $0 \leq t \leq t_D$. When one uses this notation, the differential equations describing the accumulation of A_1 are

$$\frac{d}{dt} c_{1L}(x, t) = Q_1 - k_1 c_{1L}(x, t), 0 \leq t \leq t_L \tag{2}$$

during the light interval, and

$$\frac{d}{dt} c_{1D}(x-1, t) = -k_1 c_{1D}(x-1, t), 0 \leq t \leq t_D \tag{3}$$

during the preceding dark interval.

The initial conditions for these equations are

$$\left.\begin{aligned} c_{1L}(x, 0) &= c_{1D}(x-1, t_D) \\ c_{1D}(x-1, 0) &= c_{1L}(x-1, t_L) \end{aligned}\right\} \tag{4}$$

Thus the concentration at the beginning of an interval is that existing at the end of the preceding interval. When one integrates Equations (2) and (3) over the indicated time intervals using the initial conditions given by Equations (4)

$$\left.\begin{aligned} c_{1L}(x, t_L) &= \frac{Q_1}{k_1}(1 - e^{-k_1 t_L}) + (e^{-k_1 t_L})\, c_{1D}(x-1, t_D) \\ c_{1D}(x-1, t_D) &= (e^{-k_1 t_D})\, c_{1L}(x-1, t_L) \end{aligned}\right\} \tag{5}$$

When $c_{1D}(x-1, t_D)$ is eliminated between these two equations, the following difference equation results:

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

If there is no A_1 present initially, Equation (6) sums to

$$\frac{c_{1L}(x, \theta_L)}{c_{1S}} = \frac{1 - e^{-(\theta_L + \theta_D)x}}{1 - e^{-(\theta_L + \theta_D)}}(1 - e^{-\theta_L}) \tag{7}$$

in which $c_{1S} = Q_1/k_1$ the steady state concentration of A_1 under steady irradiation, and $\theta_L = k_1 t_L$ and $\theta_D = k_1 t_D$ are the durations of the light and dark intervals in units of the mean lifetime of A_1 under steady irradiation. Equation (7) is an expression for the concentration of A_1 at the end of the xth light interval. The concentration history during a given pair of light and dark intervals may be found by substituting Equation (7) in Equations (5), each evaluated at a time t within the particular interval. Thus for the xth light interval in normalized form

$$\frac{c_{1L}(x, \theta)}{c_{1S}} = (1 - e^{-\theta}) + e^{-(\theta + \theta_D)} \frac{1 - e^{-(\theta_L + \theta_D)(x-1)}}{1 - e^{-(\theta_L + \theta_D)}} (1 - e^{-\theta_L}) \quad 0 \leq \theta \leq \theta_L \tag{8}$$

and for the xth dark interval

$$\frac{c_{1D}(x, \theta)}{c_{1S}} = \frac{1 - e^{-(\theta_L + \theta_D)x}}{1 - e^{-(\theta_L + \theta_D)}}(1 - e^{-\theta_L})e^{-\theta}, \; 0 \leq \theta \leq \theta_D \tag{9}$$

The concentration history given by Equations (8) and (9) is shown graphically in Figure 1 in which the normalized concentrations are plotted against x, the number of pairs of light and dark intervals. Three cases are shown in which the parameters θ_L and θ_D are equal and assume the values 0.1, 1, and 10. Saw-toothed responses to the intermittent initiation are obtained, with the concentration rising during light intervals and falling during dark intervals. The steady state pattern is closely approached during the first pair of intervals for $\theta_L = \theta_D = 10$. Repetition of the steady state pattern is not shown. Approximately three pairs are required for $\theta_L = \theta_D = 1$, and the subse-

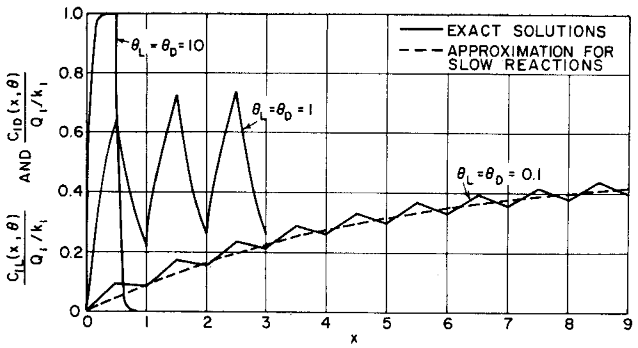

Fig. 1. Concentration transients for first-order reaction of intermediate in a batch irradiator with intermittent source.

quent repetition is not shown. A steady state is not achieved for $\theta_L = \theta_D = 0.1$ in the range of x shown. In general the approach to steady state is more rapid, and the range of concentration during a pair of light and dark intervals is greater for intervals which are long compared with the mean lifetime.

The limit of Equation (7) as $x \to \infty$ is the steady state concentration at the end of a light interval:

$$\frac{c_{1L}(\infty, \theta_L)}{c_{1S}} = \frac{1 - e^{-\theta_L}}{1 - e^{-(\theta_L + \theta_D)}} \tag{10}$$

An estimate of the time to approach steady state may be determined from this equation and Equation (7). The number of pairs of light and dark intervals required to obtain $c_{1L}(x, \theta_L) \geqslant 0.99\, c_{1L}(\infty, \theta_L)$ is found to be

$$x \geqslant \frac{4.606}{\theta_L + \theta_D} \tag{11}$$

For light and dark intervals which are short compared with the mean lifetime many cycles are required for a close approach to steady state. Little decay occurs during a dark interval, 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. The reaction system behaves as though it were exposed to steady irradiation of reduced intensity corresponding to an initiation rate of $[t_L/(t_L + t_D)]Q_1$. A single differential equation then describes the rate of accumulation of A_1. Thus without subscripts or arguments in the notation for concentration

$$\frac{dc_1}{dt} = \frac{t_L}{t_L + t_D} Q_1 - k_1 c_1 \tag{12}$$

The solution in normalized form is

$$\frac{c_1}{c_{1S}} = \frac{\theta_L}{\theta_L + \theta_D} [1 - e^{-(\theta_L + \theta_D)x}] \tag{13}$$

This equation may also be derived as the limiting form of Equations (7), (8), or (9) for small θ_L and θ_D. The transient given by Equation (13) for $\theta_L = \theta_D = 0.1$ is shown as the dashed line in Figure 1. It is seen to be a fair approximation to the corresponding curve given by Equations (8) and (9).

The mean value of the concentration of A_1 at steady state, averaged over a pair of light and dark intervals, is a quantity of interest, since this quantity determines the rate of formation of stable product P. Experimentally the rate of increase with time of the concentration of P may be accessible, whereas information on the concentration of A_1 may not be. The average concentration of A_1 at steady state is found from Equations (8) and (9) to be

$$\frac{c_{1I}}{c_{1S}} = \frac{\theta_L}{\theta_L + \theta_D} \int_0^{\theta_L} \frac{c_{1L}(x, \theta)}{c_{1S}} d\theta + \frac{\theta_D}{\theta_L + \theta_D} \int_0^{\theta_D} \frac{c_{1D}(x, \theta)}{c_{1S}} d\theta = \frac{\theta_L}{\theta_L + \theta_D} \tag{14}$$

The mean steady state rate of production of P is then given by

$$\frac{d\bar{P}}{dt} = k_1 c_{1I} = k_1 \frac{\theta_L}{\theta_L + \theta_D} c_{1S} \tag{15}$$

As far as the quantities θ_L and θ_D are concerned this rate depends only on their ratio and not on their absolute magnitudes. Therefore rotating sector experiments on first-order systems show no dependence on sector speed (5).

In the preceding treatment A_1 was assumed not to be decomposed on irradiation; that is the rate constant for first-order reaction of A_1 was taken to be the same in both the light and dark intervals. Most of the expressions developed however are applicable also when A_1 is subject to first-order radiation decomposition, provided only that in this event the augmented rate constant described at the beginning of this section be used to define θ_L. The exceptions to this statement are Equations (12), (13), and (15). As they stand, these equations are formulated with the same rate constant being used in both intervals. They can be adapted for the case of radiation decomposition of A_1 by replacing k_1 by the weighted sum of k_1 and the augmented rate constant, the weights being the fractions of the total time occupied by the dark and light intervals respectively.

Continuous Stirred Tank Irradiator

The treatment given for the batch irradiator is applicable for a perfectly mixed continuous stirred tank irradiator with an intermittent source if it is assumed that reactant A_0 is fed at the rate at which it is consumed and if in all expreessions k_1 is replaced by $k_1 + F/V$.

Plug Flow Tubular Irradiator With Recycle

In Figure 2 a tubular irradiator with a steady rather than an intermittent source is shown. The system is continuous, and a portion of the flow through the irradiator is recycled. Plug flow is assumed to exist throughout the system, and it is assumed that perfect mixing exists at the juncture of the recycle and feed streams. The rate of conversion of A_0 is small so that its concentration is effectively constant throughout the flow path. Make-up A_0 or A_0 plus inerts constitutes the feed to the system. An element of reaction mixture experiences alternate exposure to light and dark intervals as it circulates through the irradiator and along the recycle path back to the irradiator. The residence times and appropriate concentration notation for the various portions of the recirculating flow path are shown in Figure 2. It will be evident subsequently that it is convenient to imagine the irradiator to be divided

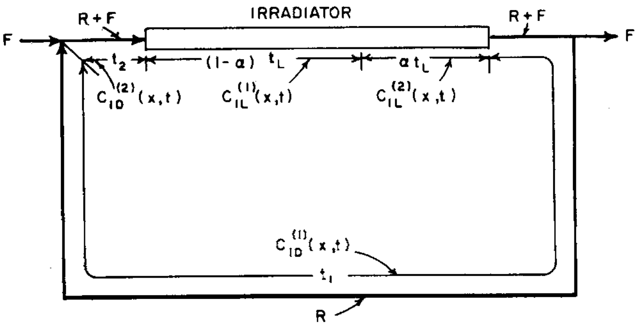

Fig. 2. Continuous plug flow tubular irradiator with recycle.

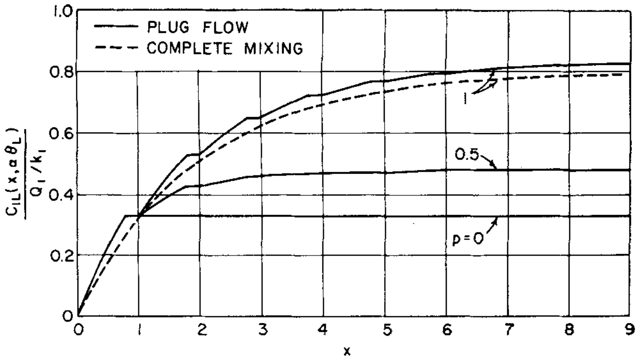

Fig. 3. Concentration transients for A_1 at outlet of irradiator of Figure 2. $\theta_L = 0.4$, $\theta_D = 0.1$.

into two parts as shown in order to accommodate a practical start-up procedure. The dark portion of the circuit is also divided into two segments, one of which runs from the irradiator outlet along the recycle path to the point at which the latter joins the feed stream. The other is the balance of the dark portion of the circuit.

With the notation in Figure 2, the differential equations describing the unsteady state concentration of A_1 in each of the segments of the recirculating flow path are as follows:

$$\left.\begin{aligned}
&\frac{d}{dt}\overset{(1)}{c}_{1L}(x,t) = Q_1 - k_1\overset{(1)}{c}_{1L}(x,t), && 0 \leqq t \leqq (1-\alpha)\,t_L\\
&\frac{d}{dt}\overset{(2)}{c}_{1L}(x,t) = Q_1 - k_1\overset{(2)}{c}_{1L}(x,t), && 0 \leqq t \leqq \alpha t_L\\
&\frac{d}{dt}\overset{(1)}{c}_{1D}(x-1,t) = -\,k_1\overset{(1)}{c}_{1D}(x-1,t), && 0 \leqq t \leqq t_1\\
&\frac{d}{dt}\overset{(2)}{c}_{1D}(x-1,t) = -\,k_1\overset{(2)}{c}_{1D}(x-1,t), && 0 \leqq t \leqq t_2
\end{aligned}\right\}\tag{16}$$

As before the initial concentration for each of the four segments is the final concentration of the preceding segment. Hence the initial conditions for Equations (16) are:

$$\left.\begin{aligned}
&\overset{(1)}{c}_{1L}(x,0) = \overset{(2)}{c}_{1D}(x-1,t_2)\\
&\overset{(2)}{c}_{1L}(x,0) = \overset{(1)}{c}_{1L}[x,(1-\alpha)\,t_L]\\
&\overset{(1)}{c}_{1D}(x-1,0) = \overset{(2)}{c}_{1L}(x-1,\alpha t_L)\\
&\overset{(2)}{c}_{1D}(x-1,0) = p\overset{(1)}{c}_{1D}(x-1,t_1)
\end{aligned}\right\}\tag{17}$$

The presence of recycle is taken into account in the last equation of Equations (17). Thus p is $R/(R+F)$, the fraction of the irradiator flow which is recycled.

When Equations (16) are integrated over the time intervals indicated, with Equations (17) as initial conditions, the following equations are obtained:

$$\left.\begin{aligned}
&\overset{(1)}{c}_{1L}[x,(1-\alpha)t_L] = e^{-k_1(1-\alpha)t_L}\,\overset{(2)}{c}_{1D}(x-1,t_2) + \frac{Q_1}{k_1}\left[1-e^{-k_1(1-\alpha)t_L}\right]\\
&\overset{(2)}{c}_{1L}(x,\alpha t_L) = e^{-k_1\alpha t_L}\,\overset{(1)}{c}_{1L}[x,(1-\alpha)t_L] + \frac{Q_1}{k_1}\left(1-e^{-k_1\alpha t_L}\right)\\
&\overset{(1)}{c}_{1D}(x-1,t_1) = e^{-k_1 t_1}\,\overset{(2)}{c}_{1L}(x-1,\alpha t_L)\\
&\overset{(2)}{c}_{1D}(x-1,t_2) = p\,e^{-k_1 t_2}\,\overset{(1)}{c}_{1D}(x-1,t_1)
\end{aligned}\right\}\tag{18}$$

Three of the five terminal concentrations may be eliminated among these four equations to obtain in normalized form

$$\frac{\overset{(2)}{c}_{1L}(x,\alpha\,\theta_L)}{c_{1S}} = 1 - e^{-\theta_L} + p\,e^{-(\theta_L+\theta_D)}\,\frac{\overset{(2)}{c}_{1L}(x-1,\alpha\,\theta_L)}{c_{1S}}\tag{19}$$

An initial condition for this difference equation may be determined by considering a practical start-up procedure. The equipment is first charged with A_0, flow with recycle is started, and at zero time the radiation source is turned on. A given volume element of reactant within the irradiator at zero time resides within the radiation field during its first pass for a time αt_L, where α varies from 0 for an element located initially at the outlet to 1 for an element at the inlet. The concentration of A_1 developed in such an element upon first reaching the irradiator outlet is given by the integration of the second of Equations (16) from 0 to αt_L with $x = 1$ and $\overset{(2)}{c}_{1L}(1,0) = 0$. Thus

$$\frac{\overset{(2)}{c}_{1L}(1,\alpha\,\theta_L)}{c_{1S}} = 1 - e^{-\alpha\theta_L}\tag{20}$$

With this initial condition for Equation (19) the solution is

$$\frac{\overset{(2)}{c}_{1L}(x,\alpha\,\theta_L)}{c_{1S}} = \frac{1-[p\,e^{-(\theta_L+\theta_D)}]^x}{1-p\,e^{-(\theta_L+\theta_D)}}\,(1-e^{-\theta_L}) + (e^{-\theta_L}-e^{-\alpha\theta_L})\,[p\,e^{-(\theta_L+\theta_D)}]^{x-1}\tag{21}$$

If Equation (21) is substituted in Equations (18), solutions for $\overset{(1)}{c}_{1D}(x,t_1)$, $\overset{(2)}{c}_{1D}(x,t_2)$, and $\overset{(1)}{c}_{1L}[x,(1-\alpha)t_L]$ may be obtained, and the solution of the problem of the plug flow irradiator with recycle may thereby readily be completed. It will be sufficient for present purposes to consider Equation (21) which is an expression for the concentration transient of A_1 at the outlet of the irradiator. Figure 3 shows a graphical representation of Equation (21) for $\theta_L = 0.4$, $\theta_D = 0.1$, and for three values of the parameter p. The transients consist of periods of exponential buildup corresponding to the breakthrough of reactant which was within the irradiator at start-up followed by periods of constant concentration corresponding to the breakthrough of reactant which was in the dark portion of the circuit at start-up. For exponential periods $0 \leqq \alpha \leqq 1$, and for the constant concentration periods $\alpha = 1$. For no recycle, that is $p = 0$, a single exponential buildup period, given by Equation (20) rather than (21), is followed by a steady state constant concentration. For total recycle $p = 1$, corresponding to the maximum accumulation of A_1 in the circuit.

The mean steady state concentration of A_1 in the recirculating flow path may be obtained by averaging the solutions of Equations (18) around the flow path and may be shown to be

$$\frac{c_{1I}}{c_{1S}} = \frac{\theta_L}{\theta_L + \theta_D}\left[1 - \frac{1 - e^{-\theta_L}}{1 - p\, e^{-(\theta_L + \theta_D)}}\, e^{-\theta_1}\frac{(1-p)}{\theta_L}\right] \tag{22}$$

In contrast to the batch irradiator and the stirred tank irradiator [see Equation (14)] the average concentration of A_1 in the plug flow tubular irradiator with recycle does depend on the absolute as well as relative magnitudes of θ_L and θ_D and in addition on θ_1 and p.

Finally one may briefly consider the transient time for the plug flow tubular irradiator with recycle. It may be seen in Figure 3 and Equation (21) that a convenient and useful point at which to examine the approach to steady state is at an integral value of x, at which $\alpha = 1$. For $\alpha = 1$ in Equation (21) one may show that for

$$x \geqq \frac{4.606 + 2.303 \log_{10} p}{\theta_L + \theta_D} \tag{23}$$

then $c_{1L}^{(2)}(x, \theta_L)/c_{1L}^{(2)}(\infty, \theta_L) \geqq 0.99$. A comparison of Equations (11) and (23) shows, when one notes that $0 \leqq p \leqq 1$ and hence $\log_{10} p \leqq 0$, that, as one would expect, increasing the proportion of through flow reduces the transient time. In the absence of through flow, that is $p = 1$, the transient times for all of the irradiators considered are identical.

Perfectly Mixed Tubular Irradiator With Recycle

This irradiator is identical to that shown in Figure 2 except that as a result of mixing in the flow direction the concentration of A_1 is uniform in all parts of the recirculating flow path. The rate of initiation is reduced in proportion to the fraction of time during which the reactant is irradiated. The appropriate differential equation and its solution are identical to Equations (12) and (13), those for slow reactions, except that in order to account for through flow k_1 is replaced by $k_1 + F/V$. The time for attainment of 99% of the steady state concentration is given by Equation (11) in which the above augmented rate constant is used.

The effect of mixing in tubular irradiators with total recycle may be seen in Figure 3. There the comparison is evident between the plug flow irradiator (solid line) and the perfectly mixed irradiator (dotted line) for the case of total recycle, the only case for which a comparison is possible. For the particular case chosen, involving as it does relatively small values of θ_L and θ_D, the agreement is good. For large θ_L and θ_D the agreement would be poor. It may nevertheless be noted that one can show that the average steady state concentration at total recycle for plug flow and for perfect mixing are equal. Mixing is therefore unimportant in first-order reactions in determining the rate of production of P.

CONSECUTIVE FIRST-ORDER REACTIONS

In this section and the following one the treatment of two additional reaction schemes will be given. Illustrative treatment will be given for the batch irradiator only, although the methods of formulation and solution appropriate for other irradiator types, as developed in the previous section, might equally well have been presented.

The first of the reaction schemes to be considered involves a sequence of first-order reactions of arbitrary length. Radioactive decay chains initiated by fission or say by (n, γ) activation are included in this category. Transient and steady state solutions for consecutive first-order reactions have been available heretofore only for isolated special cases (*14*).

The reaction scheme of interest is represented in Figure 4. As in the previous section the zeroth member of the series is subject to decomposition on irradiation, producing in this case, for the sake of generality, amounts of each of the daughter species as primary products at the rates Q_i. Each of the Q_i is proportional to the radiation flux, the concentration of A_0, and the yield of the *i*th member. It is assumed to remain constant with time. First-order decomposition of each member of the series except the zeroth is governed by the rate constant $\kappa_i = \lambda_i + \mu_i$, where the κ_i are assumed to be distinct. λ_i governs the rate of production of the daughter of i. By definition $\lambda_r = 0$. μ_i is associated with the process of removal of i by radiation decomposition. As such it is proportional to the radiation flux and is zero in the dark.

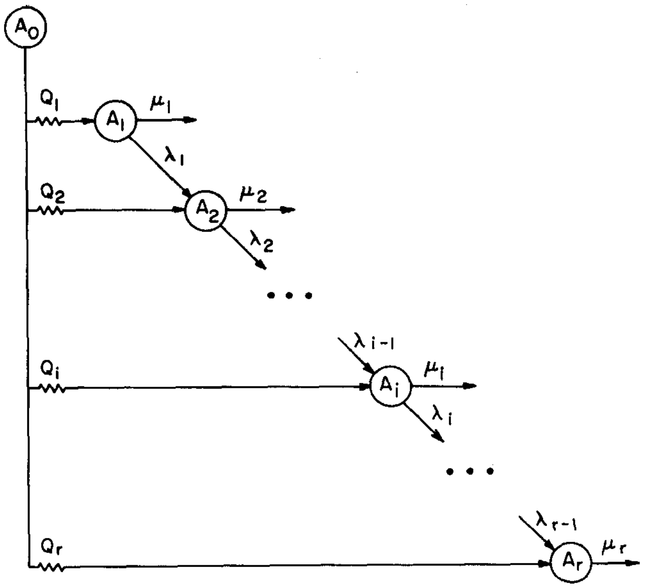

Fig. 4. Production and removal processes in consecutive first order reactions.

In a manner similar to that used previously the intermittent irradiation problem for the batch reactor may be formulated by deriving in this case a sum equation, rather than a difference equation, which relates the concentration of the *i*th member of the series at the end of the *x*th light interval to the concentration of i and in this case to those of its predecessors as well at the end of the $(x - 1)$ *st* light interval. This is done as before, by first solving the two sets of differential equations describing the net rate of production of the members of the series in the *x*th light interval

$$\left.\begin{aligned} &\frac{d}{dt} c_{1L}(x, t) = Q_1 - \kappa_1 c_{1L}(x, t) \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ &\frac{dt}{d} c_{iL}(x, t) = Q_i + \lambda_{i-1} c_{i-1L}(x, t) \\ &\qquad - \kappa_i c_{iL}(x, t), i, = 2, 3, \ldots, r \end{aligned}\right\} \tag{24}$$

and in the preceding dark interval

$$\left.\begin{aligned} &\frac{d}{dt} c_{1D}(x-1, t) = -\kappa_1 c_{1D}(x-1, t) \\ &\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ &\frac{d}{dt} c_{iD}(x-1, t) = \lambda_{i-1} c_{i-1D}(x-1, t) \\ &\qquad - \kappa_i c_{iD}(x-1, t),\ i = 2, 3, \ldots, r \end{aligned}\right\} \tag{25}$$

The initial conditions are

$$\left.\begin{aligned} c_{jL}\,(x, 0) &= c_{jD}\,(x-1, t_D) \\ c_{jD}\,(x-1, 0) &= c_{jL}\,(x-1, t_L) \end{aligned}\right\} \tag{26}$$

The solutions of Equations (24) and (25) subject to Equations (26) are (see Appendix*)

$$\left.\begin{aligned} c_{iL}\,(x, t_L) &= \sum_{j=1}^{i} [a_{ij}(t_L)\,Q_j + b_{ij}(t_L)\,c_{jD}\,(x-1, t_D)] \\ c_{iD}\,(x-1, t_D) &= \sum_{j=1}^{i} b_{ij}(t_D)\,c_{jL}\,(x-1, t_L) \end{aligned}\right\} \tag{27}$$

where

$$\left.\begin{aligned} a_{ij}(t) &= \left(\prod_{m=j}^{i-1} \lambda_m\right)\left(\sum_{m=j}^{i} \frac{1}{\prod\limits_{\substack{n=j\\ n\neq m}}^{i} (\kappa_n - \kappa_m)} \int_0^t e^{-\kappa_m t'}\,dt'\right) \\ b_{ij}(t) &= \frac{d}{dt}\,[a_{ij}(t)] \end{aligned}\right\} \tag{28}$$

The sum equation sought is obtained by substituting the second of Equations (27) in the first:

$$c_{iL}(x, t_L) = c_{iL}(1, t_L) + \sum_{j=1}^{i} b_{ij}(t_L) \sum_{k=1}^{j} b_{jk}(t_D)\,c_{kL}(x-1, t_L) \tag{29}$$

In writing Equation (29) by setting $\sum_{j=1}^{i} a_{ij}(t_L)Q_j = c_{iL}(1, t_L)$ it has been noted that no member of the series except A_0 is present prior to the onset of intermittent irradiation.

Equation (29) may be solved in step-by-step fashion, first for $i = 1$, then for $i = 2$, and so on. Thus for $i = 1$

$$c_{1L}(x, t_L) = c_{1L}(1, t_L) + b_{11}\,c_{1L}(x-1, t_L) \tag{30}$$

where $b_{11} = b_{11}(t_L)b_{11}(t_D)$. The solution is

$$c_{1L}(x, t_L) = \frac{1 - b_{11}^{\,x}}{1 - b_{11}}\,c_{1L}(1, t_L) \tag{31}$$

For $i = 2$ Equation (29) is

$$c_{2L}(x, t_L) = c_{2L}(1, t_L) + b_{22}c_{2L}(x-1, t_L) + b_{21}c_{1L}(x-1, t_L) \tag{32}$$

where

$$b_{22} = b_{22}(t_L)b_{22}(t_D)$$
$$b_{21} = b_{21}(t_L)b_{11}(t_D) + b_{22}(t_L)b_{21}(t_D)$$

After one substitutes the solution for $c_{1L}(x, t_L)$, Equation (31), in Equation (32), the solution of the resulting equation is found to be

$$c_{2L}(x, t_L) = \frac{1 - b_{22}^{\,x}}{1 - b_{22}}\,c_{2L}(1, t_L) + \left[\frac{1}{(1-b_{11})(1-b_{22})} - \frac{b_{11}^{\,x}}{(1-b_{11})(b_{11}-b_{22})} + \frac{b_{22}^{\,x}}{(b_{11}-b_{22})(1-b_{22})}\right] b_{21}c_{1L}(1, t_L) \tag{33}$$

The solutions rapidly become cumbersome and unwieldy, although the method of obtaining them is simple in principle. When they are 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 (*13*).

Steady state solutions are obtained by letting $x \to \infty$ in the solutions of Equation (29) or in Equation (29) itself. In the latter instance solution of a system of simultaneous linear algebraic equation arises.

It might be noted that in practical applications of this treatment one is most often interested in cases in which there is a direct yield of the first member of the chain only, that is, $Q_i = 0$ for $i \geqq 2$.

In the above formulation of the batch reactor problem the sum equations obtained represent systems of i coupled equations. In a review of this paper R. Aris pointed out a method which leads to uncoupled equations and which is briefly outlined below. In this method square wave excitation is applied to the system of equations heretofore used for the light interval alone, Equations (24). Then, in matrix form, Equations (24) become

$$\frac{dc}{dt} = -Kc + q(t) \tag{34}$$

Since in K the κ_i are distinct, there may be found a nonsingular matrix L such that

$$\Lambda = LKL^{-1} \tag{35}$$

Then $e = Lc$ satisfies

$$\frac{de}{dt} = -\Lambda e + p(t) \tag{36}$$

where $p(t) = Lq(t)$. These equations are uncoupled, and a solution for the concentration of the ith member may be obtained without first finding solutions for earlier members of the series.

SECOND-ORDER REACTION OF INTERMEDIATES

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. Numerical 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 can be transformed to a linear one. The reaction of interest is one which is typical of those studied by means of the rotating sector method. It involves, as rate-controlling steps in the overall mechanism, the production of radicals through irradiation and their subsequent recombination:

$$A_0 \underset{k_t}{\overset{Q_1}{\rightleftarrows}} 2A_1 \tag{37}$$

The formulation of the batch irradiator problem again parallels the treatment for first-order systems. The differential equations describing the radical concentration are

$$\frac{d}{dt}\,c_{1L}(x, t) = Q_1 - k_t c_{1L}^{2}(x, t) \tag{38}$$

for the xth light interval and

$$\frac{d}{dt}\,c_{1D}(x-1, t) = -\,k_t c_{1D}^{2}(x-1, t) \tag{39}$$

for the preceding dark interval.

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* The Appendix has been deposited as document 7826 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

It is convenient to introduce the dimensionless variables

$$C_{1D}(x, \theta) = \frac{c_{1D}(x, \theta)}{c_{1S}}, C_{1L}((x, \theta) = \frac{c_{1L}(x, \theta)}{c_{1S}}, \theta = t/\tau_1 \tag{40}$$

where $c_{1S} = (Q_1/k_t)^{1/2}$, the steady state concentration of A_1 under steady irradiation, and $\tau_1 = (Q_1 k_t)^{-1/2}$, the mean lifetime of A_1 under steady irradiation. In terms of these variables, Equations (38) and (39) are, respectively

$$\frac{d}{d\theta} C_{1L}(x, \theta) = 1 - C_{1L}^2(x, \theta) \tag{41}$$

$$\frac{d}{d\theta} C_{1D}(x-1, \theta) = - C_{1D}^2(x-1, \theta) \tag{42}$$

The initial conditions are

$$\left.\begin{aligned} C_{1L}(x, 0) &= C_{1D}(x-1, \theta_D) \\ C_{1D}(x-1, 0) &= C_{1L}(x-1, \theta_L) \end{aligned}\right\} \tag{43}$$

The solution of Equations (41) and (42) then are

$$\left.\begin{aligned} C_{1L}(x, \theta_L) &= \frac{\beta_L + C_{1D}(x-1, \theta_D)}{1 + \beta_L C_{1D}(x-1, \theta_D)} \\ C_{1D}(x-1, \theta_D) &= \frac{C_{1L}(x-1, \theta_L)}{1 + \theta_D C_{1L}(x-1, \theta_L)} \end{aligned}\right\} \tag{44}$$

in which $\beta_L = \tanh \theta_L$. From these equations, when one eliminates $C_{1D}(x-1, \theta_D)$, one finds

$$C_{1L}(x, \theta_L) = \frac{\beta_L + (1 + \beta_L \theta_D)\, C_{1L}(x-1, \theta_L)}{1 + (\beta_L + \theta_D) C_{1L}(x-1, \theta_L)} \tag{45}$$

Equation (45), the difference equation sought, is nonlinear. A linear equation can be obtained through the use of the following transformation (*1*, *9*):

$$C_{1L}(x, \theta_L) + \frac{1}{\beta_L + \theta_D} = \frac{w(x+1)}{w(x)} \tag{46}$$

In terms of $w(x)$ Equation (45) is

$$w(x+1) - \frac{2 + \beta_L\theta_D}{\beta_L + \theta_D} w(x) + \frac{1 - \beta_L^2}{(\beta_L + \theta_D)^2} w(x-1) = 0 \tag{47}$$

Equation (47) is satisfied by a solution of the form

$$w(x) = A r_1^x + B r_2^x \tag{48}$$

where A and B are constants, and

$$\left.\begin{aligned} r_1 &= \frac{1}{2(\beta_L + \theta_D)} \left[2 + \beta_L\theta_D - \sqrt{(2 + \beta_L\theta_D)^2 - 4(1 - \beta_L^2)}\right] \\ r_2 &= \frac{1}{2(\beta_L + \theta_D)} \left[2 + \beta_L\theta_D + \sqrt{(2 + \beta_L\theta_D)^2 - 4(1 - \beta_L^2)}\right] \end{aligned}\right\} \tag{49}$$

Using Equation (48) in Equation (46) and rearranging one obtains

$$C_{1L}(x, \theta_L) = r_2 - \frac{1}{\beta_L + \theta_D} + \frac{r_1 - r_2}{1 + C(r_2/r_1)^x} \tag{50}$$

where $C = B/A$.

In the first of Equations (44) if $C_{1D}(0, \theta_D) = 0$, then $C_{1L}(1, \theta_L) = \beta_L$. After this initial condition is used to evaluate C, Equation (50) may be written

$$C_{1L}(x, \theta_L) = r_2 - \frac{1}{\beta_L + \theta_D} - \frac{r_2 - r_1}{1 - \dfrac{r_1 - \beta_L - \dfrac{1}{\beta_L + \theta_D}}{r_2 - \beta_L - \dfrac{1}{\beta_L + \theta_D}} (r_2/r_1)^{x-1}} \tag{51}$$

It can be determined from Equations (49) that $r_2/r_1 > 1$, and that therefore as $x \to \infty$ the last term in Equation (51) approaches zero. Hence

$$C_{1L}(\infty, \theta_L) = r_2 - \frac{1}{\beta_L + \theta_D} = \frac{1}{2(\beta_L + \theta_D)} \left[\beta_L\theta_D + \sqrt{(2 + \beta_L\theta_D)^2 - 4(1 - \beta_L^2)}\right] \tag{52}$$

The same result can be obtained by letting $x \to \infty$ in Equation (45).

Equation (51) may be used in Equations (44), 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 Figure 5. The same general discussion applies here as was found for Figure 1 for first-order disappearance. Steady state is closely approached in the first cycle for $\theta_D = \theta_L = 10$ and in three 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

$$C_{1L}(x, \theta_L) = \left(\frac{\theta_L}{\theta_L + \theta_D}\right)^{1/2} \tanh\{[\theta_L(\theta_L + \theta_D)]^{1/2} x\} \tag{53}$$

Equation (53), which is represented by the dashed line in Figure 5 for $\theta_D = \theta_L = 0.1$, is the solution for the differential equation for slow reactions [see Equation (12)]:

$$\frac{dC}{d\theta} = \frac{\theta_L}{\theta_L + \theta_D} - C^2 \tag{54}$$

The mean steady state value of the concentration of A_1, averaged over a pair of light and dark intervals, is found to depend on the absolute values of θ_L and θ_D as

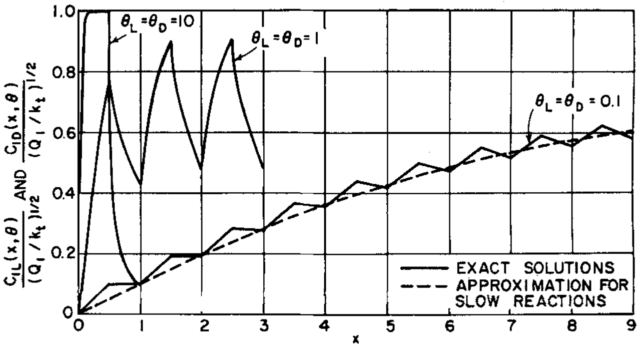

Fig. 5. Concentration transients for second-order reaction of intermediates in a batch irradiator with intermittent source.

well as on their ratio. This dependence forms the basis for the rotating sector method (*16*).

ACKNOWLEDGMENT

D. S. Trifan and R. H. Wilhelm made valuable suggestions regarding the scope of the work. Anna Potter performed the calculations for Figures 1 and 5. This work was done under the auspices of the United States Atomic Energy Commission.

NOTATION

$a_{ij}(t)$ = coefficient defined by Equation (28)
A = constant
A_i = *i*th 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 $i = 2$, Equation (32)
$b_{ij}(t)$ = coefficient defined by Equation (28)
B = constant
c = column matrix with elements c_i
c_i = concentration of species i
$c_{iD}(x,t)$ = concentration of *i*th member of a series at a time t during the *x*th dark interval, with superscripts (1) or (2) as defined in Figure 2
c_{iI} = mean steady state concentration of i under intermittent irradiation
$c_{iL}(x,t)$ = concentration of *i*th member of a series at a time t during the *x*th light interval, with superscripts (1) or (2) as defined in Figure 2
c_{iS} = steady state concentration of i under steady irradiation
C = constant
$C_{iD}(x,\theta)$ = dimensionless concentration defined by Equation (40)
$C_{iL}(x,\theta)$ = dimensionless concentration defined by Equation (40)
e = Lc
E_0 = molar extinction coefficient of A_0
F = flow rate through stirred tank irradiator or through irradiator with recycle
I = radiation intensity incident on reactant mixture
k_t = rate constant for radical-radical termination of a chain reaction
k_1 = rate constant for first-order disappearance of A_1
K = matrix of coefficients of $c_{iL}(x,t)$ in Equation (24)
L = transforming matrix defined by Equation (35)
$p(t)$ = $Lq(t)$
p = $R/(R+F)$
P = reaction product
$\overline{P}$ = mean concentration of P
$q(t)$ = column matrix with elements which are zero in a dark interval and Q_i in a light interval
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 Equation (49)
R = flow rate of recycled reactant (Figure 2)
t = time
t_D = duration of dark interval
t_L = duration of light interval
t_1, t_2 = times of passage through segments of dark portion of flow circuit (see Figure 2), $t_1 + t_2 = t_D$
V = reactant volume in stirred tank irradiator or in tubular irradiator including recycle path
$w(x)$ = function defined by Equation (46)
x = number of dark or light interval following onset of intermittent irradiation, sequences start with a light interval

Greek Letters

α = plug flow residence time within tubular irradiator during first pass of an element of reactant volume initially within irradiator, expressed as a fraction of t_L the maximum residence time
β_L = $\tanh \theta_L$
γ_i = direct fission yield of i
θ = t/τ_1
θ_D = t_D/τ_1
θ_L = t_L/τ_1
κ_i = total rate constant for first order reaction of A_i
λ_i = rate constant for production of A_{i+1} from A_i
Λ = diagonal matrix defined by Equation (35)
μ_i = rate constant for radiation decomposition of A_i
σ_a = microscopic neutron absorption cross section of A_1
Σ_f = macroscopic fission cross section of A_0
τ_1 = mean lifetime of A_1 under steady irradiation
ϕ = neutron flux
ϕ_1 = quantum yield of A_1

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Manuscript received February 6, 1963; revision received August 16, 1963; paper accepted August 22, 1963. Paper presented at A.I.Ch.E. Buffalo meeting.