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The Progression of Sequential Reactions

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The Progression of Sequential Reactions

Abstract

Sequential reactions consist of linked reactions in which the product of the first reaction becomes the substrate of a second reaction. Sequential reactions occur in industrially important processes, such as the chlorination of methane. A generalized series of three sequential reactions was analyzed in order to determine the times at which each chemical species reaches its maximum. To determine the concentration of each species as a function of time, the differential rate laws for each species were solved. The solution of each gave the concentration curve of the chemical species. The concentration curves of species A_1 and A_2 possessed discrete maxima, which were determined through slope-analysis. The concentration curve of the final product, A_3 , did not possess a discrete maximum, but rather approached a finite limit.

Keywords

Sequential Reactions, Chemical Concentration, Process Optimization

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PROBLEM STATEMENT

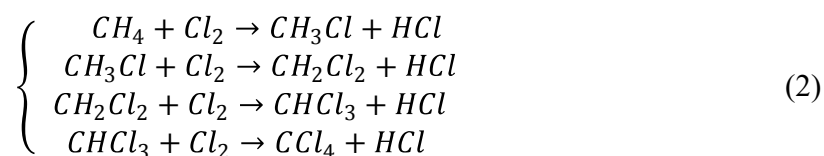
When the product of an initial chemical reaction becomes the substrate for further reactions, the step-wise series of transformations are known as sequential reactions. Since each reaction in the series is linked, the rate of each reaction is dependent on the reaction which precedes it. Therefore, the concentration of each product should rise and fall during the course of the reaction. The following generic sequential reactions will be studied.



This analysis seeks equations which describe the time of each product's maximal concentration. In order to confirm this result, the concentration of each product as a function of time will be graphed. These results will be expanded into general formulae which describe the n -th chemical species of any sequential reaction.

MOTIVATION

Sequential reactions occur both in nature and industry. In living organisms, the biosynthesis of fatty acids from acetyl Co-A proceeds sequentially, whereby acetyl groups are successively added to the growing tail of a fatty acid and reduced. The commercially important chlorination of methane also proceeds in a sequential manner. In this series of reactions, each step substitutes one chlorine atom for a hydrogen atom, ultimately resulting in a fully chlorinated product.



Typically, chlorination is performed as a batch process; thus, the composition of the chemical reactor changes as the process progresses. Throughout the course of the sequential reactions, the concentration of starting material will fall continuously and the concentration of the final product will rise continuously. It is trivial to demonstrate that the concentration of starting material will decrease to zero and that the concentration of the final product will assume a maximum, given sufficient time. The concentration of each intermediate product, however, will rise and fall in series. Thus, each intermediate will possess a distinct time at which its concentration is maximal.

To a chemical manufacturer, some reaction intermediates may be more desirable than others. For instance, market conditions may produce more demand for dichloromethane than chloromethane or chloroform. A manufacturer would thus seek to maximize the production of dichloromethane. If a particular intermediate product is desired, then determining the time at which each product reaches its maximum concentration assumes great practical importance, for the production of the desired intermediate can be maximized by adjusting reaction time.

MATHEMATICAL DESCRIPTION AND SOLUTION APPROACH

Over the course of any chemical reaction, the concentration of a chemical species will change, either increasing or decreasing, depending on the reaction conditions. A rate law is a differential equation which describes the rate of this change as a function of the concentration of the species and its precursors. In simple terms, the rate law considers the rate of both formation

and the rate of degradation of a chemical species. The differential equations which describe each rate law appear below.

$$\frac{d[A_0]}{dt} = -k[A_0] \quad (3)$$

$$\frac{d[A_1]}{dt} = k[A_0] - k[A_1] \quad (4)$$

$$\frac{d[A_2]}{dt} = k[A_1] - k[A_2] \quad (5)$$

$$\frac{d[A_3]}{dt} = k A_2 \quad (6)$$

The constant k is a rate law constant, which relates concentration to rate. For the purposes of this study, k is a pseudo-rate constant, which incorporates the concentration of R . The reagent R is assumed to be present in great excess and thus its concentration is constant over the course of the reaction. In order to simplify the analysis, each reaction is assumed to possess the same value for k .

Notice that the starting material, A_0 , undergoes exponential decay, since no other reaction replenishes its concentration. The intermediates, A_1 and A_2 , are the products of previous reactions which undergo further reaction. Thus, their rate of formation and rate of reaction compete to determine their concentration. Due to this competition, each is expected to rise to a maximum and then decline to zero as time progresses. The rate law which describes the final product, A_3 , is controlled by the concentration of A_2 alone. Since the concentration of A_2 rises, peaks and falls to zero, the concentration of A_3 should also rise and then level-off to a finite quantity. This is fitting, since the concentration of A_3 should never exceed the initial concentration of starting material; otherwise, the law of mass conservation would be violated.

Solving the differential rate laws yields the concentration curves for each chemical species. The concentration curve is a function which describes the concentration a chemical species as a function of time. Naturally, the concentration curve can be studied to determine t_{max} , the time at which a species reaches its maximal concentration. The solutions of the differential equations are discussed below.

The rate law (3) describes the concentration of A_0 . A separation of variables followed by integration yields the equation

$$[A_0](t) = e^{-kt} + C_0 \quad (7)$$

which describes the A_0 concentration as a function of time. Assuming that $[A_0](t) = 1$ at time zero yields the equation

$$[A_0](t) = e^{-kt}. \quad (8)$$

The rate laws which describe the intermediate products, A_1 and A_2 , are both first-order differential equations, which follow the standard form

$$\frac{dy}{dx} + P(x)y = Q(x). \quad (9)$$

First order differential equations of form (9) are solved by the formula

$$y = \frac{1}{e^{\int P(x)dx}} \int Q(x)e^{\int P(x)dx} dx. \quad (10)$$

In the case of A_1 , the differential (4) can be expressed as

$$\frac{dA_1}{dt} + k[A_1] = k[A_0] \quad (11)$$

and substituting the previous result for $[A_0]$ found on line (8) yields

$$\frac{d[A_1]}{dt} + k[A_1] = k(e^{-kt}). \quad (12)$$

Solving the first-order differential equation with formula (10) yields the general equation

$$[A_1](t) = \frac{kt}{e^{-kt}} + \frac{C_1}{e^{-kt}}. \quad (13)$$

Assuming that $[A_1](t) = 0$ at time zero results in

$$[A_1](t) = \frac{kt}{e^{-kt}}. \quad (14)$$

The rate law (5) describing A_2 is

$$\frac{d[A_2]}{dt} + k[A_2] = k[A_1]. \quad (15)$$

When (14) is substituted for $[A_1]$, (15) becomes

$$\frac{d[A_2]}{dt} + k[A_2] = \frac{k^2t}{e^{-kt}}. \quad (16)$$

Solving this first-order differential equation using (10) yields

$$[A_2](t) = \frac{k^2t^2}{2e^{-kt}} + \frac{C_2}{e^{-kt}}. \quad (17)$$

Assuming that $[A_2](t) = 0$ at time zero gives

$$[A_2](t) = \frac{k^2t^2}{2e^{-kt}}. \quad (18)$$

The differential rate law (6) which describes the final product, A_3 , is

$$\frac{d[A_3]}{dt} = k[A_2]. \quad (19)$$

Substituting (18) for $[A_2]$ yields

$$\frac{d[A_3]}{dt} = \frac{k^3 t^2 e^{-kt}}{2}. \quad (20)$$

The solution to (20) entails integrating by parts, which ultimately yields the following general solution

$$[A_3](t) = C_4 - \left(\frac{k^2 t^2 e^{-kt}}{2} + k t e^{-kt} + e^{-kt} \right). \quad (21)$$

Note the sum resulting from several iterations of integration by parts. Since $[A_3](t) = 0$ at time zero, $C_4 = 1$. Substituting the value for C_4 into equation (21) yields

$$[A_3](t) = 1 - \left(\frac{k^2 t^2 e^{-kt}}{2} + k t e^{-kt} + e^{-kt} \right). \quad (22)$$

Equations (8), (14), (18) and (22) describe the concentration of each species as a function of time. Thus, the time at which each species reaches its maximum concentration can be determined from these equations. In the case of the intermediate products A_1 and A_2 , the derivatives of the functions $[A_1](t)$ and $[A_2](t)$ equated to zero in order to determine t_{max} :

$$\frac{d[A_1](t)}{dt} = \frac{1}{e^{-kt}} (k - k^2 t) = 0 \rightarrow t_{max} = \frac{1}{k} \quad (23)$$

$$\frac{d[A_2](t)}{dt} = \frac{1}{e^{-kt}} \left(k^2 - \frac{k^3 t}{2} \right) = 0 \rightarrow t_{max} = \frac{2}{k}. \quad (24)$$

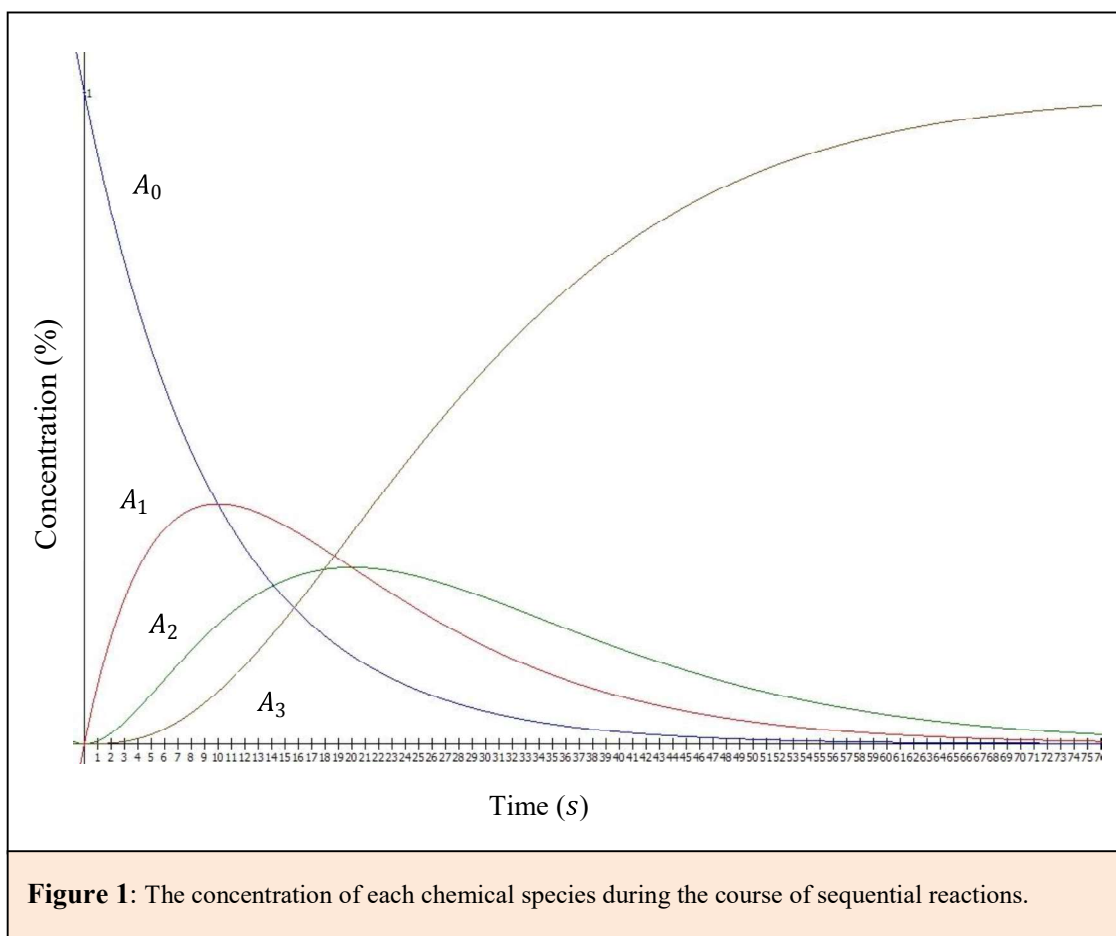
The slope analysis of $[A_0](t)$ and $[A_3](t)$ provides the intuitive solution, because their slopes continuously decrease and continuously increase, respectively. It is trivial to demonstrate that $[A_0](t)$ possesses a maxima at $t = 0$, given that its initial concentration decreases continuously. The function $[A_3](t)$ displays asymptotic behavior as $t \rightarrow \infty$. The finite quantity which $[A_3](t)$ approaches is

$$\lim_{t \rightarrow \infty} 1 - \left(\frac{k^2 t^2 e^{-kt}}{2} + k t e^{-kt} + e^{-kt} \right) = 1. \quad (25)$$

The exponential terms approach zero as time increases. Thus, $[A_3](t)$ approaches one as $t \rightarrow \infty$.

No discrete maxima exists for $[A_3](t)$, however.

In order to confirm the results of maxima-analysis and gain additional insight into the behavior of the chemical species during the progress of the sequential reactions, the equations which describe the concentration of each product as a function of time were graphed using MathGV graphing software. The chosen value for the pseudo-rate law constant, $k = 0.1$, was selected for convenience. The resultant graph appears below in Figure 1.



DISCUSSION

Solving the differential rate laws yielded the following equations which describe the concentration of each chemical species as a function of time:

$$\begin{cases} [A_0](t) = e^{-kt} \\ [A_1](t) = \frac{kt}{e^{kt}} \\ [A_2](t) = \frac{k^2 t^2}{2e^{kt}} \\ [A_3](t) = 1 - \left(\frac{k^2 t^2 e^{-kt}}{2} + kt e^{-kt} + e^{-kt} \right) \end{cases}$$

These equations assume initial conditions of $[A_0] = 1$ and $[A_1] = [A_2] = [A_3] = 0$, at $t = 0$.

The form of each equation fits with the predicted behavior of each chemical species. The first equation indicates that the starting material, A_0 , undergoes exponential decay as the reaction progresses; this is expected, since no reaction replenishes its concentration. The second and third equations, which describe the intermediate products, A_1 and A_2 , each contain a linear term and a negative exponential term. Since the linear term increases faster initially, the equations are expected to rise initially. This initial increase, however, is counteracted by the negative exponent, which approaches zero as time increases. The balance of these two terms produces an equation which initially rises to a maximum value and then decreases to approach zero; both $[A_1](t)$ and $[A_2](t)$ possess discrete maxima. These functions fit the expected behavior of A_1 and A_2 , which are intermediate products that are consumed by further reactions. In contrast, A_3 is the final product of the series of reactions and, as such, is expected to accumulate to a finite concentration as the reaction progresses. This is exactly the behavior of $[A_3](t)$. It is important to note that this limit is equal to the initial concentration of the starting material, A_0 .

While these particular results are useful, they do not predict the behavior of higher order sequential reactions consisting of more than three reactions. The results of the above analysis, however, can be generalized for any chemical species. The remainder of this discussion will now address these generalized results.

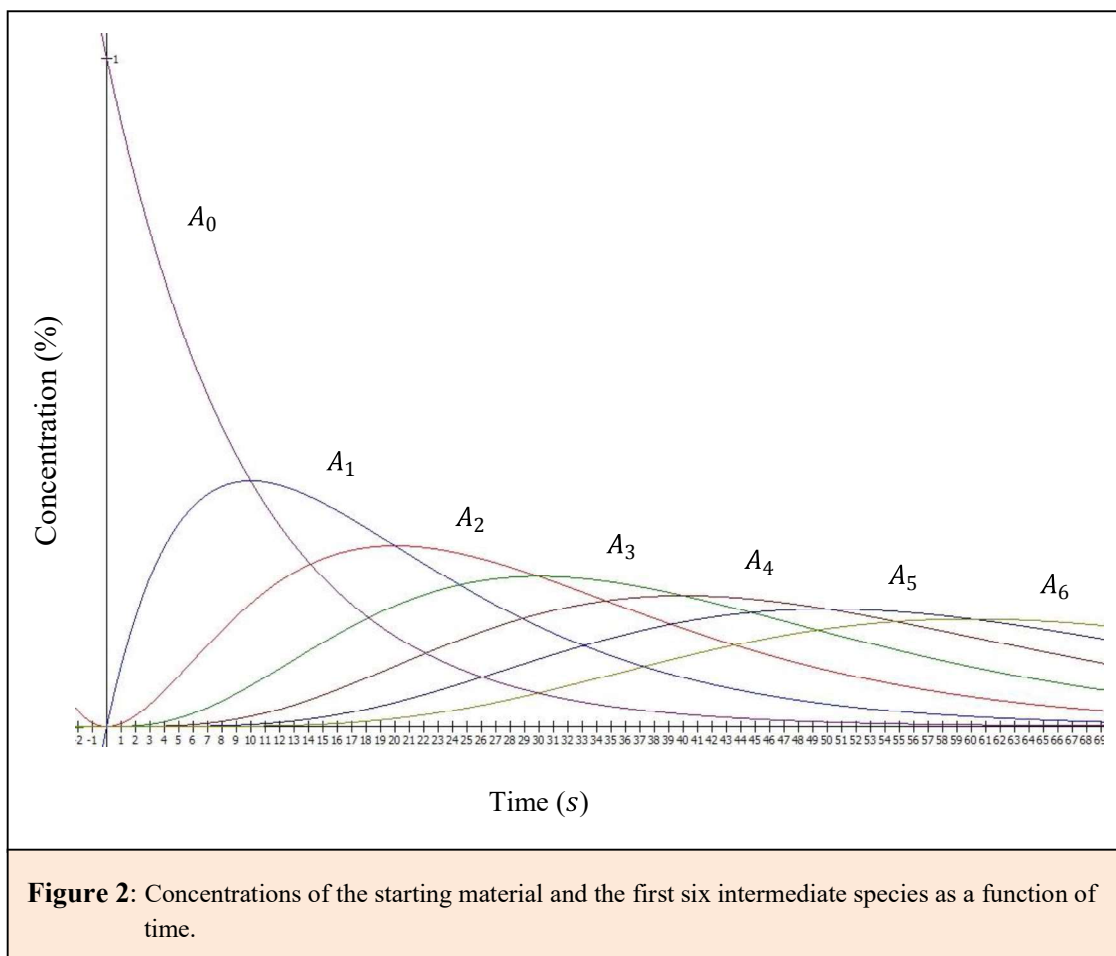
The results for the intermediate products A_1 and A_2 suggest a pattern for A_n . The fact that each successive rate law incorporates the solution of the previous rate law motivates expression

$$[A_n](t) = \frac{k^n t^n}{n! e^{kt}} \quad (26)$$

which is the result of n iterations of first-order differential equations. Note that this general form also applies to the starting material, A_0 , which is the special case $n = 0$.

As this result indicates, the behavior of all intermediate species is similar (excluding the A_0 species, which exhibits only exponential decay). Their concentration increases to a maxima and then decreases, approaching zero. Moreover, since the factorial term increases faster than the exponential time term, the maxima of each successive intermediate will occur later. This is an expected result and it reinforces the behavior of the sequential reactions. Interestingly, equation (26) also indicates that the maximum concentration of each successive intermediate species will decrease. Thus the concentration curves tend to flatten as the reaction progresses.

The flattening of concentration curves can be conceptualized as an increase in the entropy of the system, whereby the initially high concentration of starting material degenerates into a mixture of various intermediates at low individual concentrations. As the reaction progresses, the “impulse” of the highly concentrated starting material is muffled like a damped wave. This phenomenon is illustrated in Figure 2.



Since the concentration curves of the intermediate products possess discrete maxima, they are amenable to derivative analysis. When the derivative of the generalized concentration curve is equated to zero,

$$\frac{d[A_n]}{dt} = \left(\frac{1}{e^{kt}}\right) (t^{n-1}) \left(\frac{k^n}{(n-1)!} - \frac{k^{n+1}t}{n!}\right). \quad (27)$$

According to (27), $\frac{d[A_n]}{dt} = 0$ when $t = 0$ and $\frac{d[A_n]}{dt} = \frac{n}{k}$ as $t \rightarrow \infty$.

The first two results are unsurprising, since concentration is at a minimum when $t = 0$. By definition, concentration approaches zero as $t \rightarrow \infty$. The third solution, however, is very

useful, as it predicts the time at which concentration reaches its maximum. As expected, t_{max} is larger for later products; the further along a chemical species is in the order of a sequential reaction, the later it occurs during the progress of the reactions.

Of course, these generalized results do not predict the behavior of the final product. While the concentration curve of the final product is more difficult to generalize than that of the intermediate species, the iterative integration by parts employed to solve the rate law for $[A_{n+1}](t)$ suggest a pattern. In this result, the successive rounds of integration by parts are expressed as the series:

$$[A_{n+1}](t) = 1 - \sum_{p=0}^n \frac{k^p t^p}{p! e^{kt}}. \quad (28)$$

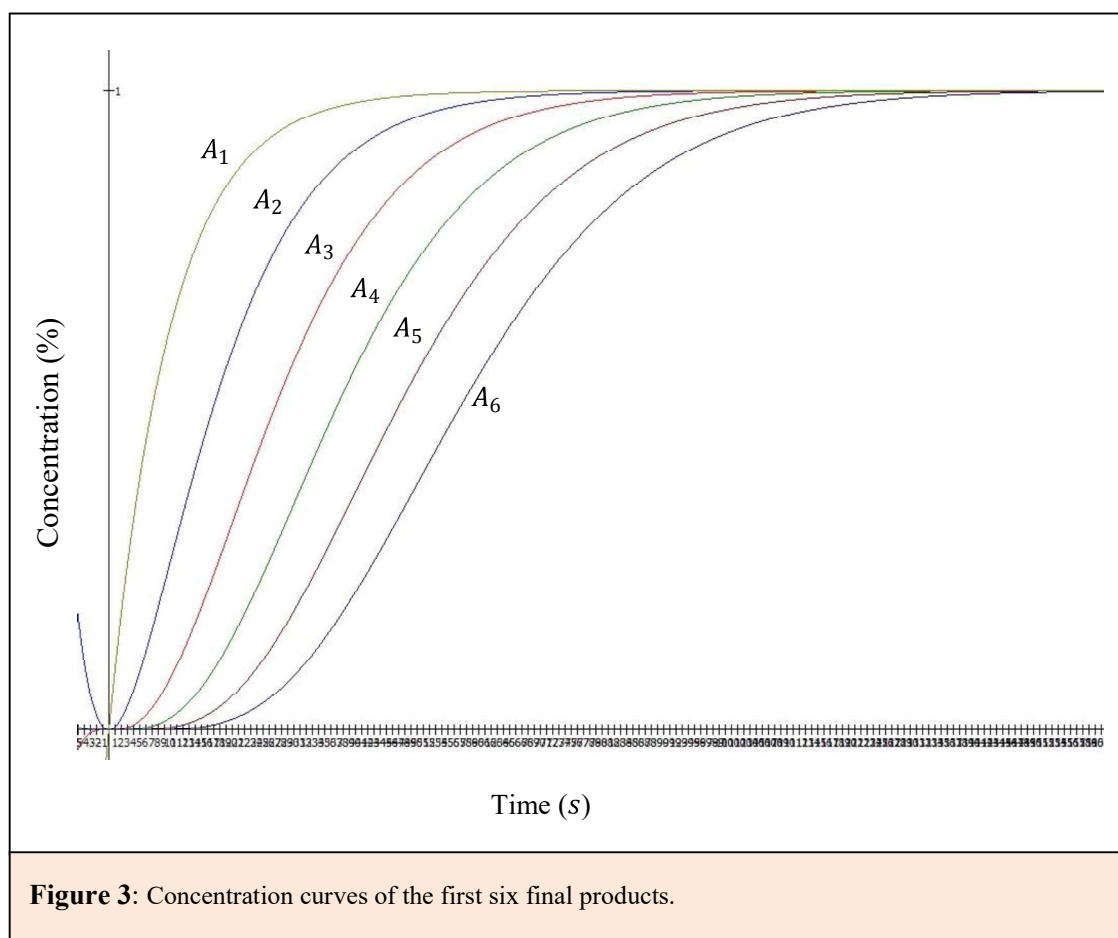
The finite sum increases with n , which causes the concentration curve to flatten. Thus, the curve approaches its limit slower at higher values of n . This is not surprising, since $[A_{n+1}](t)$ depends on $[A_n](t)$ and, as already demonstrated, $[A_n](t)$ flattens as n increases (Figure 3).

CONCLUSION AND RECOMMENDATIONS

The chemical species which participate in sequential reactions belong to either of two classes: intermediate species or the final product. Intermediate species are produced and then consumed in the course of the reactions. Thus, the concentration of an intermediate species will rise to a maximum and then fall, approaching zero. The starting material is the only exception to this rule; by definition, its maximum occurs at $t = 0$. The concentration curve for any intermediate species, A_n , is described by (26).

One consequence of this expression is that higher order concentration curves tend to flatten, with lower and later maxima. This is an important consideration for the design of batch reactions. If a high-order intermediate species is desired, yield will be less than for a low-order intermediate species. Moreover, the broadening of high-order concentration curves ensures that the composition of late reaction mixtures will be more complex than that of earlier reaction mixtures, which complicates purification. Thus, the production of high-order intermediates present two challenges in batch reactions, low yield and increased difficulty in purification.

The time at which any intermediate species reaches its maximum concentration was found by analysis of the derivative of the above function and is found to be $t_{max} = \frac{n}{k}$.



The value t_{max} can be used to determine the reaction time required to optimize the yield of a desired chemical species in a batch reaction. Intuitively, t_{max} is greater for higher order species.

The concentration curve for the final product differs in behavior from that of the intermediate species. Since the final product accumulates as the reaction progresses, its concentration rises continuously and approaches a finite limit. In contrast to the intermediate species, the final product possesses no discrete maximum. The concentration curve for any final product, A_{n+1} , is expressed in (28).

As evident from the expression, the speed at which the final product approaches its limit depends on the number of reactions intermediates before it. The final products of low order sequential reactions accumulate quickly, while those of high order sequential reactions accumulate slowly. Even though a discrete t_{max} is not appropriate to A_{n+1} , the concentration curve still provides a useful guide to reaction progress. If the final product is desired from a batch reactor, then analysis of the graph of $[A_{n+1}](t)$ would provide guidelines for how long the reaction should be run to approach completion.

The above generalized results can be employed to model the progression of any finite series of sequential reactions in a batch reactor. This analysis, however, relies on certain assumptions, which limits the equations' utility. First, the results assume that the reactions of a series do not generate by-products. While some reactions follow this assumption, many do not. The chlorination of methane, for instance, generates hydrochloric acid with each chlorination reaction. Such by-products will build-up over the course of the process. The increasing concentration of by-product will tend to slow later reactions. The second assumption made is that each reaction in a series possesses an identical rate constant. This is not true of any series of

sequential reactions; thus, the concentration curves of actual sequential reactions will differ accordingly from the standardized curves reported for these results.

NOMENCLATURE

A_n	The chemical species A_n
$[A_n]$	The concentration of the chemical species A_n
$[A_n](t)$	The concentration of the chemical species A_n as a function of time
k	pseudo-rate law constant ($k = 0.1$)
t	Time
t_{max}	Time at which $[A_n]$ is maximal
