Mathematical Model of Catalytic Chemical Reactor

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Abstract

This study concerns mathematical modeling, analyzing and simulation aspect of a catalytic reaction kinetics. The paper has the form a feasibility study, and is not referring to actual industrial chemical reactors. The catalytic reaction equations are modeled in the form of non-linear ordinary differential equations. These equations are composed of kinetic parameters such as kinetic rate constants, concentration of substances and the initial concentrations. The modeling consists of establishing the model and discuss variations and simplifications by applying generic modeling tools like scaling, perturbation analysis and numerical experiments. Numerical simulations help corroborate theoretical results. The analysis here considers a revised model with permanent poisoning of the catalyst with no reversibility. To show that the numerical solution and the perturbation solution give approximate or identical results and to observe the actual functional behavior over the interval of interest, the equations of solutions are implemented, evaluated, and plotted using Matlab™. The perturbation solutions are compared to numerical solutions obtained by the Matlab™ ODE solver ODE45.

Key Words: Chemical reactor, Modeling, Scaling, Regular and Singular perturbation, Numerical experiments.

Introduction

Chemical engineering is a rich source of mathematical modeling problems, and the aim of this paper is to analyze the catalytic chemical reactor. A chemical reactor is, stated in simple terms, a chemical experiment carried out on an industrial scale [5].

Catalytic reactors are used a lot familiar examples are the catalytic converters for automobile exhaust treatment. A catalytic converter is an exhaust emission control device which converts toxic chemicals in the exhaust of an internal combustion engine into less noxious substances.

Catalyst poisoning occurs when the catalytic converter is exposed to exhaust containing substances that coat the working surfaces, thus encapsulating the catalyst so that it cannot contact and treat the exhaust. It is well known that leaded fuel on a modern car will immediately spoil the catalyst. In fact, this deactivation or poisoning of the catalyst over time is a serious problem for catalytic reactors. If we want a continuous operation, it is necessary to replace poisoned catalyst continuously with cleaned, re-activated catalyst [5].

The idea behind the paper comes from Alternative analysis of the Michaelis-Menten equations [2], Kiros Gebrearegawi [3] master thesis entitled in Mathematical Model of a Catalytic Counter-Current Chemical Reactor, and a Mathematical Modeling project at NTNU [5]. Krogstad, E. H. et al (2011) [2] developed the alternative analysis of the Michaelis-Menten equations. They were analyzing the model by applying generic modeling tools like simplification, scaling, perturbation analysis and numerical experiments. The alternative analysis contains regular as well as singular perturbation. The perturbation analysis of the alternative analysis model, which involves several different reaction time scales, should be based on the ratio between short and long time scales. Kiros Gebrearegawi (2011) [3] developed the modeling aspects of a counter-current catalytic moving bed chemical reactor, based on a study in the book Mathematical Modeling Techniques by R. Aris (1994)[1]. The modeling aspects include catalytic reaction kinetics, transport in the reactor and conservation laws. Kiros analyzed the model by using different techniques such as simplification, scaling, perturbation analysis and numerical analysis.

The main objective of the present paper is to carry out a mathematical model development and analysis of kinetic reactions in the case of permanent poisoning of catalyst and identify the important dimensionless parameters. The paper has the form a feasibility study, and is not referring to actual industrial chemical reactor. Some ordinary differential equations in mathematics do not possess a simple analytic solution. Such type of equations require approximate solutions by different methods available in applied mathematics and perturbation methods is a huge and important family of such methods. One of the aims of this study is therefore to investigate a problem and find approximate solutions by perturbation methods.

Mathematical Model Development of the Catalytic Reaction Equations

We assume the chemical reactor consists of a long cylinder of length L and volume V containing fluid and catalyst, and a mechanism that transports the catalyst through the reactor. The catalyst consists of granulated, solid material. At the same time, a fluid, containing the substrate A to be converted, moves through the cylinder in the opposite direction. Since the cylinder contains the catalyst in the form of a solid granulate, only a volume fraction $\emptyset$ of open space will be available for the fluid. We also assume that the catalyst and the solution are entered and removed continuously, and that the cylinder is always completely filled up. The substrate A interacts with the catalyst (K) by sticking to its surface, where a series of chemical reactions, called the catalytic pathway, takes place. During this process, the additive A is changed to a variant B which may disintegrate back to A, remain stuck to the surface of catalyst(K), or converted to a product P, which immediately dissolves into the fluid. The direct reaction $A \rightarrow P$ is typically situation that is hampered by an energy barrier, and the catalyst's role is to lower the barrier and hence ease the conversion. When some of B remains stuck on the surface of the catalyst (K), less catalyst surface area becomes available for the reaction, and the efficiency of the catalyst decreases. This is called a poisoning of the catalyst. As shown in figure1, the product P is dissolved in the fluid and follows the fluid out from the reactor, where a separator may take P out and re-inject A that has not been converted.
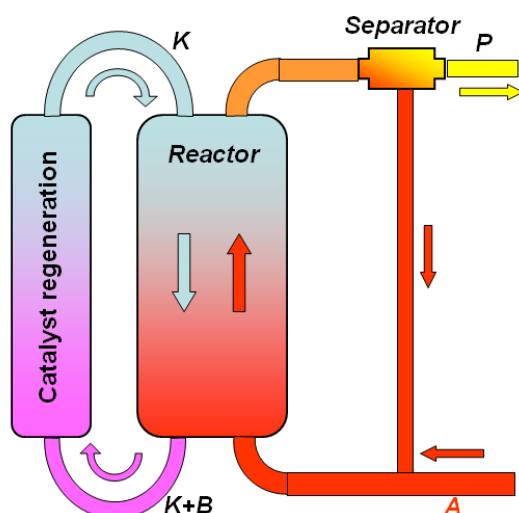

Figure 1: Sketch of the reactor concept.

We now consider the situation where the substrate A is changed to B, which is either changed back to A or converted to a product P. In this case B may temporary stick on the surface of the catalyst, and we call this a temporary poisoning. The schematic of catalytic equation with temporary poisoning may be represented as follow [5]:

$$A \underset{k_d}{\overset{k_a}{\underset{\leftarrow}{\rightarrow}}} B \overset{k_r}{\rightarrow} P \tag{1}$$

In the case of permanent nature of poisoning of catalyst we shall also assume that some reversibility in the reaction $A \rightarrow B$, but no reversibility in the transformation from B to the product P or C, where C is staying on the catalyst permanently. From equation(1), similarly to B, the material C is also attached to the catalyst, but contrary to B, which over time decays to the product P or back to substrate A, the C version is inert and stays on the catalyst permanently. This is therefore the most serious source for the contamination of the catalyst. The catalytic equation with permanent poisoning may be summarized by the following chemical reaction equation [3]:

$$A \underset{k_d}{\overset{k_a}{\underset{\leftarrow}{\rightarrow}}} B \begin{cases} \overset{k_r}{\rightarrow} P, \\ \overset{k_c}{\rightarrow} C. \end{cases} \tag{2}$$

Here k_a, k_d, k_r and k_c are dimensional reaction rate constants whose sizes will greatly influence the performance of the reaction and that must be determined empirically. The double arrows indicate the reactions taking place in both directions, whereas the single arrow only to the forward direction.

If we assume there is no reversibility from B to A, chemical reaction equation (2) is modified to

$$A \overset{k_a}{\rightarrow} B \begin{cases} \overset{k_r}{\rightarrow} P, \\ \overset{k_c}{\rightarrow} C. \end{cases} \tag{3}$$

The overall mechanism is a conversion of the substrate A, via catalyst(K), into a product P. We shall start the modeling by considering only the catalytic reaction, thus neglecting the motion through the reactor. Consider a closed reactor chamber filled with catalyst and fluid. At the start of the reaction, the catalyst is clean, and the fluid contains the substrate A. We also assume that no substrate is entered and no product removed after the reaction has started. The concentration of A is denoted $a^*(t^*)$, and the concentration of B within the reactor $b^*(t^*)$, etc.

When it comes to adsorption, the amount sticking to the catalyst's surface is proportional to the concentrations a^* and $(1 - \frac{b^*}{B_M})$, where B_M is maximum possible concentration of b^*. The product P is immediately dissolved and we assume that the product is staying in the fluid without taking further part in the reaction . We shall assume that no heat exchange is involved in the reactions, and an additional heat energy balance, which is usually needed, will not be required here. Following this description, from equation (1) the reaction equations become

$$\emptyset \frac{da^*}{dt^*} = -k_a \emptyset a^* \left(1 - \frac{(1-\emptyset)b^*}{B_M}\right) + k_d(1-\emptyset)b^*, \tag{4}$$

$$(1-\emptyset)\frac{db^*}{dt^*} = k_a \emptyset a^* \left(1 - \frac{(1-\emptyset)b^*}{B_M}\right) - k_d(1-\emptyset)b^* - k_r(1-\emptyset)b^*, \tag{5}$$

$$\emptyset \frac{dp^*}{dt^*} = k_r(1-\emptyset)b^*. \tag{6}$$

It is possible to reduce a^*, b^*, p^* and B_M so as to include $\emptyset$ and $(1-\emptyset)$, and reduce the above equations to the more convenient form

$$\frac{da^*}{dt^*} = -k_a a^* \left(1 - \frac{b^*}{B_M}\right) + k_d b^*, \tag{7}$$

$$\frac{db^*}{dt^*} = k_a a^* \left(1 - \frac{b^*}{B_M}\right) - k_d b^* - k_r b^*, \tag{8}$$

$$\frac{dp^*}{dt^*} = k_r b^*. \tag{9}$$

The analysis of these equations is discussed in [2].

From equation(2), the reaction equations for permanent poisoning are modified as

$$\frac{da^*}{dt^*} = -k_a a^* \left(1 - \frac{b^* + c^*}{B_M}\right) + k_d b^*, \tag{10}$$

$$\frac{db^*}{dt^*} = k_a a^* \left(1 - \frac{b^* + c^*}{B_M}\right) - k_d b^* - k_r b^* - k_c b^*, \tag{11}$$

$$\frac{dp^*}{dt^*} = k_r b^*, \tag{12}$$

$$\frac{dc^*}{dt^*} = k_c b^*. \tag{13}$$

The detail analysis of these equations has been discussed in [3].

In the irreversible case in equation(3), the reaction equations further modified to

$$\frac{da^*}{dt^*} = -k_a a^* \left(1 - \frac{b^* + c^*}{B_M}\right), \tag{14}$$

$$\frac{db^*}{dt^*} = k_a a^* \left(1 - \frac{b^* + c^*}{B_M}\right) - k_r b^* - k_c b^*, \tag{15}$$

$$\frac{dp^*}{dt^*} = k_r b^*, \tag{16}$$

$$\frac{dc^*}{dt^*} = k_c b^*. \tag{17}$$

The analysis of these equations is discussed in this paper.

Analysis of the Reaction Equations

In this section, we focus on the mathematical analysis of the reaction equations, and not on how to build models of catalytic reaction equations. Here, by considering the system of equations, which represents a model for reaction of equations, it is possible to analyze those equations using a number of mathematical techniques. Analysis of the reaction equations below are dealt with a closed reactor.

We now consider the differential equations $(14) - (17)$, in the irreversible case in equation (3), with the initial conditions

$$a^*(0) = a_I, \ b^*(0) = 0, \ p^*(0) = 0, \ c^*(0) = 0. \tag{18}$$

By adding all equations $(14) - (17)$, we obtain

$$\frac{d}{dt^*}(a^* + b^* + c^* + p^*) = 0 \tag{19}$$

This equation can be integrated directly to yield

$$a^*(t^*) + b^*(t^*) + c^*(t^*) + p^*(t^*) = a_I, \tag{20}$$

in which the initial conditions have been imposed in order to determine the constant of integration. From equation (16) and (17) it follows that c^* and p^* will always increase, whereas equation (20) then implies that $a^* + b^*$ always decreases. Starting, e.g. with $p^*(0) = 0$ and $c^*(0) = 0$, equation (16) and (17) give immediately

$$p^*(t^*) = \frac{k_r}{k_c} c^*(t^*) \tag{21}$$

Scaling

The aim of scaling in [8] is to reduce the number of parameters in a model. So, a prerequisite of the technique of scaling is knowledge of the equations governing the system, because scaling can only be performed when the governing equations are known. The detail discussion of scaling which are essential to our discussion has been discussed in [4] and [7].

The above system has time scales

$$T_a = \frac{1}{k_a}, T_r = \frac{1}{k_r}, T_c = \frac{1}{k_c}, \tag{22}$$

leading to two dimensionless ratios

$$\varepsilon = \frac{k_r}{k_a} = \frac{T_a}{T_r}, \qquad \delta = \frac{T_r}{T_c}. \tag{23}$$

In addition, we define as above

$$k = \frac{B_M}{a_I} \tag{24}$$

For an efficient process, it is reasonable to consider $T_a \ll T_r \leq T_c$ and hence, as above, ε becomes a small parameter.

Now applying the (initial phase or inner) scaling

$$a^* = a_I a, \ b^* = B_M b, \ p^* = a_I p, \ c^* = B_M c, \ t^* = T_a \tau, \tag{25}$$

the dimensionless form of the equations $(14) - (17)$ becomes

$$\frac{da}{d\tau} = -a\big(1 - (b + c)\big),$$

$$k\frac{db}{d\tau} = a\big(1 - (b + c)\big) - k\varepsilon b - k\varepsilon\delta b,$$

$$\frac{dp}{d\tau} = k\varepsilon b,$$

$$\frac{dc}{d\tau} = \varepsilon\delta b.$$

Equation (20) takes the dimensionless form

$$a(\tau) + kb(\tau) + \frac{k}{\delta}c(\tau) + kc(\tau) = a(0) + kb(0) + \frac{k}{\delta}c(0) + kc(0),$$

so that with

$$a(0) = 1, b(0) = 0, c(0) = 0, p(0) = 0,$$

we obtain

$$a + kb + \frac{k}{\delta}c + kc = 1. \tag{26}$$

We shall apply these initial conditions below. From equation (26), it follows that

$$b \leq \min\left(1, \quad \frac{1}{k}\right), \qquad c \leq \min\left(1, \quad \frac{\delta}{k(1+\delta)}\right), \ p = \frac{k}{\delta}c \leq \frac{1}{1+\delta}.$$

Since $p = \frac{k}{\delta}c$, we may just consider the 3-dimensional system

$$\frac{da}{d\tau} = -a\big(1 - (b + c)\big), \tag{27}$$

$$k\frac{db}{d\tau} = a\big(1 - (b + c)\big) - k\varepsilon b - k\varepsilon\delta b, \tag{28}$$

$$k\frac{dc}{d\tau} = k\varepsilon\delta b. \tag{29}$$

For small amount of A, we would expect the asymptotic state to be

$$a(\infty) = 0, \qquad b(\infty) = 0,$$

and hence, from equation (26),

$$c(\infty) = \frac{\delta}{k(1 + \delta)}, \qquad p(\infty) = \frac{1}{(1 + \delta)}.$$

On the other hand, if the initial amount of A is large, the catalyst will be saturated with C along before all A has been converted, that is,

$$c(\infty) = 1, \qquad b(\infty) = 0,$$

leading to

$$a(\infty) = 1 - \frac{k}{\delta} - k, \qquad p(\infty) = \frac{k}{\delta},$$

(assuming $1 - \frac{k}{\delta} - k \geq 0$).

Although c looks as a natural candidate to eliminate b. From equation(26), we then obtain

$$b = \frac{1}{k}\left(1 - a - ck - c\frac{k}{\delta}\right) = \frac{1 - a}{k} - c\left(1 + \frac{1}{\delta}\right), \tag{30}$$

leading to the system

$$\frac{da}{d\tau} = -a\left(1 - \frac{1}{k}(1 - a) + \frac{c}{\delta}\right), \tag{31}$$

$$\frac{dc}{d\tau} = \varepsilon\delta\left(\frac{1 - a}{k} - c\left(1 + \frac{1}{\delta}\right)\right), \tag{32}$$

With the initial conditions $a(0) = 1$ and $c(0) = 0$. For brevity, we only consider equations (31) and (32) in this section. Stationary points occurs, as already observed above, for

$$a = 0, \qquad c = \frac{\delta}{k(1 + \delta)},$$

or

$$a = 1 - k\frac{1 + \delta}{\delta}, \qquad c = 1.$$

As above, the solution for $a \neq 0$ requires that $k\frac{1+\delta}{\delta} < 1$.

In general, since $c(\tau)$ is strictly increasing and bounded, one asymptotic limit point when $\tau \to \infty$ will necessary exist. Moreover, it is clear from the equations that the corresponding

limit for $b(\tau)$ has to be 0. In summary, it follows from equation (26) that the limit state will either be caused by $c(\tau) \to 1$, or $a(\tau) \to 0$.

Perturbation Analysis

In [7] once a problem has been correctly scaled, one can in principle derive arbitrarily accurate approximations by systematic exploitation, via perturbation theory, of the presence in the equations of a small parameter. Singular perturbation is discussed in the classic book [4]. A singular perturbation case study of the famous Michaelis-Menten enzyme reaction in [6], different to the standard one in [4], is given in [2]. Singular perturbation is often identified by a small parameter in front of the highest derivative.

With the present "inner" time scale and ε as the small parameter, equations (31) and (32) is a regular perturbation problem with leading order system

$$\frac{dA_0}{d\tau} = -A_0 \left(1 - \frac{1}{k}(1 - A_0) + \frac{C_0}{\delta}\right), \tag{33}$$

$$\frac{dC_0}{d\tau} = 0. \tag{34}$$

For $A_0(0) = 1$ and $C_0(0) = 0$, the solution for C_0 is trivial, $C_0(\tau) = 0$, but the solution for A_0 have different forms and different asymptotic limits for $\tau \to \infty$ according to the size of k:

$$A_0(\tau) = \begin{cases} \frac{1-k}{1-k\exp(\tau(k-1)/k)}, & k < 1 \\ \frac{1}{1+\tau}, & k = 1 \\ \frac{k-1}{k\exp\left(\tau(k-1)/k\right)-1}, & 1 < k \end{cases} \tag{35}$$

(Of course, the forms for $k \neq 1$ are identical, but the sign of the exponential switches as k passes 1).

For the outer solution, we substitute $\tau = t/\varepsilon$ and obtain the singularly perturbed system

$$\varepsilon \frac{da_0}{dt} = -a_0 \left(1 - \frac{1}{k}(1 - a_0) + \frac{c_0}{\delta}\right), \tag{36}$$

$$\frac{dc_0}{dt} = \delta \left(\frac{1 - a_0}{k} - c_0 \left(1 + \frac{1}{\delta}\right)\right). \tag{37}$$

Now setting $\varepsilon = 0$, the leading order system for $a(t)$ and $a(t)$ becomes (as long as $a \neq 0$)

$$0 = \left(1 - \frac{1}{k}(1 - a_0) + \frac{c_0}{\delta}\right), \tag{38}$$

$$\frac{dc_0}{dt} = \delta\left(\frac{1 - a_0}{k} - c_0\left(1 + \frac{1}{\delta}\right)\right). \tag{39}$$

Here, the initial conditions for a and c functions are uncertain. Leaving the initial conditions unspecified, the solution for $a_0(t)$ and $c_0(t)$ are:

$$a_0(t) = 1 - k - \frac{k}{\delta}c_0(t) \tag{40}$$

$$c_0(t) = De^{-\delta t} + 1, D \text{ is a free constant} \tag{41}$$

However, since the asymptotic limit for $A_0(\tau)$ may be 0, we also need to consider the outer system for the trivial case that $a_0(t) \equiv 0$. The equation for c_0 then becomes

$$\frac{dc_0}{dt} = \delta\left(\frac{1}{k} - c_0\left(1 + \frac{1}{\delta}\right)\right), \tag{42}$$

and the general outer solution is

$$a_0(t) = 0, \tag{43}$$

$$c_0(t) = De^{-(1+\delta)t} + \frac{\delta}{k(1 + \delta)}. \tag{44}$$

Case I: Consider first $k \geq 1$, where

$$\lim_{\tau\to\infty} A_0(\tau) = \lim_{\tau\to\infty} C_0(\tau) = 0. \tag{45}$$

Clearly, the outer solution to use is now $a_0(t) \equiv 0$ with the corresponding $c_0(t)$ matching $c_0(\infty) = 0$ for $t \to \infty$. Hence, we may determine the constant D and obtain

$$a_0(t) \equiv 0, \tag{46}$$

$$c_0(t) = \frac{1 - e^{-(1+\delta)t}}{k\left(1 + \frac{1}{\delta}\right)}. \tag{47}$$

The uniform solution becomes

$$a_0{}^u(t) = A_0(t/\varepsilon) \tag{48}$$

$$c_0{}^u(t) = \frac{1 - e^{-(1+\delta)t}}{k\left(1 + \frac{1}{\delta}\right)} \tag{49}$$

Where A_0 follows from equation (35).

Case II: When $k < 1$,

$$\lim_{\tau\to\infty} A_0(\tau) = 1 - k, \qquad \lim_{\tau\to\infty} C_0(\tau) = 0. \tag{50}$$

The outer solution match for

$$a_0(t) = 1 - k + \frac{k}{\delta}\left(e^{-\delta t} - 1\right), \tag{51}$$

$$c_0(t) = 1 - e^{-\delta t}, \tag{52}$$

and the uniform solutions become

$$a_0{}^u(t) = A_0(t/\varepsilon) + \frac{k}{\delta}\left(e^{-\delta t} - 1\right), \tag{53}$$

$$c_0{}^u(t) = 1 - e^{-\delta t} \tag{54}$$

Note that the asymptotic limits for $t \to \infty$ for the full problem and the leading order outer system are identical when $\frac{k(1+\delta)}{\delta} < 1$. When $a_0(t)$ becomes 0 at t_p, we may derive the solution for the two cases $a_0 > 0$ and $a_0 = 0$.

The leading order outer system is

$$0 = \left(1 - \frac{1}{k}(1 - a_0) + \frac{c_0}{\delta}\right)$$

$$\frac{dc_0}{dt} = \delta\left(\frac{1 - a_0}{k} - c_0\left(1 + \frac{1}{\delta}\right)\right),$$

and the leading order solution matching to the inner solution for $t < t_p$ where $a_0(t) > 0$ is

$$a_0(t) = 1 - k - \frac{k}{\delta}c_0(t), \tag{55}$$

$$c_0(t) = 1 - e^{-\delta t}. \tag{56}$$

However, when $a_0(t)$ hits 0, at t_p, we need to change to the solution of

$$a_0(t) = 0,$$

$$\frac{dc_0}{dt} = \delta\left(\frac{1}{k} - c_0\left(1 + \frac{1}{\delta}\right)\right),$$

for $t > t_p$. Since the last equation is linear, it is easy to solve, and the general solution (as shown earlier) becomes

$$c_0(t) = De^{-(1+\delta)t} + \frac{\delta}{k(1 + \delta)}.$$

It has now the correct limit for $t \to \infty$ (when $\frac{\delta}{k(1+\delta)} \leq 1$ but must also match the other solution at $t = t_p$). This determines D :

$$De^{-(1+\delta)t_p} + \frac{\delta}{k(1 + \delta)} = 1 - e^{-\delta t_p}.$$

Thus,

$$D = \left(1 - e^{-\delta t_p} - \frac{\delta}{k(1 + \delta)}\right)e^{(1+\delta)t_p}.$$

We have to consider when t_p is a positive number (That is, that $a_0(t)$ is really crossing 0).

The expression is

$$t_p = -\frac{1}{\delta} \ln\left(\frac{1}{k}(k - \delta + k\delta)\right),$$

and in order for t_p to be positive, we need

$$0 < \frac{1}{k}(k - \delta + k\delta) < 1,$$

that is, $k < 1$, but

$$k\frac{1 + \delta}{\delta} > 1.$$

Then

$$D = -\frac{\delta(k - \delta + k\delta)}{(k + k\delta)} \frac{1}{\left(\frac{1}{k}(k - \delta + k\delta)\right)^{\frac{1}{\delta}(\delta+1)}}.$$

However, for $k\left(1 + \frac{1}{\delta}\right) > 1$ and $k < 1$, the leading order outer solution does not have the correct behavior for large times since it does not converge to 0.

$$a_0(t) = \begin{cases} 1 - k + \frac{k}{\delta}\left(e^{-\delta t} - 1\right), & t \le t_p \\ 0 & t_p < t. \end{cases} \tag{57}$$

$$c_0(t) = \begin{cases} \dfrac{1 - e^{-\delta t}}{\delta} & t \le t_p \\ \dfrac{1}{k(1 + \delta)} - \dfrac{\delta(k - \delta + k\delta)}{k + k\delta} \dfrac{1}{\left(\frac{1}{k}(k - \delta + k\delta)\right)^{\frac{1}{\delta}(\delta+1)}} e^{-(1+\delta)t}, & t_p < t \end{cases} \tag{58}$$

and the uniform solutions becomes

$$a_0{}^u(t) = \begin{cases} A_0(t/\varepsilon) + \dfrac{k}{\delta}\left(e^{-\delta t} - 1\right), & t \le t_p \\ 0 & t_p < t. \end{cases} \tag{59}$$

$$c_0{}^u(t) = \begin{cases} \dfrac{1 - e^{-\delta t}}{\delta} & t \le t_p \\ \dfrac{1}{k(1 + \delta)} - \dfrac{\delta(k - \delta + k\delta)}{k + k\delta} \dfrac{1}{\left(\frac{1}{k}(k - \delta + k\delta)\right)^{\frac{1}{\delta}(\delta+1)}} e^{-(1+\delta)t}, & t_p < t \end{cases} \tag{60}$$

Thus, equations (59) and (60) have been used in the numerical experiment as an approximated analytical solutions of the scaled system of differential equations.

Numerical Experiments

Numerical experiments provide a check on our reasoning. The time scale in all presentations is chosen to be the fast inner scale T_a. The solution is not very sensitive to δ when it is order of one, and all graphs here use $\delta = 1$.

The graphs display $a(t)$, $b(t)$, $p(t)$ and $c(t)$ from the numerical simulations (solid lines), the leading order uniform solutions (dashed lines). We compute $b(t)$ and $p(t)$ from

$$b(t) = \frac{1 - a(t)}{k} - \left(1 + \frac{1}{\delta}\right)c(t),$$

$$p(t) = \frac{k}{\delta}c(t).$$

For $k > 1$, b has been scaled by k (in the graphs), so that $a(t)$, $b(t)$, $p(t)$ and $c(t)$ range between 0 and 1.

In the first graphs, k is moderately larger than 1, $k = 5$, $\varepsilon = 0.05$. The inner solution $A_0(\tau)$ tends to 0. Whereas $B_0(\tau) = 1/5$ (rescaled to one in the graphs) since $C_0(\tau) = 0$, $P_0(\tau) = 0$ and the summation should be 1. All figures show the solution for $0 \le t \le 20$ to the left and $0 \le t \le 400$ to the right side.

Figure 2 shows that for $\varepsilon = 0.1$ there is very small decreases in substrate concentration, whereas c rises to close to unity. As expected, reducing ε by a factor of 10, the leading order uniform solution has a better agreement with the numerical simulation as shown in figure 3.

Figure 4 shows that for $\varepsilon = 0.01$, there are tendencies for $a_0{}^u$ to approach 0 too fast and small difference between $b_0{}^u$ and the numerical solution because of t_p. However, apart from the neighborhood of t_p the overall agreement is good for a long time. Decreasing ε by a factor of 10, we get a better simulation as shown in figure 5. Although the numerical solution has a smooth change when k passes through 1, the uniform solution does not, as illustrated in figure 4 and 8. But the long term behavior is acceptable.

Generally, for sufficiently large initial amount a_I, the conversion of A is very slow, and differ very drastically from the small initial amount a_I.
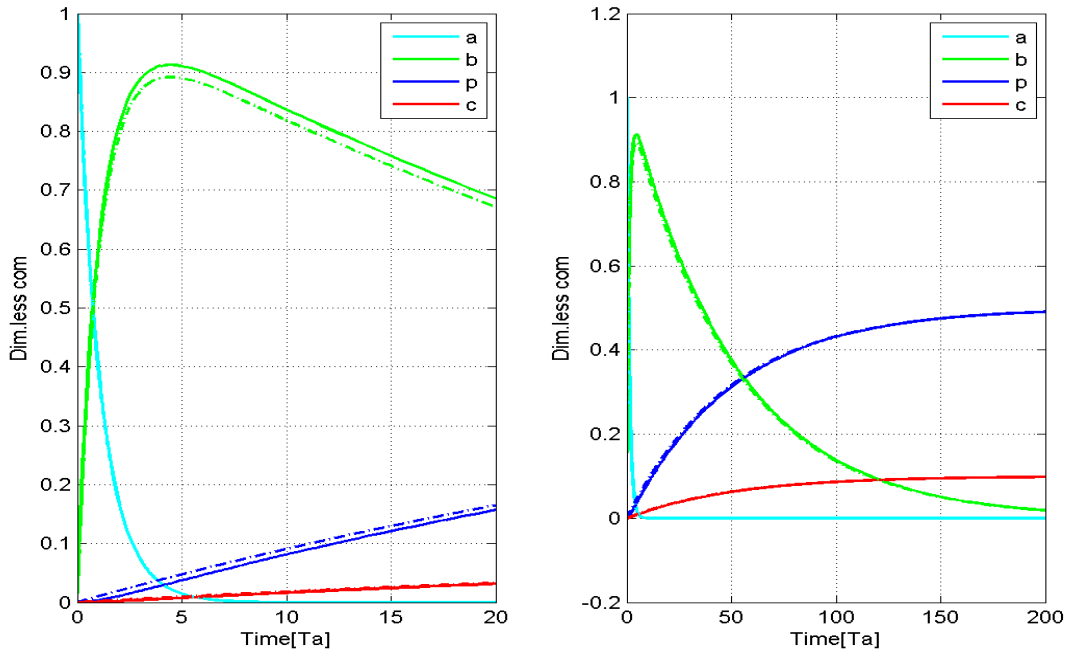
Figure 1: Numerical and leading order uniform solutions for $k = 5$, $\varepsilon = 0.05$ and $\delta = 1$.
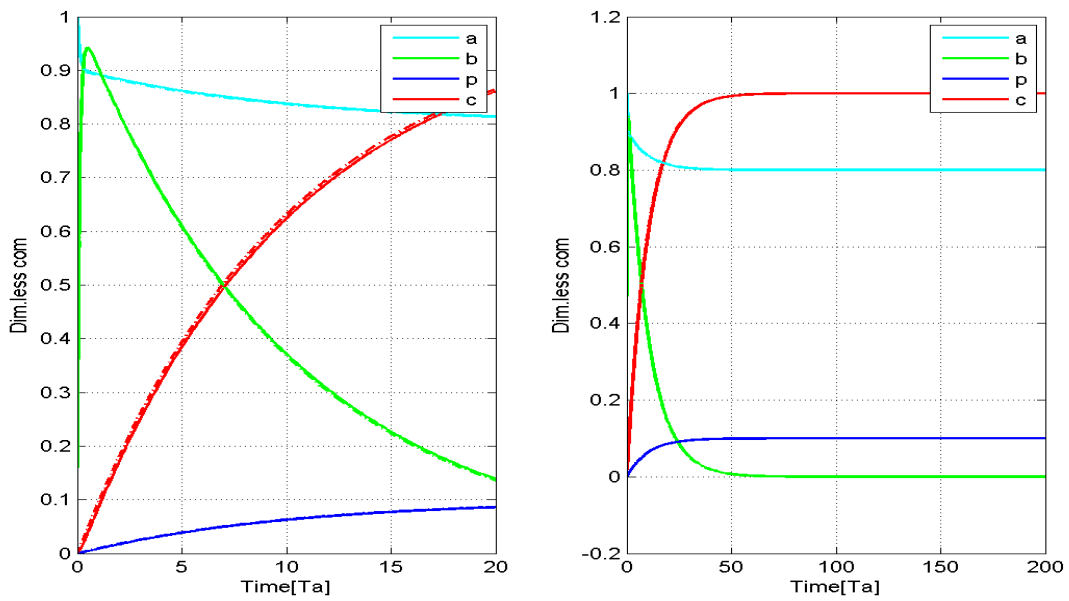

Figure 2: Numerical and leading order uniform solutions for $k = 0.1$, $\varepsilon = 0.1$ and $\delta = 1$.
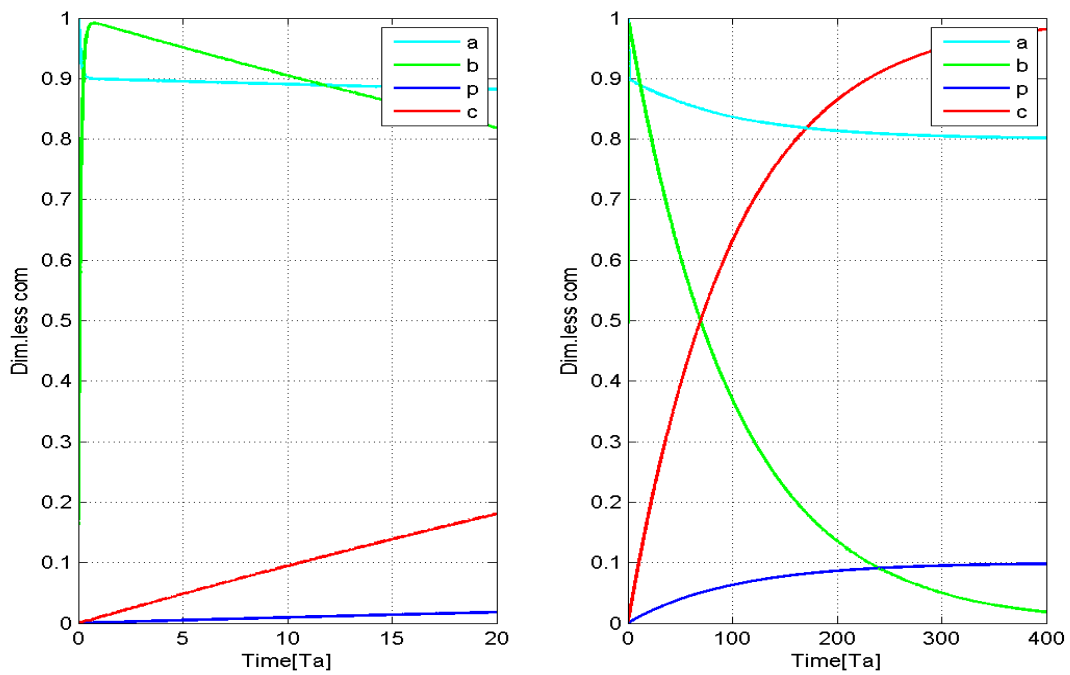
Figure 3: Numerical and leading order uniform solutions for $k = 0.1$, $\varepsilon = 0.01$ and $\delta = 1$.
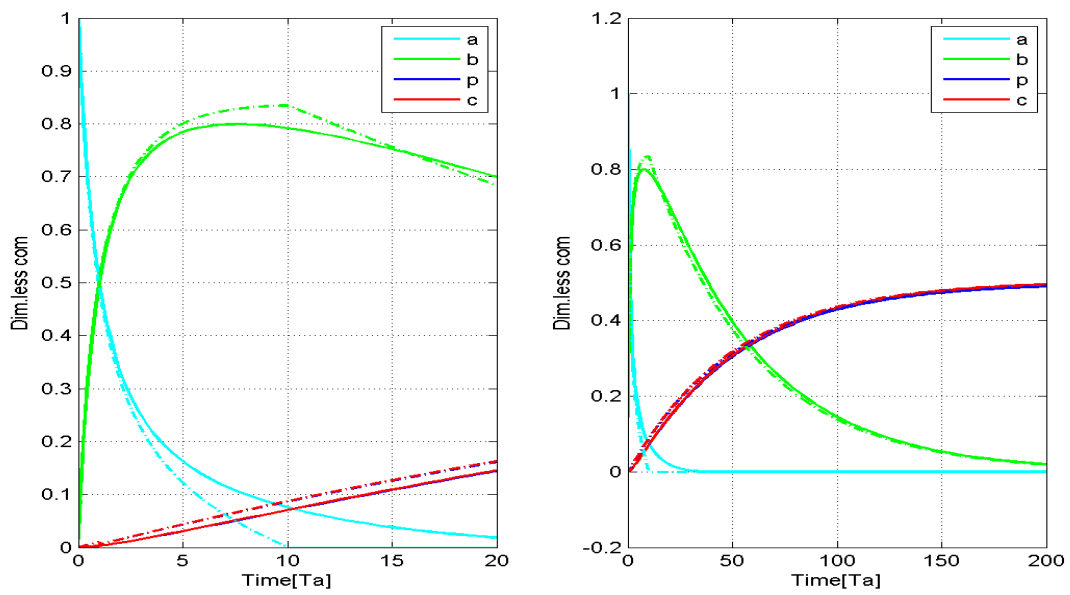

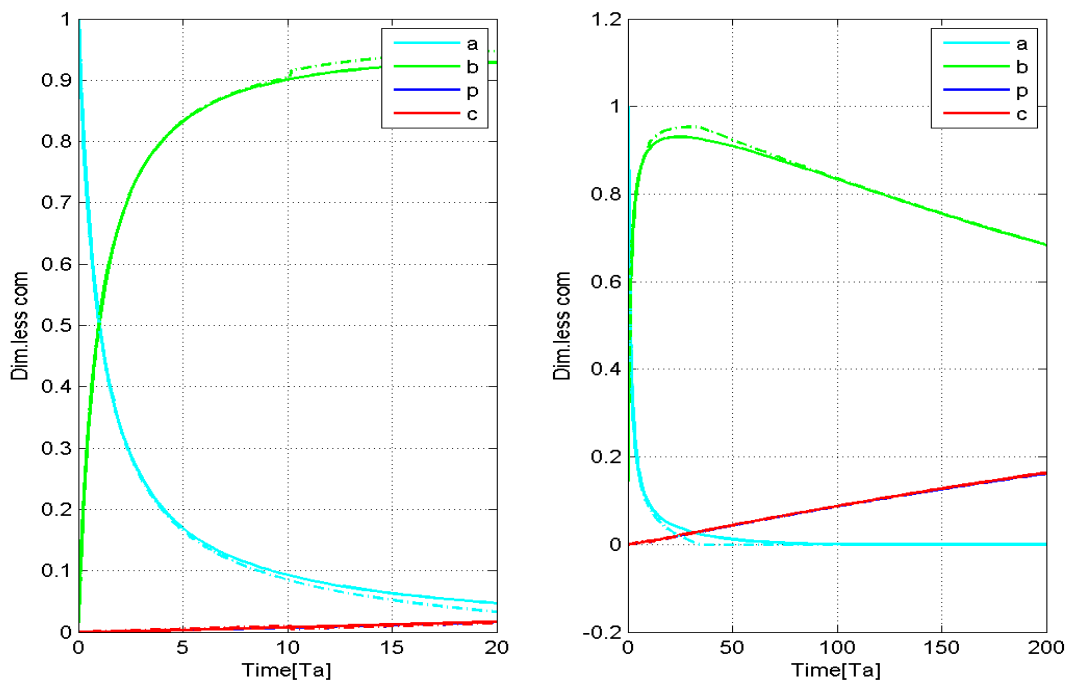Figure 4: Numerical and leading order uniform solutions for $k = 0.99$, $\varepsilon = 0.01$ and $\delta = 1$.

Figure 5: Numerical and leading order uniform solutions for $k = 0.99$, $\varepsilon = 0.001$ and $\delta = 1$.
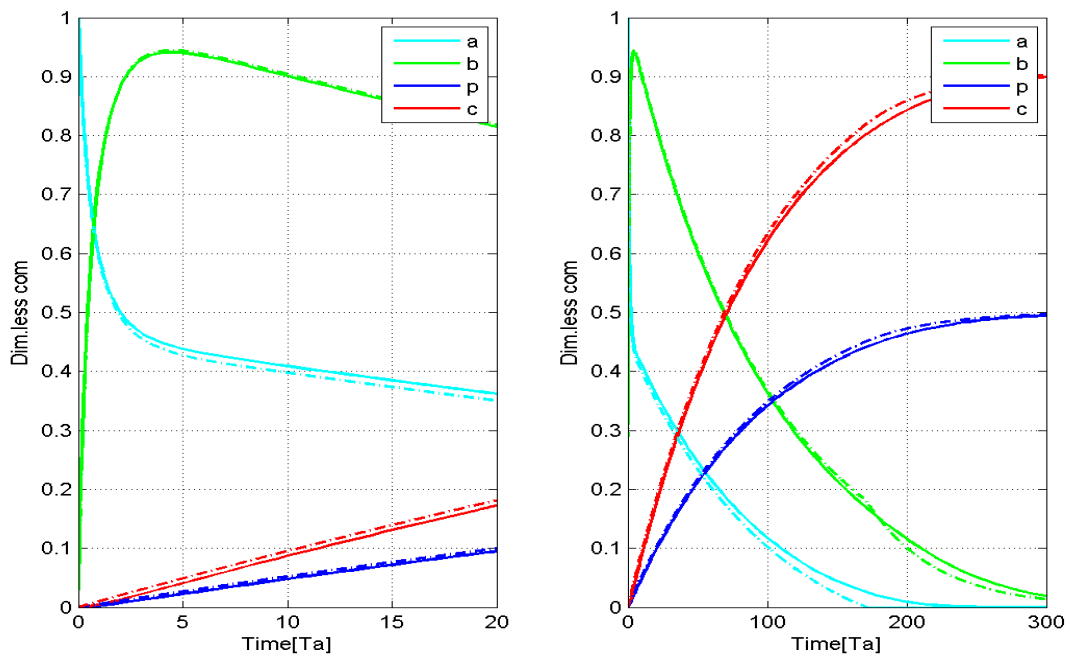

Figure 6: Numerical and leading order uniform solutions for $k = 0.55$, $\varepsilon = 0.01$ and $\delta = 1$.
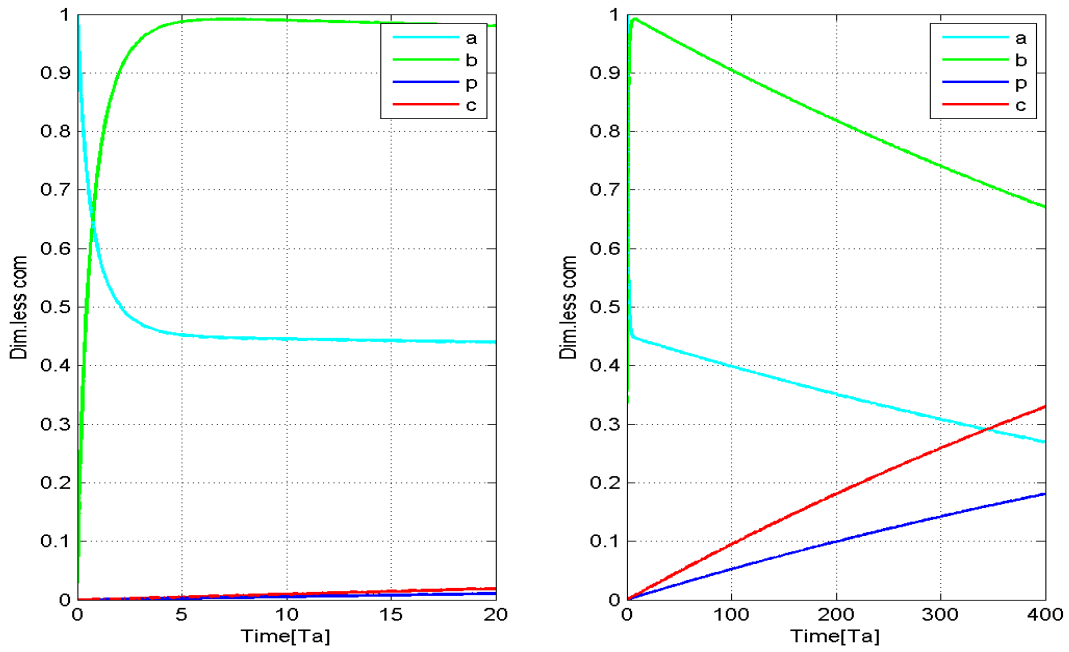
Figure 7: Numerical and leading order uniform solutions for $k = 0.55$, $\varepsilon = 0.001$ and $\delta = 1$.
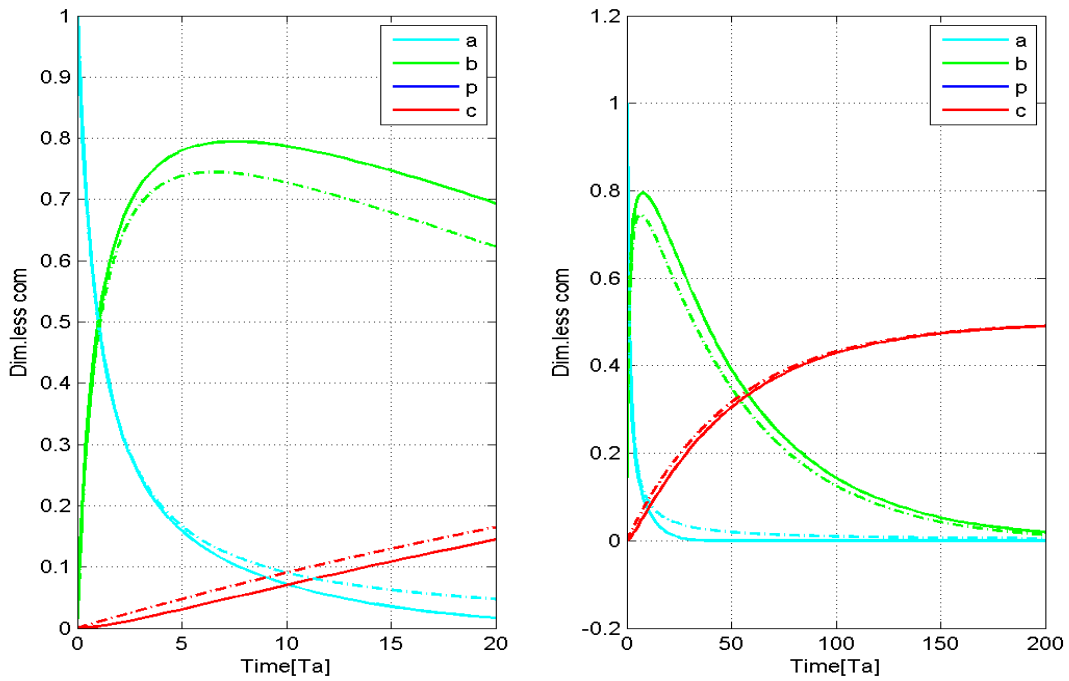

Figure 8: Numerical and leading order uniform solutions for $k = 1$, $\varepsilon = 0.01$ and $\delta = 1$.

Conclusion and Recommendation

This paper has presented mathematical models for the catalytic reaction kinetics. The basic equations have turned out to be equivalent to the well-known Michaelis-Menten catalytic enzyme-substrate reaction [6]. The study applies the alternative perturbation analysis of the Michaelis-Menten reaction based on ratios between times scales discussed in [2], leading to a completely different picture compared to the standard analysis found in the textbooks, like [4]. The analysis here considers permanent poisoning of catalyst with no reversibility, that is, no reversibility in the forward reaction from substrate to the complex forming on the surface of the catalyst, and is analyzed in a similar manner as in [2].

In this paper we have spent much time attempting to determine approximate analytical solutions of the ordinary differential equation models since the ordinary differential equations originating from the models do not admit simple analytic solutions. The system of the model shows nice example of regular as well as singular perturbation in addition to situations where the straightforward singular perturbation does not cover the terminal behavior of the solution.

The modification of the kinetic reactions with permanent poisoning of the catalyst and no reversibility in the substrate to complex has been analyzed by considering the case where the maximum concentration of the complex, B_M, is of the order of the input substrate concentration, a_I, or less. In this model, the ratio between the adsorption (to the catalyst) and reaction time scales defines the small parameter ε, and this formulation leads to a singular perturbation situation. The leading order uniform solution from the singular perturbation analysis compares very well with the numerical solution of the system up to the final stages of the reaction. However, the leading order outer solution has not correct behavior as the time tends to infinity for some values of the ratio $k = B_M/a_I$. In this case, it is necessary to introduce some modification to the outer solution in the asymptotic limit $t \to \infty$. We recommend that the result of the study should help for advanced research in the field of chemical engineering and chemistry.

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Appendix

Table 1: List of variables, parameters and their dimensions

A: Substrate to be transformed. Dimension: Mass.

B: Intermediate product which Stick to the catalysts surface. Dimension: Mass.

C: The material which stick permanently to the catalysts surface. Dimension: Mass.

P: Product. Dimension: Mass.

K: Catalyst. Dimension: Mass.

a^*: Concentration of A. Dimension: Mass per unit Volume.

b^*: Concentration of B. Dimension: Mass per unit Volume.

p^*: Concentration of P. Dimension: Mass per unit Volume.

c^*: Concentration of C. Dimension: Mass per unit Volume.

k_a: The rate constant of formation of the intermediate product B. Dimension: per time.

k_d: The rate constant of dissociation of the intermediate product B. Dimension: per time.

k_r: Reaction rate constant. Dimension: per time.

k_c: Rate constant of formation of C. Dimension: per time.

T_a: The time it takes to convert A to B. Dimension: Time.

T_r: The time it takes to convert B to P. Dimension: Time.

T_d: The time needed to reverse B to A. Dimension: Time.

T_c: The time required to convert B to C. Dimension: Time.

B_M: The maximum concentration of the complex B. Dimension: Mass per unit Volume

a_I : The input concentration of the substrate A. Dimension: Mass per unit Volume