SOME REMARKS ON THE KINETIC OF SUCCESSIVE CHEMICAL REACTIONS

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Abstract. Successive chemical reactions, often found in technological practice, in agreement with kinetic features available, can be modelled using mathematical equations or systems of differential equations. This paper presents a generalized differential model, for a given number, finite successive reactions; track parameters are changes in concentrations of compounds that generate the chemical reaction.

***Keywords*:** Successive chemical reactions, mathematical models

Introduction

The literature describes several differential models that characterize quantitative and qualitative changes occurring in successive chemical reactions [IKAI, 1973; LIN, 2004; ONDAA, 1970].

Most often studies are focused on determining the concentration of a useful product in the chain of reactions to maximize the quantity of this product [WOINAROSCHY, 1990].

General expression of two consecutive reactions is:

$$A_1 \xrightarrow{k_1} A_2 \xrightarrow{k_2} A_3$$

Where k_1, k_2 are reaction rate constants.

In this paper we generalized the problem for *n–1* successive reactions, and after the analysis of the differential model attached were found several features of the kinetics of chemical reactions [WOINAROSCHY, 1990; SCHECHTER, 1991].

The differential model for two and three consecutive chemical reactions. If two consecutive chemical reactions like those presented in the introduction. We will note with $c_{A_i}(t)$ and $k_i, k_1 < k_2 < k_3$, concentration at a fixed time t, and reaction rate constants for each component A_i, at time t. The differential model attached is [RUTHERFORD, 1989; SEGEL, 1980;]:

$$\begin{cases} (1)\ \dfrac{dc_{A_1}(t)}{dt} = -k_1 c_{A_1}(t) \\ (2)\ \dfrac{dc_{A_2}(t)}{dt} = k_1 c_{A_1}(t) - k_2 c_{A_2}(t) \\ (3)\ \dfrac{dc_{A_3}(t)}{dt} = k_2 c_{A_2}(t) \end{cases}$$

Substituting equation (3) in (2) is obtained:

$$\frac{dc_{A_2}(t)}{dt} = k_1 c_{A_1}(t) - \frac{dc_{A_3}(t)}{dt}$$

Or equivalent:

$$(4)\ k_1 c_{A_1}(t) = \frac{dc_{A_2}(t)}{dt} + \frac{dc_{A_3}(t)}{dt}$$

Substituting than equation (4) in (1) we have:

$$\frac{dc_{A_1}(t)}{dt} = -\left(\frac{dc_{A_2}(t)}{dt} + \frac{dc_{A_3}(t)}{dt}\right)$$

Or we can write that:

$$\frac{dc_{A_1}(t)}{dt} + \frac{dc_{A_2}(t)}{dt} + \frac{dc_{A_3}(t)}{dt} = 0$$

$$(5)\ \frac{d}{dt}\left(\sum_{i=1}^{3} c_{A_i}(t)\right) = 0$$

Now be three consecutive chemical reactions:

$$A_1 \xrightarrow{k_1} A_2 \xrightarrow{k_2} A_3 \xrightarrow{k_3} A_4$$

The differential model attached becomes:

$$\begin{cases} \dfrac{dc_{A_1}(t)}{dt} = -k_1 c_{A_1}(t) \\ \dfrac{dc_{A_2}(t)}{dt} = k_1 c_{A_1}(t) - k_2 c_{A_2}(t) \\ \dfrac{dc_{A_3}(t)}{dt} = k_2 c_{A_2}(t) - k_3 c_{A_3}(t) \\ \dfrac{dc_{A_4}(t)}{dt} = k_3 c_{A_3}(t) \end{cases}$$

Making similar substitutions as the previous we achieve:

$$(6)\ k_1 c_{A_1}(t) = \frac{dc_{A_2}(t)}{dt} + \frac{dc_{A_3}(t)}{dt} + \frac{dc_{A_3}(t)}{dt}$$

Finally we obtain:

$$\frac{dc_{A_1}(t)}{dt} + \frac{dc_{A_2}(t)}{dt} + \frac{dc_{A_3}(t)}{dt} + \frac{dc_{A_4}(t)}{dt} = 0$$

Or gathered:

$$(7)\quad \frac{d}{dt}\left(\sum_{i=1}^{4} c_{A_i}(t)\right)=0.$$

Generalization of the differential model for *n–1* consecutive chemical reactions. Now be *n-1* consecutive chemical reactions:

$$A_1 \xrightarrow{k_1} A_2 \xrightarrow{k_2} \ldots \xrightarrow{k_{i-1}} A_i \ldots \xrightarrow{k_{n-1}} A_n,$$

With $k_i > k_{i-1}, i = 2,\ldots,n-1$.

In this case, the differential model attached becomes:

$$(8)\quad \begin{cases} \frac{dc_{A_1}(t)}{dt} = -k_1 c_{A_1}(t) \\ \frac{dc_{A_2}(t)}{dt} = k_1 c_{A_1}(t) - k_2 c_{A_2}(t) \\ \frac{dc_{A_3}(t)}{dt} = k_2 c_{A_2}(t) - k_3 c_{A_3}(t) \\ \ldots \\ \frac{dc_{A_i}(t)}{dt} = k_{i-1} c_{A_{i-1}}(t) - k_i c_{A_i}(t) \\ \ldots \\ \frac{dc_{A_n}(t)}{dt} = k_{n-1} c_{A_{n-1}}(t) \end{cases}$$

Making similar substitutions as the previous we achieve:

$$(9)\quad k_i c_{A_i}(t) = \frac{dc_{A_{i+1}}(t)}{dt} + \frac{dc_{A_{i+2}}(t)}{dt} + \ldots + \frac{dc_{A_n}(t)}{dt}$$

Or gathered:

$$(10)\quad k_i c_{A_i}(t) = \sum_{\substack{j>i \\ j\le n}} \frac{dc_{A_j}(t)}{dt}$$

Finally we obtain:

$$\frac{dc_{A_1}(t)}{dt} + \frac{dc_{A_2}(t)}{dt} + \frac{dc_{A_3}(t)}{dt} + \ldots + \frac{dc_{A_n}(t)}{dt} = 0$$

or:

$$(11)\quad \frac{d}{dt}\left(\sum_{i=1}^{n} c_{A_i}(t)\right) = 0,$$

Equation that will be discussed below; indicating that the derivative of the sum of concentrations of all products from the consecutive reactions is canceled.

We return to equations (8) that gathered can be written:

$$(12)\quad \frac{dc_{A_i}(t)}{dt} = \begin{cases} -k_1 c_{A_1}(t),\ i=1 \\ k_{i-1} c_{A_{i-1}}(t) - k_i c_{A_i}(t),\ i \ne \{1,n\} \\ k_{n-1} c_{A_{n-1}}(t),\ i=n \end{cases}$$

We place now the problem of determining the concentration of product from the consecutive chain reaction, at a time t. This is achieved by integrating the differential equations (12). We have:

a)For $i=1 \Rightarrow \frac{dc_{A_1}(t)}{dt} = -k_1 c_{A_1}(t)$

$$\frac{dc_{A_1}(t)}{c_{A_1}(t)} = -k_1 dt \Rightarrow \ln(c_{A_1}(t)) = -k_1 t + a_0,\ a_0 \in \Re$$

$$c_{A_1}(t) = a_1 e^{-k_1 t},\ a_1 \in \Re$$

Since at the initiation process is known in quantitative terms the value of the initial product concentration, the model requires the inclusion of initial conditions, which generally are of the form:

$$(13)\quad c_{A_1}(0) = c_{A_0} > 0,$$

Representing the initial product concentration at the time $t=0$, than:

$$(14)\quad c_{A_2}(0) = c_{A_3}(0) = \ldots = c_{A_n}(0) = 0.$$

So we have $a_1 = c_{A_0}$ and:

$$(15)\quad c_{A_1}(t) = c_{A_0} e^{-k_1 t}$$

b) For $i \ne \{1,n\} \Rightarrow$

$$\frac{dc_{A_i}(t)}{dt} = k_{i-1} c_{A_{i-1}}(t) - k_i c_{A_i}(t) \text{ or}$$

$$\frac{dc_{A_i}(t)}{dt} + k_i c_{A_i}(t) = k_{i-1} c_{A_{i-1}}(t)$$

So a linear inhomogeneous differential equation.

We solves first the homogeneous equation attached and than will use Lagrange method of constants variation. Its solution is:

$$(16)\quad c_{A_i}(t) = e^{-k_i t}\left(a_i + \int k_{i-1} c_{A_{i-1}}(t) e^{k_i t} dt\right)$$

The constant $a_i \in \Re$ will be determined from the initial conditions (14).

So we have:

$$(16')\quad c_{A_2}(t) = c_{A_0} \frac{k_1 k_2}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

$$(16'')\ c_{A_i}(t)=c_{A_0}\frac{\prod_{j=1}^{i-1}k_j}{k_2-k_1}\left(\frac{e^{-k_1t}}{\prod_{j=3}^{i}(k_j-k_1)}-\frac{e^{-k_2t}}{\prod_{j=3}^{i}(k_j-k_2)}\right)$$

if $3\le i\le n-1$

c)For $i=n\Rightarrow\dfrac{dc_{A_n}(t)}{dt}=k_{n-1}c_{A_{n-1}}(t)$

From this, by direct integration we obtain:

$$(17)\ c_{A_n}(t)=\int k_{n-1}c_{A_{n-1}}(t)dt+a_n$$

Also the constant $a_n\in\Re$ is determined from initial conditions (14).

Results and discussion

If we analyze equation (11) we observe that:

$$(18)\sum_{i=1}^{n}c_{A_i}(t)=C,\ C\in\Re\ .$$

Practically, the sum of all products concentration is constant. Than, equations (15, 16 and 17) can be written:

$$(19)\,c_{A_i}(t)=\varphi(t,C),\ c\in\Re$$

That can lead to determine the value of a product concentration, at time t.

Determination of maximum of equation (19) is made after annulling the derivative of order I. So we have:

$$(20)\frac{dc_{A_i}(t)}{dt}=\frac{d}{dt}(\varphi(t,C))=0$$

In this context, a solution for equation (20), $t = t_{optim}$, for $2 < i < n$,

$$(21)\,t_{optim}=\frac{k_2}{k_1}\ln\left(\frac{k_2\prod_{j=3}^{i-1}(k_j-k_1)}{k_1\prod_{j=3}^{i-1}(k_j-k_2)}\right)$$

Leads to optimum concentration (maximum) of form:

$$(22)\,c_{A_i}(t_{optim})=\varphi(t_{optim},C)$$

Conclusion

a) Equations of type (15, 16 and 17) in which we expressed a product concentration at time t, can be a support for solving optimization problems due to the concentration of a particular product, which is reflected in the string of successive reactions. Issues of this nature can often find very practical applicability, because in such a consecutive process, the compounds in intermediate phases can be very unstable. If recovery is sought, the process must be stopped at a timely moment to minimize such potential losses due to product failing to process the previous compounds or possibly to prevent the transformation/ degradation of product. Such optimization problems can be resolved empirically, than when the technical characteristics of the process for monitoring concentrations at each time point. These assumptions are however difficult to achieve in practice, and empirical process perhaps even lead to considerable error.

b) Equations of form(18)

$$\sum_{i=1}^{n}c_{A_i}(t)=C,\ C\in\Re$$

Represent a somewhat expected result. In particular conclusion: according to this, the sum of all concentrations at a given time is constant; the equation is in accord with the general balance equation. Basically, between inputs and outputs of the successive processes, there is strict dependency relationship.

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