

Stability of solutions to a reaction diffusion system based upon chemical reaction kinetics

Jisun Lim

Department of Applied Mathematics, 526 UCB, University of Colorado at Boulder, Boulder,
CO 80309-0526, USA

E-mail: jisun@colorado.edu

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In this paper, we deal with the stability problem to some mathematical models that describe chemical reaction kinetics. One is a set of ordinary differential equations induced by one reversible chemical reaction mechanism containing three chemical species. The other is a set of reaction diffusion equations based on the same chemical reaction. We show that all solutions of the model are asymptotically stable by applying the Liapunov method. We thus find that the concentration of each species has certain limits as time proceeds.

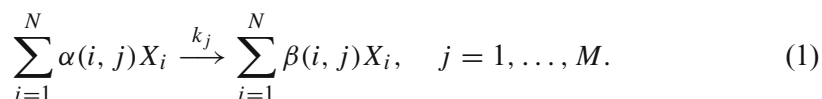
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1. Introduction

The mathematical model of chemical reaction kinetics is used in various fields, such as in physical chemistry, biochemistry, and atmospheric or aquatic chemistry. However, the stability of such mathematical models is not well studied. We here are concerned with their global stability of two certain models, which is described later, that is, their global behavior of solutions for our models as time proceeds. We briefly introduce some notions of the reaction kinetics below.

Suppose we have a complex chemical reaction containing N chemical species X_1, X_2, \dots, X_N . Assume that M reaction steps are taking place as follows:



Here the positive values of k_j are the reaction rate constants, and the non-negative integers $\alpha(i, j)$, and $\beta(i, j)$ are the stoichiometric coefficients.

The order of the j th reaction step in (1) is defined to be $\sum_{i=1}^N \alpha(i, j)$ and the order k of the reaction is obtained if $\max \sum_{i=1}^N \alpha(i, j) \leq k$ holds [7]. The j th reaction step is said to be reversible if the reverse reaction also occurs among the reaction steps; otherwise it is irreversible. The reaction (1) is said to be mass conserving if there exist positive real numbers θ_i ($i = 1, \dots, N$) for which

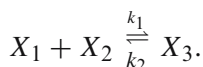
$$\sum_{i=1}^N \alpha(i, j)\theta_i = \sum_{i=1}^N \beta(i, j)\theta_i, \quad j = 1, \dots, M.$$

Let us define the concentrations of species $x_i \equiv [X_i]$ as dependent variables and time as an independent variable. The mass action type model of the reaction (1) is formulated as

$$\frac{dx_i}{dt} = \sum_{j=1}^M (\beta(i, j) - \alpha(i, j))k_j \prod_{p=1}^N x_p^{\alpha(p, j)}, \quad i = 1, \dots, N.$$

This induced kinetic differential equation of reaction is deterministic.

Now, we establish a mathematical model which explains kinetics mechanism obtained by a chemical reaction. The second-order reversible chemical reaction involving three species, X_1, X_2, X_3 , with the forward rate constant k_1 and backward rate constant k_2 is as follows.



The model is a system of the ordinary differential equations

$$\begin{aligned} \frac{du_1}{dt} &= -k_1 u_1 u_2 + k_2 u_3, \\ \frac{du_2}{dt} &= -k_1 u_1 u_2 + k_2 u_3, \\ \frac{du_3}{dt} &= k_1 u_1 u_2 - k_2 u_3 \end{aligned} \tag{2}$$

with $u_i \equiv [X_i]$. The initial conditions are given by $u_1(0) = u_{1,0}$, $u_2(0) = u_{2,0}$, and $u_3(0) = u_{3,0}$.

Letting $C_1 = u_{1,0} + u_{3,0}$, $C_2 = u_{2,0} + u_{3,0}$, we thus obtain that the solution of (2) is asymptotically stable, applying the Liapunov stability theorem [3] (p. 293).

We present the results:

Theorem 1.1. Assume that u_1 , u_2 , and u_3 are the solutions of the initial value problem (2). Let

$$C_1 = u_{1,0} + u_{3,0} \quad \text{and} \quad C_2 = u_{2,0} + u_{3,0}. \tag{3}$$

Then $u_1(x, t)$, $u_2(x, t)$, and $u_3(x, t)$ converge uniformly to $C_1 - u_{3,\infty}$, $C_2 - u_{3,\infty}$, and $u_{3,\infty}$, respectively, as $t \rightarrow \infty$.

That is,

$$\begin{aligned} \lim_{t \rightarrow \infty} u_1(t) &= C_1 - u_{3,\infty}, \\ \lim_{t \rightarrow \infty} u_2(t) &= C_2 - u_{3,\infty}, \\ \lim_{t \rightarrow \infty} u_3(t) &= u_{3,\infty}, \end{aligned} \tag{4}$$

where

$$u_{3,\infty} = \frac{C_1 + C_2 + K}{2} - \frac{\sqrt{(C_1 - C_2)^2 + K^2 + 2K(C_1 + C_2)}}{2} \tag{5}$$

with $K = k_2/k_1$.

Further, we investigate the stability of the previous model including the diffusion phenomena, which it turns out a system of parabolic partial differential equations. Define a domain $\Omega = U \times [0, \infty)$, where $U = \{x \mid 0 < x < l\}$. This model is represented by the parabolic partial differential equations

$$\begin{cases} \partial_t u_1 = \partial_{xx} u_1 - k_1 u_1 u_2 + k_2 u_3, \\ \partial_t u_2 = \partial_{xx} u_2 - k_1 u_1 u_2 + k_2 u_3, \\ \partial_t u_3 = \partial_{xx} u_3 + k_1 u_1 u_2 - k_2 u_3 \end{cases} \tag{6}$$

in Ω . Here, the diffusion is assumed to be equally diffusive; the diffusion does not depend on the individual chemical species.

The initial conditions assume the form

$$u_i(x, 0) = g_i(x) \text{ in } \Omega, \tag{7}$$

where all $g_i(x)$ ($i = 1, 2, 3$) are bounded and belong to $L^1(\Omega)$.

We consider this initial value problems (6) and (7) under three different cases, such as, periodic condition, Neumann boundary condition and an infinite domain in space. More precisely, they are expressed as in the followings: the periodic condition

$$u_i(x + 2l, t) = u_i(x, t) \text{ on } \Omega. \tag{8}$$

Neumann boundary conditions

$$\frac{\partial u_i}{\partial x} = 0 \text{ on } \Omega \tag{9}$$

and the infinite domain U , that is,

$$\Omega \equiv \mathbb{R} \times [0, \infty). \tag{10}$$

Based on the previous result for ordinary differential equation, we prove the stability of the solutions of a set of partial differential equations. The Liapunov stability theorem is also applied. We now state:

Theorem 1.2. Assume that u_1 , u_2 , and u_3 are solutions of the initial/boundary value problem for diffusion equations (6)–(8) (or (6), (7), (9) or (6), (7), (10)). Let

$$C_1 = \frac{1}{U} \int_U (g_1(x) + g_3(x))dx, \tag{11}$$

$$C_2 = \frac{1}{U} \int_U (g_2(x) + g_3(x))dx \tag{12}$$

in Ω . Let $u_{3,\infty}$ be defined previously in (5).

Then $u_1(x, t)$, $u_2(x, t)$, and $u_3(x, t)$ converge uniformly to $C_1 - u_{3,\infty}$, $C_2 - u_{3,\infty}$, and $u_{3,\infty}$, respectively, as $t \rightarrow \infty$.

In the next section, we first prove the stability of the solutions of ordinary differential equations and then prove it for partial differential equations.

2. Stability analysis of the model

Proof of Theorem 1 To prove this, it is enough to show that the solution $u_3(t) = u_{3,\infty}$ is asymptotically stable as $t \rightarrow \infty$.

Define a positive definite function $V: E \rightarrow \mathbb{R}$, E open in \mathbb{R} ,

$$V(u_3(t)) = (u_3 - u_{3,\infty})^2. \tag{13}$$

Then $V(u)$ is a Liapunov function on E . Letting $w_3 = u_{3,\infty} - u_3$,

$$\begin{aligned} \frac{dV}{dt} &= 2(u_3 - u_{3,\infty})(k_1u_1u_2 - k_2u_3) \\ &= -2w_3 [k_1(C_1 - u_3)(C_2 - u_3) - k_2u_3] \\ &= -2w_3^2 [k_1(C_1 + C_2 - u_{3,\infty} - u_3) + k_2] \\ &< 0. \end{aligned}$$

Applying the Liapunov stability theorem [3], the solution $u_3(t)$ converges uniformly to $u_{3,\infty}$ as $t \rightarrow \infty$.

Furthermore, the solution $u_1(t)$ converges uniformly to $C_1 - u_{3,\infty}$ as $t \rightarrow \infty$. Similarly, the solution $u_2(t)$ converges uniformly to $C_2 - u_{3,\infty}$ as $t \rightarrow \infty$. These complete our assertion. □

Remark. We remark that $u_{3,\infty}$ defined above is an equilibrium point of the equation $\frac{du_3}{dt} = k_1u_1u_2 - k_2u_3$. Indeed, one can easily see that (5) is a root of the (RHS = 0) equation $k_1(C_1 - u_3)(C_2 - u_3) - k_2u_3 = 0$, or $u_3^2 - [(C_1 + C_2) + k_2/k_1]u_3 + C_1C_2 = 0$ by (3).

Proof of Theorem 2 We first prove that $u_3(x, t)$ converges to $u_{3,\infty}$ as t goes to infinity.

Let $w_1 = u_1 + u_3$. Then we have the initial value problem

$$\begin{cases} \frac{\partial w_1}{\partial t} = \frac{\partial^2 w_1}{\partial x^2} & \text{in } \Omega = U \times (0, \infty), \\ w_1(x, 0) = g_1(x) + g_3(x) \equiv \tilde{g}_1(x) & \text{in } U. \end{cases} \tag{14}$$

We claim that the solution $w_1(x, t)$ converges to C_1 as $t \rightarrow \infty$. Here C_1 is determined later.

Case:

(a) Assume that $w_1(x + 2l, t) = w_1(x, t)$ in $\bar{\Omega}$.

By the method of separation of variables, we obtain the solution

$$w_1(x, t) = \sum_{n=1}^{\infty} e^{-(n\pi)^2 t / l^2} \left[a_n \cos\left(\frac{n\pi x}{l}\right) + b_n \sin\left(\frac{n\pi x}{l}\right) \right],$$

where $a_n = \frac{2}{l} \int_0^l \tilde{g}_1(x) \cos\left(\frac{n\pi x}{l}\right) dx$, $b_n = \frac{2}{l} \int_0^l \tilde{g}_1(x) \sin\left(\frac{n\pi x}{l}\right) dx$ ($n=1, 2, \dots$). Thus, $w_1(x, t) \rightarrow 0$ as $t \rightarrow \infty$.

(b) Assume that $\frac{\partial w_1}{\partial n} = 0$ on Ω .

By the method of separation of variables, it can be shown that the eigenvalues and the eigenfunctions are $\lambda_0=0, \varphi_0=1$, and $\lambda_n = \frac{n^2 \pi^2}{l^2}, \varphi_n = \cos\left(\frac{n\pi x}{l}\right)$, $n = 1, 2, \dots$, respectively. Thus, the solution is

$$w_1(x, t) = \frac{1}{2} a_0 + \sum_{n=1}^{\infty} a_n e^{-(n\pi)^2 t / l^2} \cos\left(\frac{n\pi x}{l}\right),$$

where $a_n = \frac{2}{l} \int_0^l \tilde{g}_1(x) \cos\left(\frac{n\pi x}{l}\right) dx$, ($n = 0, 1, 2, \dots$). Consequently, $w_1(x, t) \rightarrow \frac{a_0}{2}$ as $t \rightarrow \infty$.

(c) Consider $\Omega \equiv \mathbb{R} \times [0, \infty)$.

The solution $w_1(x, t)$ is given by

$$w_1(x, t) = \frac{1}{(4\pi t)^{n/2}} \int_{-\infty}^{\infty} e^{-\frac{|x-y|^2}{4t}} \tilde{g}_1(y) dy.$$

Clearly, we see that $e^{-\frac{|x-y|^2}{4t}} < 1$ on a ball with radius large enough. Since \tilde{g}_1 is integrable, we conclude that $w_1(x, t) \rightarrow 0$ as $t \rightarrow \infty$.

In each case of (a)–(c), we have shown $w_1(x, t) \rightarrow C_1$, that is, it has been shown $u_1 + u_3 \rightarrow C_1$ as $t \rightarrow \infty$. In a similar way, it is easy to see that $w_2(x, t) \rightarrow C_2$ as $t \rightarrow \infty$.

It remains to prove $u_3(x, t) \rightarrow u_{3,\infty}$ as $t \rightarrow \infty$.

Define a positive definite function $V : \Omega \rightarrow \mathbb{R}$, Ω open in \mathbb{R} ,

$$V(u_3(x, t)) = (u_3 - u_{3,\infty})^2. \tag{15}$$

Via direct computations, we have $V_{xx} = 2[(\partial_x u_3)^2 + (u_3 - u_{3,\infty})\partial_{xx}u_3]$.

Letting $w_3 = u_{3,\infty} - u_3 (> 0)$,

$$\begin{aligned} \dot{V} &= 2(u_3 - u_{3,\infty})(\partial_{xx}u_3 + k_1u_1u_2 - k_2u_3) \\ &= \partial_{xx}V - 2(\partial_x u_3)^2 - 2w_3(k_1u_1u_2 - k_2u_3) \\ &= \partial_{xx}V - 2(\partial_x u_3)^2 - 2w_3^2[k_1(C_1 + C_2 - u_3 - u_{3,\infty}) + k_2] \\ &\leq \partial_{xx}V - 2V[k_1(C_1 + C_2 - 2u_{3,\infty} + w_3) + k_2]. \end{aligned}$$

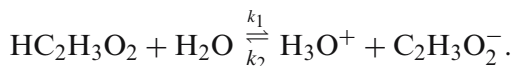
Here, the last step is followed from the previous proof of theorem 1. By weak maximum principle, it follows that $V(u(x, t))$ goes to zero as $t \rightarrow \infty$.

By applying Liapunov’s method, we conclude that $u_3(x, t) \rightarrow u_{3,\infty}$ as $t \rightarrow \infty$. Furthermore, it follows that $u_1(x, t) \rightarrow C_1 - u_{3,\infty}$ and $u_2(x, t) \rightarrow C_2 - u_{3,\infty}$ as $t \rightarrow \infty$, respectively. This completes the proof. \square

3. Example

We have shown that the concentration of chemical species has certain amount of limit as time proceeds. In this section, we determine the equilibria in an chemical solutions of weak acids and strong acids by applying previous theorem.

Consider a reversible reaction



Here, the ionization constant $K_a = 1.74 \times 10^{-5}$ (for convenience, $k_1 = 1.74 \times 10^{-5}$, $k_2 = 1$). Refer to Petrucci [6].

We determine concentrations $[\text{H}_3\text{O}^+]$, and $[\text{C}_2\text{H}_3\text{O}_2^-]$ in a solution that is 0.1 M both in $\text{HC}_2\text{H}_3\text{O}_2$ and HCL.

Let’s define $u_1 = [\text{H}_3\text{O}^+]$, $u_2 = [\text{C}_2\text{H}_3\text{O}_2^-]$, and $u_3 = [\text{HC}_2\text{H}_3\text{O}_2]$. Then based on reaction equations, the rate for each chemical species can be found in the model

$$\begin{aligned} \frac{du_1}{dt} &= k_1u_3 - k_2u_1u_2, \\ \frac{du_2}{dt} &= k_1u_3 - k_2u_1u_2, \\ \frac{du_3}{dt} &= -k_1u_3 + k_2u_1u_2. \end{aligned}$$

We expect u_2 to be small because the strong acid HCL represses the ionization of the weak acid $\text{HC}_2\text{H}_3\text{O}_2$ through the common ion, H_3O^+ . This yields two conservation equations:

$$u_1 = 0.1 + u_2,$$

$$u_3 = 0.1 - u_2.$$

According to theorem 1.1, we can see $u_2(t)$ converges to $u_{2,\infty} = 1.74 \times 10^{-5} \text{ M}$ as time increases. Indeed, one can check that the value $u_{2,\infty}$ is one of roots of an equation

$$u_2^2 + (0.1 + k_1/k_2)u_2 - 0.1(k_1/k_2) = 0,$$

which is derived from $\frac{du_2}{dt} = 0$.

Further, we find that $u_1(t)$ converges to $0.1 + u_{2,\infty}$ as $t \rightarrow \infty$. Hence, it follows that $[\text{C}_2\text{H}_3\text{O}_2^-] = 1.74 \times 10^{-5} \text{ M}$ and $[\text{H}_3\text{O}^+] = 0.1 + 1.74 \times 10^{-5} \text{ M}$.

References

- [1] W. Chen, C. Li and E.S. Wright, *Commun. Pure Appl. Anal.* 4 (2005) 889–899.
- [2] L.C. Evans, *Partial Differential Equations* (AMS, Rhode Island, 2002).
- [3] J.K. Hale, *Ordinary Differential Equations* (Wiley, New York, 1969).
- [4] C. Li and E.S. Wright, *Discrete Contin. Dyn. Syst.* 7(2) (2001) 377–384.
- [5] C. Li and E.S. Wright, *Commun. Pure Appl. Anal.* 1 (2002) 77–84.
- [6] R.H. Petrucci, *General Chemistry* (New York, 1982), p. 440.
- [7] J. Toth, G. Li, H. Rabitz and A.S. Tomlin, *Siam J. Appl. Math.* 57 (1997) 1531–1556.