

# Kinetics of irreversible consecutive processes with first order second steps: analytical solutions

Gábor Lente

Received: 25 October 2014 / Accepted: 20 January 2015 / Published online: 29 January 2015  
© Springer International Publishing Switzerland 2015

**Abstract** Analytical solutions are derived for a family of two-stage reactions, in which the later process is first order with respect to the product of the previous, non-first order step. A general strategy is shown that is suitable to handle typical cases. The strategy is demonstrated by considering, zeroth order, second order, mixed second order and third order initial reactions, analytical solutions for all of which can be obtained and advantageously used. The solutions can also be used as archetypes of intermediate formation and decay in chemical kinetics.

**Keywords** Reaction kinetics · Dynamical system · Mathematical modelling · Intermediate · Two-stage process

## 1 Introduction

The mathematically most demanding part of chemical kinetics is finding analytical solutions for rate equations. Rate equations describe how the rate of concentration change depends on concentrations, so these are typically non-linear, autonomous differential equations, in which the time dependence of concentrations are sought. While the solutions of the rate equations for single step reactions are often well known and available in widely used textbooks (the relevant chapters of the textbook written by Espenson [1] are still the most authoritative source for kineticists), this is seldom the case for reaction sequences. Basically, the only case when analytical solutions are known is the one of first order reaction networks [2–9]. In such networks, each reac-

---

G. Lente (✉)  
Department of Inorganic and Analytical Chemistry, University of Debrecen,  
P.O.B. 21, Debrecen 4010, Hungary  
e-mail: lenteg@science.unideb.hu

tion rate is directly proportional to a single concentration, so the overall system of differential equations remains linear, and, therefore, reasonably easy to solve.

In experimental chemical kinetics, the computational and theoretical background is now suitable to use numerical solutions when analytical solutions are unavailable. There are numerous commercial (or even free) software packages for generating numerical solutions for cases of reasonably high complexity, where the number of species may reach 20 and the number of reaction steps may easily exceed 100 [10–14]. With these computational opportunities, one might even think that the analytical solutions have lost their significance in practice. Yet, from a mathematical point of view, it is clear that analytical solutions take precedence whenever they can be found, so searching for them is not in vain. Actually, they can provide insight and conceptual novelty, which is impossible for numerical solutions, and analytical solutions for kinetic problems are still sought in an active field of research, both practically and theoretically [9, 15–23]. Such analytical solutions in dynamical systems are also viewed as highly valuable because the parameter dependence of the solution is much clearer than for a numerical solution. In fact, approximate solutions with explicit mathematical forms, such as using the steady state or pre-equilibrium approaches [1], are also often very useful as they make the information content of the observations easier to understand. This is even true for more complicated cases such as chain reactions [1] or rubber vulcanization [18, 20], where approximations yield experimentally testable rate equations even when consolidated closed exact forms are absent.

In this paper, analytical solutions will be presented for a family of irreversible two-stage reaction schemes in which a first order step follows an initial, non-first order process. Emphasis will be mostly given to the intermediate, which is the species that forms in the first process and decays in the second. The concentration change of this species may be considered as an archetype of the kinetic behavior of intermediates.

## 2 General solution method

The general strategy presented in this paper relies on first determining the time dependence of the concentration of the reactant in the initial step. This is possible independently of the rest of the concentrations because the reactions are irreversible, so in effect, the rate equation of a single-stage scheme needs to be solved. After this, the concentration of the intermediate,  $c(t)$ , can be defined by the following general differential equation:

$$\frac{dc(t)}{dt} = f(t) - kc(t) \quad (1)$$

Unlike a rate equation, this differential equation is not autonomous. Conceptually, this is understandable as solving the rate equation for the initial substance necessarily involved identifying the initial time ( $t = 0$ ), at which the reaction started. Equation 1 is a first order, inhomogeneous, linear ordinary differential equation, which can be solved generally using the following substitution:

$$c(t) = x(t)e^{-kt} \quad (2)$$

In effect, a new variable,  $x(t)$  is introduced instead of  $c(t)$ . The rationale in this substitution is that the resulting differential equation for  $x(t)$  is much simpler than the original:

$$\frac{dx(t)}{dt} = e^{kt} f(t) \quad (3)$$

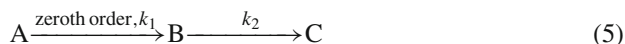
Equation 3 is one of the simplest possible differential equations, it can be solved by finding the primitive function of the right side. Using  $c(0)$  as the value of the concentration at zero time, the solution of the original equation (Eq. 1) for  $c(t)$  is given as:

$$c(t) = c(0)e^{-kt} + e^{-kt} \int_0^t e^{k\tau} f(\tau) d\tau \quad (4)$$

The ability to find the analytical solution of Eq. 1 in an explicit way depends on the analytical possibilities for evaluating the integral of the right side of Eq. 4. The use of this strategy will be demonstrated in the next sections through examples, which have high relevance and importance in chemical kinetics.

### 3 Zeroth order first step

If the first reaction is zeroth order with respect to its reagent, the consecutive reactions are represented by the following scheme:



In the remaining text,  $[A]$ ,  $[B]$ , and  $[C]$  will denote the concentrations of species A, B, and C, in order. The initial concentrations (at  $t = 0$ , which is the instance at which the reaction is started) will be  $[A]_0$ ,  $[B]_0$ , and  $[C]_0$ . The simultaneous differential equations describing the system shown in Eq. 5 are as follows:

$$\begin{aligned} \frac{d[A]}{dt} &= -\text{sgn}([A])k_1 \\ \frac{d[B]}{dt} &= \text{sgn}([A])k_1 - k_2[B] \\ \frac{d[C]}{dt} &= k_2[B] \end{aligned} \quad (6)$$

The notation  $\text{sgn}$  refers to the signum function [24], the value of which is 1 for positive arguments,  $-1$  for negative arguments and 0 for 0. The relevance of this term is often neglected in the usual textbook examples of zeroth order processes, where the statement that the rate equation is only valid for  $[A] > 0$  is typically made instead of this mathematical trick. However, for the purposes of this work, reaction times at

which  $[A] = 0$  are clearly significant. The inclusion of the  $\text{sgn}$  function ensures that the value of  $[A]$  remains non-negative. The time dependence of the concentration of A is easily given in a zeroth order process:

$$[A](t) = \begin{cases} [A]_0 - k_1 t & \text{if } t \leq [A]_0/k_1 \\ 0 & \text{if } t > [A]_0/k_1 \end{cases} \quad (7)$$

Consequently, the  $f(t)$  term in Eq. 1 assumes the following form:

$$f(t) = \begin{cases} k_1 & \text{if } t \leq [A]_0/k_1 \\ 0 & \text{if } t > [A]_0/k_1 \end{cases} \quad (8)$$

The solution for the concentration of B is readily obtained as:

$$[B](t) = \begin{cases} k_1/k_2 + ([B]_0 - k_1/k_2)e^{-k_2 t} & \text{if } t \leq [A]_0/k_1 \\ (k_1/k_2)e^{k_2[A]_0/k_1} + [B]_0 - k_1/k_2 e^{-k_2 t} & \text{if } t > [A]_0/k_1 \end{cases} \quad (9)$$

Finally, the concentration of C is given easily from mass balance equations (i.e. noting that the sum  $[A](t) + [B](t) + [C](t)$  is independent of time):

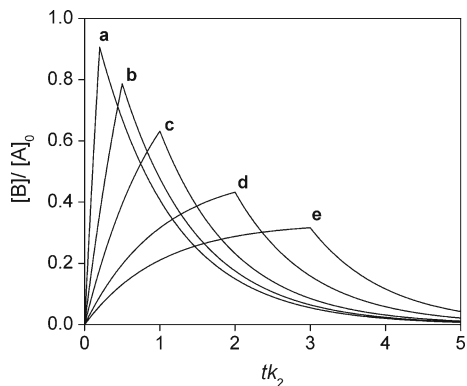
$$[C](t) = [A]_0 + [B]_0 + [C]_0 - [A](t) - [B](t) \quad (10)$$

For the practice of chemical kinetics, it is clear that the most significant case is when the reaction starts purely from species A, so that  $[B]_0 = [C]_0 = 0$ . These are the classical conditions for the observation of B as an intermediate and C as a final product. Figure 1 gives some sample kinetic curves calculated using the derived formulas. The figure uses special scaling to emphasize the curve shapes: concentrations on the y axis are given in  $[A]_0$  units, whereas time on the x axis is given in  $1/k_2$  units. The entire system has three parameters:  $[A]_0$ ,  $k_1$  and  $k_2$ . Scaling shows that two of these three parameters only provide the scales for time and concentration, so the actual shape of the curves is only determined by a single parameter, which is the combination  $k_2[A]_0/k_1$ . This parameter will be called a shape parameter. Figure 1 shows curves for 5 different values of this shape parameter. Similar scaling will be used throughout this paper.

The curves displayed in Fig. 1 show that a break point occurs at time  $[A]_0/k_1$  on the concentration–time traces. This is not unexpected as a break point occurs on the corresponding concentration–time curves for species A as well, this is the time at which  $[A]$  reaches the value of 0. As the shape parameter increases, the maximum B concentration attained decreases. Again, this is fully understandable as the increase in the shape parameter implies an increase in the rate constant of the second process relative to that of the first. This basic phenomenon (smaller maximum concentration of the intermediate as the decay process gets faster) will be observable for all the rest of the examples used in this paper.

It can also be noted that setting  $[A]_0 = \infty$  in the first line Eq. 9 (before the break point) also gives the analytical solution for an open system into which B is introduced

**Fig. 1** Representative scaled kinetic traces for the intermediate in the zeroth order–first order consecutive reaction (Eq. 5). The values of the shape parameter  $k_2[A]_0/k_1$ : 0.2 (a), 0.5 (b), 1 (c), 2 (d), 3 (e)



at a constant rate ( $k_1$ ) and removed in a first order process characterized by rate constant  $k_2$ .

#### 4 First order first step

When the first step in the sequence of reactions is a first order process, the following scheme is used:



The simultaneous differential equations describing this system are as follows:

$$\begin{aligned} \frac{d[A]}{dt} &= -k_1[A] \\ \frac{d[B]}{dt} &= k_1[A] - k_2[B] \\ \frac{d[C]}{dt} &= k_2[B] \end{aligned} \quad (12)$$

Following the presented general method gives formulas for the concentrations:

$$[A](t) = [A]_0 e^{-k_1 t} \quad (13)$$

$$[B](t) = \frac{[A]_0 k_1}{k_1 - k_2} \left( e^{-k_2 t} - e^{-k_1 t} \right) + [B]_0 e^{-k_2 t} \quad (14)$$

Equation 14 can only be used if  $k_1 \neq k_2$ . If  $k_1 = k_2$ , the solution is assumed a different form:

$$[B](t) = ([A]_0 k_1 t + [B]_0) e^{-k_1 t} \quad (15)$$

These solutions are not discussed any further because they are well known and are given in most textbooks about chemical kinetics under the title ‘two consecutive

irreversible first order reactions' [1]. In fact, this model is a simple case of a linear compartmental system, which can always be analytically solved irrespectively of the size of the problem [7–9].

## 5 Second order first step

When the first step is a second order process, the kinetic scheme has the following form:



The simultaneous differential equations for the concentrations are as follows:

$$\begin{aligned} \frac{d[A]}{dt} &= -2k_1[A]^2 \\ \frac{d[B]}{dt} &= k_1[A]^2 - k_2[B] \\ \frac{d[C]}{dt} &= k_2[B] \end{aligned} \quad (17)$$

Note that the multiplication factor 2 in the first differential equation is needed to satisfy IUPAC conventions [25,26] of the definition of reaction rate and shows that two molecules of A is consumed in the first step. As one molecule of B is produced in the same step, this multiplication factor is no longer necessary in the second differential equation. Again, the first of these differential equations, describing only the concentration change of A, can be solved easily and the solution is given in standard textbooks of chemical kinetics [1]:

$$[A](t) = \frac{[A]_0}{1 + 2k_1[A]_0 t} \quad (18)$$

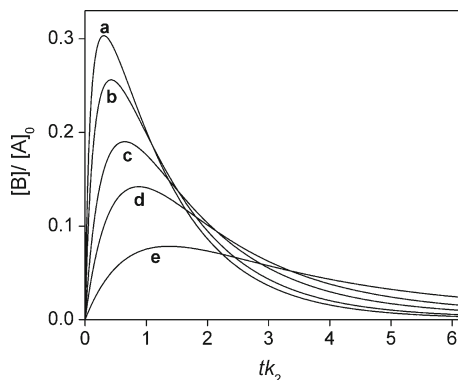
Consequently, function  $f(t)$  in Eq. 1 is given as:

$$f(t) = k_1 \left( \frac{[A]_0}{1 + 2k_1[A]_0 t} \right)^2 \quad (19)$$

After finding the integral shown in Eq. 4, the concentration of B can be given as:

$$\begin{aligned} [B](t) &= \frac{4k_1[B]_0 + 2k_1[A]_0 - k_2 e^{-k_2/(2k_1[A]_0)} Ei \left( \frac{k_2}{2k_1[A]_0} \right)}{4k_1} e^{-k_2 t} \\ &+ \frac{-2k_1[A]_0 + k_2 e^{-k_2 t - k_2/(2k_1[A]_0)} (1 + 2k_1[A]_0 t) Ei \left( k_2 t + \frac{k_2}{2k_1[A]_0} \right)}{4k_1(1 + 2k_1[A]_0 t)} \end{aligned} \quad (20)$$

**Fig. 2** Representative scaled kinetic traces for the intermediate in the second order–first order consecutive reaction (Eq. 16). The values of the shape parameter  $k_2/(k_1[A]_0)$ : 0.1 (a), 0.2 (b), 0.5 (c), 1 (d), 3 (e)



In this equation,  $Ei$  denotes the exponential integral function [27], which is defined for real numbers as follows:

$$Ei(a) = - \int_{-a}^{\infty} \frac{e^{-\tau}}{\tau} d\tau \quad (21)$$

Finally, the concentration of C can be calculated by a mass conservation equation similar to Eq. 10 (the difference is that  $[A]_0$  and  $[A](t)$  both need to be multiplied by 2). Figure 2 gives some sample kinetic curves calculated using the derived formulas. In this graph,  $[A]_0$  and  $k_2$  are used as scaling parameters, whereas the shape parameter assumes the form  $k_2/(2k_1[A]_0)$ .

## 6 Mixed second order first step

A mixed second order step is one in which two different molecules (rather than two identical molecules in the ‘normal’ second order case) react to give some sort of a product. So a mixed second order step followed by a first order reaction is represented by the following scheme:



This is probably the most important two-stage consecutive schemes of all, as the underlying concept is that two different reactants ( $A_1$  and  $A_2$ ) give final product C through the intervention of intermediate B. In this case, four concentrations are involved and the differential equations are as follows:

$$\begin{aligned} \frac{d[A_1]}{dt} &= -k_1[A_1][A_2] \\ \frac{d[A_2]}{dt} &= -k_1[A_1][A_2] \end{aligned}$$

$$\begin{aligned} \frac{d[B]}{dt} &= k_1 k_1 [A_1][A_2] - k_2 [B] \\ \frac{d[C]}{dt} &= k_2 [B] \end{aligned} \tag{23}$$

Again, the solutions for  $[A_1]$  and  $[A_2]$  (note that equation  $[A_1](t) - [A_2](t) = [A_1]_0 - [A_2]_0$  holds at all values of  $t$ ) can be found in textbooks [1]:

$$\begin{aligned} [A_1](t) &= \frac{([A_2]_0 - [A_1]_0)[A_1]_0}{[A_2]_0 e^{([A_2]_0 - [A_1]_0)k_1 t} - [A_1]_0} \\ [A_2](t) &= \frac{([A_1]_0 - [A_2]_0)[A_2]_0}{[A_1]_0 e^{([A_1]_0 - [A_2]_0)k_1 t} - [A_2]_0} \end{aligned} \tag{24}$$

Consequently, the function  $f(t)$  in Eq. 1 assumes the following form, which is somewhat more complex than in previous cases:

$$f(t) = k_1 \frac{[A_1]_0 [A_2]_0 ([A_1]_0 - [A_2]_0)^2}{([A_2]_0^2 e^{([A_2]_0 - [A_1]_0)k_1 t} + [A_1]_0^2 e^{([A_1]_0 - [A_2]_0)k_1 t} - 2[A_1]_0 [A_2]_0)} \tag{25}$$

The integral shown in Eq. 4 with this  $f(t)$  is not very simple, but can in fact be found. The integral yields the following time dependence for the concentration of B:

$$\begin{aligned} [B](t) &= [B]_0 e^{-k_2 t} + [A_1]_0 e^{-k_2 t} - \frac{k_2 [A_1]_0 ([A_2]_0 - [A_1]_0) H(0)}{[A_2]_0 (k_1 [A_1]_0 - k_1 [A_2]_0 + k_2)} e^{-k_2 t} \\ &+ \frac{[A_1]_0 ([A_2]_0 - [A_1]_0) e^{([A_1]_0 - [A_2]_0)k_1 t}}{[A_1]_0 e^{([A_1]_0 - [A_2]_0)k_1 t} - [A_2]_0} \\ &+ \frac{k_2 [A_1]_0 ([A_2]_0 - [A_1]_0) e^{([A_1]_0 - [A_2]_0)k_1 t} H(t)}{[A_2]_0 (k_1 [A_1]_0 - k_1 [A_2]_0 + k_2)} \\ H(t) &= {}_2F_1 \left( 1, 1 + \frac{k_2}{k_1 ([A_1]_0 - [A_2]_0)}, 2 + \frac{k_2}{k_1 ([A_1]_0 - [A_2]_0)}, \right. \\ &\left. \times \frac{[A_1]_0}{[A_2]_0} e^{([A_1]_0 - [A_2]_0)k_1 t} \right) \end{aligned} \tag{26}$$

The notation  ${}_2F_1$  means the first hypergeometric function [28], which is defined as follows:

$${}_2F_1(p, q, r, y) = 1 + \sum_{n=1}^{\infty} \frac{p(p+1) \cdots (p+n-1) q(q+1) \cdots (q+n-1)}{r(r+1) \cdots (r+n-1)} \frac{y^n}{n!} \tag{27}$$

The product  $p(p+1) \cdots (p+k-1) = (p)_k$  in this definition is also called the (rising) Pochhammer symbol [29]. Because of the special cases  $p = 1$  and  $r = q + 1$ , the calculation of  $H(t)$  is simplified into the following infinite series:



$$H(t) = 1 + \sum_{n=1}^{\infty} \frac{k_1[A_1]_0 - k_1[A_2]_0 + k_2}{n \{(n+1)(k_1[A_1]_0 - k_1[A_2]_0) + k_2\}} \left( \frac{[A_1]_0}{[A_2]_0} \right)^n e^{([A_1]_0 - [A_2]_0)nk_1t} \quad (28)$$

It should be remarked that the solution shown is technically only valid for  $[A_2]_0 > [A_1]_0$ . However, this does not limit the usefulness of the formula as the notations  $A_1$  and  $A_2$  can simply be exchanged in order to satisfy this condition (i.e.  $A_1$  must be the limiting reagent).

More substantial limitations on the use of the stated solution happen when some coincidences occur. The first such case is  $[A_1]_0 = [A_2]_0$  (identical initial concentrations for the two reagents). This is already a problem in the use of Eq. 24. In this case, the differential equations actually take the form that is already given in Eq. 17 (except the multiplication factor 2 in the first equation), so the solution presented in the previous section can be used directly. This is actually the known strategy of dealing with the same problem in the case of the one-step mixed second order rate equation [1].

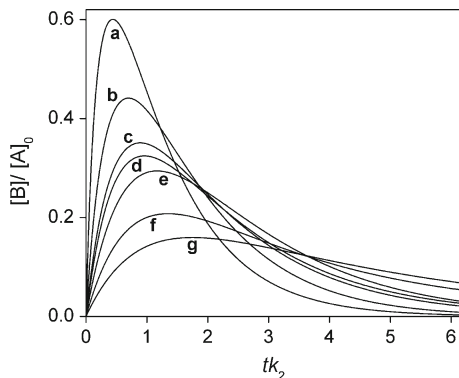
Another coincidence that renders Eq. 26 unusable is when  $k_2 = k_1([A_2]_0 - [A_1]_0)$ , as it would result in 0 appearing in the denominator. Conceptually, this is very similar to the  $k_1 = k_2$  singular case of the two consecutive irreversible first order reactions (cf. Eq. 15). The solution of Eq. 23 for  $k_2 = k_1([A_2]_0 - [A_1]_0)$  can actually be given in a form that is significantly simpler than Eq. 26:

$$[B](t) = [B]_0 e^{-k_2t} + e^{-k_2t} [A_1]_0 \left( 1 - \frac{[A_1]_0}{[A_2]_0} \right) \ln \frac{[A_2]_0 e^{k_2t} - [A_1]_0}{[A_2]_0 - [A_1]_0} + \frac{[A_1]_0^2 (1 - e^{-k_2t})}{[A_2]_0 e^{k_2t} - [A_1]_0} \quad (29)$$

An even more nuanced singular case is  $k_2 = ik_1([A_2]_0 - [A_1]_0)$  where  $i$  is an integer (it can only be positive because  $[A_2]_0 > [A_1]_0, k_1 > 0$ , and  $k_2 > 0, i = 1$  is the case for which Eq. 29 gives the solution). The phenomenon is caused by the fact that the  ${}_2F_1(p, q, r, y)$  first hypergeometric function remains undefined for cases when  $r$  is zero or a negative integer. The deeper background is that the  $e^{kt} f(t)$  function appearing in Eq. 3 is, by accident, a rational function of  $e^{kt}$  in this case. The solution can be obtained for each value of  $i$  by decomposing this rational function into a sum of partial fractions. As an example, the solution for  $i = 2$  is shown here:

$$[B](t) = [B]_0 e^{-2k_2t} + [A_1]_0 \left( 1 - \frac{[A_1]_0}{[A_2]_0} \right) (1 - e^{-k_2t/2}) e^{-k_2t/2} + e^{-k_2t} \frac{2[A_1]_0^2}{[A_2]_0^2} ([A_2]_0 - [A_1]_0) \ln \frac{[A_2]_0 e^{k_2t/2} - [A_1]_0}{[A_2]_0 - [A_1]_0} + \frac{[A_1]_0^3 (1 - e^{-k_2t/2}) e^{-k_2t/2}}{[A_2]_0 ([A_2]_0 e^{k_2t/2} - [A_1]_0)} \quad (30)$$

**Fig. 3** Representative scaled kinetic traces for the intermediate in the mixed second order–first order consecutive reaction (Eq. 22). The values of the shape parameters  $[A_2]_0/[A_1]_0 = 2$  (a), 2 (b), 2 (c), 2 (d), 6 (e), 2 (f), 6 (g);  $k_2/(k_1[A_2]_0 - k_1[A_1]_0) = 0.4$  (a), 1 (b), 1.7 (c), 2 (d), 1.7 (e), 4.5 (f), 4.5 (g)



Finally, in all cases, the usual mass balance equation is used to obtain the concentration of C:

$$[C](t) = [A_1]_0 + [B]_0 + [C]_0 - [A_1](t) - [B](t) \tag{31}$$

Figure 3 gives some sample kinetic curves calculated using the derived formulas (Eqs. 26, 29, 30). The scaling parameters are  $[A_1]_0$  for concentration and  $1/k_2$  for time, whereas there are two shape parameters in this case:  $[A_2]_0/[A_1]_0$  and  $k_2/(k_1[A_2]_0 - k_1[A_1]_0)$ .

### 7 Third order first step

A third order step is one in which three identical molecules are needed to give a product. If the first process is third order, the sequence of reactions of interest here can be given by the following scheme:



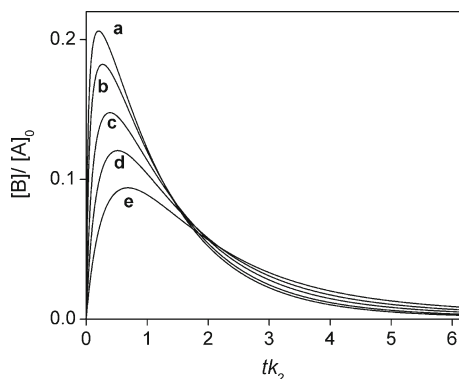
The differential equations describing the concentration changes are as follows:

$$\begin{aligned} \frac{d[A]}{dt} &= -3k_1[A]^3 \\ \frac{d[B]}{dt} &= k_1[A]^3 - k_2[B] \\ \frac{d[C]}{dt} &= k_2[B] \end{aligned} \tag{33}$$

Again, the time dependence of the concentration of A can be given solely from the first differential equation:

$$[A](t) = [A]_0 \sqrt{\frac{1}{1 + 6k_1[A]_0^2 t}} \tag{34}$$

**Fig. 4** Representative scaled kinetic traces for the intermediate in the third order–first order consecutive reaction (Eq. 32). The values of the shape parameter  $k_2/(k_1[A]_0^2)$ : 0.1 (a), 0.2 (b), 0.5 (c), 1 (d), 2 (e)



Consequently,  $f(t)$  in Eq. 1 is of the following form:

$$f(t) = k_1[A]_0^3 \left(1 + 6k_1[A]_0^2 t\right)^{-3/2} \quad (35)$$

The integral shown in Eq. 4 can be evaluated analytically and the final solution for [B] is obtained as follows:

$$\begin{aligned} [B](t) = & [B]_0 e^{-k_2 t} - \sqrt{\frac{\pi k_2}{54k_1}} e^{-k_2 t - k_2/(6k_1[A]_0^2)} \operatorname{erfi}\left(\sqrt{\frac{k_2}{6k_1[A]_0^2}}\right) + \frac{[A]_0}{3} e^{-k_2 t} \\ & + \sqrt{\frac{\pi k_2}{54k_1}} e^{-k_2 t - k_2/(6k_1[A]_0^2)} \operatorname{erfi}\left(\sqrt{\frac{k_2(1 + 6k_1[A]_0^2 t)}{6k_1[A]_0^2}}\right) - \frac{[A]_0}{3\sqrt{1 + 6k_1[A]_0^2 t}} \end{aligned} \quad (36)$$

In this formula,  $\operatorname{erfi}$  is the imaginary error function [30], which is related to the usual error function  $\operatorname{erf}$  as:

$$\operatorname{erfi}(a) = -i \times \operatorname{erf}(i \times a) \quad (37)$$

The imaginary error function returns real values for real arguments. The concentration of C can again be given using mass balance equation after noting that the sum  $3[A](t) + [B](t) + [C](t)$  is independent of time. Figure 4 gives some sample kinetic curves calculated using the derived formulas. The scaling parameters are  $[A]_0$  for concentration and  $1/k_2$  for time, whereas the shape parameter is  $k_2/(k_1[A]_0^2)$ .

## 8 Conclusions

This paper has shown that analytical solutions for a class of two-stage chemical reactions can be found if the second process is first order with respect to the intermediate. The general strategy presented can be used for other cases not shown in this paper. The

solutions show some moderate degree of mathematical sophistication because special functions such as the exponential integral function, the hypergeometric function, and the imaginary error function appear in them. On the other hand, these functions are routinely implemented in common mathematical software packages, so the author recommends the use of the derived analytical formulas instead of the numerical solutions.

**Acknowledgments** The research was supported by the EU and co-financed by the European Social Fund under the project ENVIKUT (TÁMOP-4.2.2.A-11/1/KONV-2012-0043).

## References

1. J.H. Espenson, *Chemical Kinetics and Reaction Mechanisms*, 2nd edn. (McGraw-Hill, New York, 1995)
2. F.A. Matsen, J.L. Franklin, *J. Am. Chem. Soc.* **72**, 3337–3341 (1950)
3. C.R. Quezada, T.P. Clement, K.K. Lee, *Adv. Water Resour.* **27**, 507–520 (2004)
4. C. Gadgil, C.H. Lee, H.G. Othmer, *Bull. Math. Biol.* **67**, 901–946 (2005)
5. W.J. Heuett, H. Qian, *Bull. Math. Biol.* **68**, 1383–1399 (2006)
6. T. Jahnke, W. Huisinga, *J. Math. Biol.* **54**, 1–26 (2007)
7. G. Lente, *J. Chem. Phys.* **137**, 164101 (2012)
8. F. Garcia-Sevilla, M. Garcia-Moreno, M. Molina-Alarcon, M.J. Garcia-Meseguer, J.M. Villalba, E. Arribas, R. Varon, *J. Math. Chem.* **50**, 1598–1624 (2012)
9. P. Érdi, G. Lente, *Stochastic Chemical Kinetics (Theory and (Mostly) Systems Biological Applications)* (Springer, New York, 2014)
10. *ZiTa* by Gábor Peintler, <http://www.staff.u-szeged.hu/~peintler/enprogs.htm>
11. COPASI, <http://www.copasi.org/>
12. Pro-KIV™ Kinetic Analysis & Data Simulation Software, <http://www.photophysics.com/software/pro-kiv-kinetic-analysis-data-simulation-software>
13. KINSIM/FITSIM, <http://www.biochem.wustl.edu/cflab/message.html>
14. SPECFIT Global Analysis, <http://www.hi-techsci.com/products/specfitglobalanalysis/>
15. G. Milani, F. Milani, *J. Math. Chem.* **50**, 2577–2605 (2014)
16. D. Vogt, *J. Math. Chem.* **51**, 826–842 (2013)
17. P. Miškinis, *J. Math. Chem.* **51**, 1822–1834 (2013)
18. G. Milani, *J. Math. Chem.* **51**, 2033–2061 (2013)
19. V. Vlasov, *React. Kinet. Mech. Catal.* **110**, 5–13 (2013)
20. G. Milani, F. Milani, *J. Math. Chem.* **52**, 464–488 (2014)
21. D. Belkić, *J. Math. Chem.* **52**, 1201–1252 (2014)
22. A.A. Khadom, A.A. Abdul-Hadi, *React. Kinet. Mech. Catal.* **112**, 15–26 (2014)
23. A. Izadbakhsh, A. Khatami, *React. Kinet. Mech. Catal.* **112**, 77–100 (2014)
24. <http://mathworld.wolfram.com/Sign.html>
25. P. Muller, *Pure Appl. Chem.* **66**, 1077–1184 (1994)
26. K.J. Laidler, *Pure Appl. Chem.* **68**, 149–192 (1996)
27. <http://mathworld.wolfram.com/ExponentialIntegral.html>
28. <http://mathworld.wolfram.com/HypergeometricFunction.html>
29. <http://mathworld.wolfram.com/PochhammerSymbol.html>
30. <http://mathworld.wolfram.com/Erfi.html>