Alternate solutions for two particular third order kinetic rate laws

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Abstract   Alternate solutions to third order rate law expressions which are first order in one reactant and second order in another for the generalized reaction $aA + bB \xrightarrow{k_A} P$ with a limiting reactant and for simple cubic autocatalysis $A + 2B \xrightarrow{k_A} 3B$ are presented and discussed. These solutions are expressed in terms of the Lambert function $W[x]$ with argument $x(t) = \alpha \exp(\alpha - \beta t)$, where α and β are empirical parameters. These expressions permit the concentrations of the reactant species to be explicitly represented as dependent functions of time. For the generalized reaction, the solution involves considering exactly which species is limiting, so that the correct branch of the Lambert function can be determined. For simple cubic autocatalysis, the solution is shown to be consistent with the characteristics associated with clock reactions. An exact expression for the "induction time" associated with a clock reaction described by this mechanism is also derived.

Keywords   Third order rate law · Kinetics · Lambert W · Cubic autocatalysis · Clock reaction

1 Introduction

One class of third order chemical kinetic rate laws involve differential expressions which are first order in one reactant and second order in another: $d[A]/dt = -k_A[A]^2[B]$. At first glance, the form of the rate law would appear to imply a trimolecular mechanism of the form $2A + B \xrightarrow{k_A} P$, where P is a product. But, this type of rate law is

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also consistent with mechanisms involving bimolecular steps, either as an exact form involving a dimeric intermediate subject to pre-equilibrium, or as a limiting form for the case of formation of a dimeric intermediate which may then dissociate or go on to react. This connection to bimolecular mechanisms means this type of rate law is applicable to more chemical systems than might be expected. The most well-known chemical reactions described by this type of rate law involve nitric oxide; among these, the best characterized is nitric oxide oxidation by diatomic oxygen [1–3]. However, many other inorganic and organic reactions are also described by this type of rate law, including the Cannizzaro reaction [4] and the bromination of olefins [5].

The purpose of this communication is to present novel solutions for this type of rate law. These solutions complement those previously known [6,7], in that the concentrations of the reactants can be explicitly represented in terms of time acting as an independent variable. This permits a direct, straightforward fit of this rate law to kinetic data where concentrations have been determined as a function of time. Since cubic autocatalysis represents a particular case of this type of rate law, a novel, alternate solution for this mechanism is also presented. This solution permits determination of an exact expression for the "incubation time" for consumption of half of the original concentration of the non-catalytic reagent. Previously, only approximate expressions for this incubation time appear to have been presented.

2 The general rate law $d[A]/dt = -k_A[A]^2[B]$

Begin by considering the generalized reaction $aA + bB \xrightarrow{k_A} P$ with the rate law $d[A]/dt = -k_A[A]^2[B]$. The stoichiometric coefficients a and b are both positive; for any reaction to take place, the initial reactant concentrations $[A]_0$ and $[B]_0$ must also be positive as well. Next, consider representing the rate law in terms of an unknown function of time $x(t)$ representing how the reaction progresses. The reactant concentrations will then be given by $[A](t) = [A]_0 - ax(t)$ and $[B](t) = [B]_0 - bx(t)$. Substitution into the rate law expression gives

$$\frac{d[[A]_0 - ax(t)]}{dt} = -k_A[[A]_0 - ax(t)]^2[[B]_0 - bx(t)]$$
$$a\frac{dx(t)}{dt} = k_A[[A]_0 - ax(t)]^2[[B]_0 - bx(t)]. \tag{1}$$

Defining real, positive constants $\delta = [A]_0/a$ and $\gamma = [B]_0/b$ then gives the differential equation

$$\frac{dx(t)}{dt} = k_A ab[\delta - x(t)]^2[\gamma - x(t)] \tag{2}$$

for $x(t)$. When $\delta = \gamma$, the reactants A and B are present in exact stoichiometric proportions, with neither acting as a limiting reagent. Equation (2) becomes $dx(t)/dt = k_A ab[\delta - x(t)]^3$, which is easily integrated. The novel solution to the rate law under consideration here only arises for the case $\delta \neq \gamma$, where one of the two species is limiting, and both parameters are positive.

The traditional approach to finding a solution for the general rate law leading to a closed form expression relating $[A](t)$, $[B](t)$ and time t involves the separation of variables and integration. This approach leads to the solutions noted in Refs. [6] and [7]. However, starting with Eq. (2), an alternate solution can be found by considering the properties of the Lambert function $W[x]$ with argument $x(t) = \alpha \exp(\alpha - \beta t)$.

3 The Lambert function $W[x]$ and an associated differential equation

The Lambert function $W[x]$ is defined so that for $y \exp(y) = x$, $W[x] = y$. The properties of this function and many of its applications, including some in chemical kinetics (such as for the Michaelis-Menten rate law) have been previously described [8–14]. Also, $W[x]$ can be numerically evaluated using the mathematical packages MATLAB [15] or Mathematica [16]. Three properties of the function $W[x]$ are important here. First, it is necessary to note that when $-1/\exp(1) < x < 0$, $W[x]$ has two real valued branches $W[0, x]$ and $W[-1, x]$ (Fig. 1). Second, the substitution $x(t) = \alpha \exp(\alpha - \beta t)$ into $W[x]$ leads to the result

$$\frac{d}{dt} W[\alpha \exp(\alpha - \beta t)] = \frac{-\beta W[\alpha \exp(\alpha - \beta t)]}{(1 + W[\alpha \exp(\alpha - \beta t)])} \tag{3}$$

or equivalently, that setting $f(t) = W[\alpha \exp(\alpha - \beta t)]$ means that $f(t)$ represents a solution to the differential equation $f'(t) = -\beta f(t)/(1 + f(t))$. Finally, from the definition of $W[x]$, $W[\alpha \exp(\alpha)] = \alpha$.
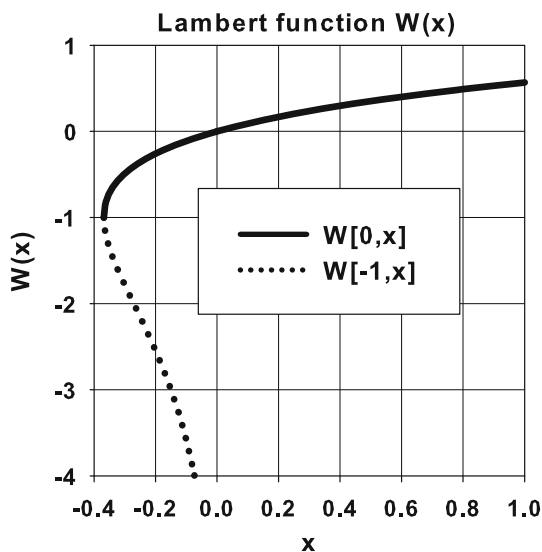

Fig. 1 Two real-valued branches of the Lambert function $W[x]$. The branch $W[0, x]$ meets the condition $-1 < W[0, x] < \infty$ for $-1/\exp(1) < x < \infty$; the branch $W[-1, x]$ meets the condition $-1 > W[-1, x] > -\infty$ for $-1/\exp(1) < x < 0$

The connection between $f(t)$ and the third order rate law considered here begins with the definition of a new function $g(t) = (\gamma + \delta f(t))/(1 + f(t))$, where δ and γ are positive real constants. In terms of $g(t)$, $f(t) = (\gamma - g(t))/(g(t) - \delta)$. Taking the derivative of $g(t)$ then gives

$$
\begin{aligned}
\frac{d}{dt} g(t) &= \left(\frac{-(\gamma + \delta f(t))}{(1 + f(t))^2} + \frac{\delta}{(1 + f(t))} \right) \left(\frac{-\beta f(t)}{(1 + f(t))} \right) \\
&= \left(\frac{(\gamma - \delta)}{(1 + f(t))^3} \right) \beta f(t) \\
&= \left(\frac{\beta}{(\gamma - \delta)^2} \right) (\delta - g(t))^2 (\gamma - g(t))
\end{aligned}
\tag{4}
$$

upon final substitution of $g(t)$ for $f(t)$. As long as $\delta \neq \gamma$, $g(t)$ represents a solution of a differential equation having exactly the same functional form as Eq. (2), where one term is quadratic and the other is linear.

4 The solutions $[A](t)$ and $[B](t)$

Comparing Eqs. (2) and (4), the definition $\beta = k_A \, ab \, (\delta - \gamma)^2$ gives $x(t)$ as

$$
x(t) = \frac{\gamma + \delta W[\alpha \exp(\alpha - \beta t)]}{1 + W[\alpha \exp(\alpha - \beta t)]} = \delta + \frac{(\gamma - \delta)}{1 + W[\alpha \exp(\alpha - \beta t)]}
\tag{5}
$$

At $t = 0$, the initial condition $x(0) = 0$ gives $\alpha = -\gamma/\delta$, so $x(t)$ can be completely defined for all positive t. Substitution of $x(t)$ into the expressions for $[A](t)$ and $[B](t)$ finally gives:

$$
\begin{aligned}
[A](t) &= \frac{\left([A]_0 - \frac{a[B]_0}{b} \right)}{1 + W[\alpha \exp(\alpha - \beta t)]} \\
[B](t) &= \frac{([B]_0 - \frac{b}{a}[A]_0) W[\alpha \exp(\alpha - \beta t)]}{1 + W[\alpha \exp(\alpha - \beta t)]}
\end{aligned}
\tag{6}
$$

Substitution of the initial condition $\alpha = -\gamma/\delta = -a[B]_0/b[A]_0$ confirms these expressions meet the initial conditions $[A](0) = [A]_0$ and $[B](0) = [B]_0$.

Careful examination of the values the parameters α and β can take on reveals an important consideration for these solutions for $[A](t)$ and $[B](t)$. As $\delta > 0, \gamma > 0$ and $\delta \neq \gamma$ by definition, the parameter $\alpha = -\gamma/\delta < 0$ and the parameter $\beta = k_A \, ab \, (\delta - \gamma)^2 > 0$. For non-negative t, this means the argument $\alpha \exp(\alpha - \beta t)$ of $W[\alpha \exp(\alpha - \beta t)]$ will be negative and also satisfy the condition $0 \geq \alpha \exp(\alpha - \beta t) > -1/\exp(1)$. For these negative arguments, Fig. 1 shows that $W[x]$ has two branches, $W[0, x]$ and $W[-1, x]$. So, finding the proper solutions for $[A](t)$ and $[B](t)$ from Eq. (6) means choosing the correct branch for $W[\alpha \exp(\alpha - \beta t)]$. The two branches have different values and different limits as $t \to \infty$:

$$W[-1, \alpha \exp(\alpha - \beta t)] < -1; \quad \lim_{t \to \infty} W[-1, \alpha \exp(\alpha - \beta t)] = -\infty$$
$$W[0, \alpha \exp(\alpha - \beta t)] > -1; \quad \lim_{t \to \infty} W[0, \alpha \exp(\alpha - \beta t)] = 0 \tag{7}$$

The choice of the correct branch then finally depends upon which of the two reactants A and B is limiting. If A is the limiting reagent (where $\gamma > \delta$), as $t \to \infty$, $[A] \to 0$ and $[B] \to [B]_0 - b[A]_0/a$; the correct branch is $W[-1, \alpha \exp(\alpha - \beta t)]$. If B is the limiting reagent (where $\delta > \gamma$), $[B] \to 0$ and $[A] \to [A]_0 - a[B]_0/b$; the correct branch is $W[0, \alpha \exp(\alpha - \beta t)]$. These choices not only give the correct limiting behavior in each case, but ensure that both $[A](t)$ and $[B](t)$ are positive but decreasing in time.

5 Simple cubic autocatalysis

Simple cubic autocatalysis represents a special case of the general rate law. Cubic autocatalysis has previously been used as the initial mechanistic step in reaction schemes leading to oscillatory behavior. Simple cubic autocatalysis has also served as a simplified description of the iodine clock reaction [17,18]. This starts with the mechanistic step $A + 2B \xrightarrow{k_A} 3B$ and the stoichiometric condition $[A]_0 + [B]_0 = [A] + [B]$. Substitution of this condition into the rate law leads to

$$\frac{d[A]}{dt} = -k_A[A][([A]_0 + [B]_0) - [A]]^2 \tag{8}$$

With the definitions $\delta = [A]_0 + [B]_0$, $\gamma = 0$ and $\beta = k_A([A]_0 + [B]_0)^2$, $[A](t)$ exactly matches $g(t)$ in Eq. (4). This gives

$$[A](t) = \frac{([A]_0 + [B]_0)W[\alpha \exp(\alpha - \beta t)]}{1 + W[\alpha \exp(\alpha - \beta t)]} \tag{9}$$

Applying the initial condition $[A]_0 = ([A]_0 + [B]_0)W[\alpha \exp(\alpha)]/(1 + W[\alpha \exp(\alpha)])$ $= ([A]_0 + [B]_0)\alpha/(1 + \alpha)$ then gives $\alpha = [A]_0/[B]_0$. As both α and β are positive, only the branch $W[0, \alpha \exp(\alpha - \beta t)]$ needs to be considered. Since $W[0, \alpha \exp(\alpha - \beta t)] \to 0$ as $t \to \infty$, $[A] \to 0$ as expected.

Some other results are useful. As $[A](t)$ is known, $[B](t)$ is also known through the original stoichiometric condition

$$[B](t) = [A]_0 + [B]_0 - [A](t)$$
$$= \frac{([A]_0 + [B]_0)}{1 + W[0, \alpha \exp(\alpha - \beta t)]} \tag{10}$$

and the result $[B](t = \infty) = [A]_0 + [B]_0$ is obtained as expected.

Figure 2 shows how $[A](t)$ and $[B](t)$ can demonstrate the time dependence expected for a clock reaction. The choice of parameters here was based on those used in earlier work; the results essentially reproduce the observations given in Ref. [17].

The concentration $[A](t)$ remains more or less constant for a certain period, while $[B](t)$ remains small. After some period of time, $[A](t)$ suddenly becomes negligible, while $[B](t)$ increases rapidly to a steady value. Earlier works on cubic autocatalysis [17,18] also gave an approximate expression for the "induction time" t_{ind} defined as the time at which $[A](t_{ind}) = [A]_0/2$. The analytical solution here permits determination of an exact expression. First, note that for $W[0, \alpha \exp(\alpha - \beta t_{ind})] = \alpha/(\alpha + 2)$,

$$
\begin{aligned}
[A](t_{ind}) &= \frac{([A]_0 + [B]_0)\frac{\alpha}{(\alpha+2)}}{(1 + \frac{\alpha}{\alpha+2})} \\
&= \frac{[A]_0(1 + \frac{1}{\alpha})(\frac{\alpha}{\alpha+2})}{(\frac{2\alpha+2}{\alpha+2})} \\
&= \frac{[A]_0}{2}
\end{aligned}
\tag{11}
$$

giving a relationship to be solved for t_{ind}. From the definition of $W[0, \alpha \exp(\alpha - \beta t_{ind})]$, inversion of the function gives $\alpha \exp(\alpha - \beta t_{ind}) = (\alpha/\alpha + 2) \exp(\alpha/\alpha + 2)$ leading to

$$
t_{ind} = \frac{\alpha - \ln\left(\frac{\exp(\frac{\alpha}{\alpha+2})}{\alpha+2}\right)}{\beta} = \frac{\alpha - \frac{\alpha}{(\alpha+2)} + \ln(\alpha + 2)}{\beta}
\tag{12}
$$

For Fig. 2, evaluation of Eq. (12) for the chosen parameters matches the value of t_{ind} determined from the intersection of the plots for $[A](t)$ and $[B](t)$.
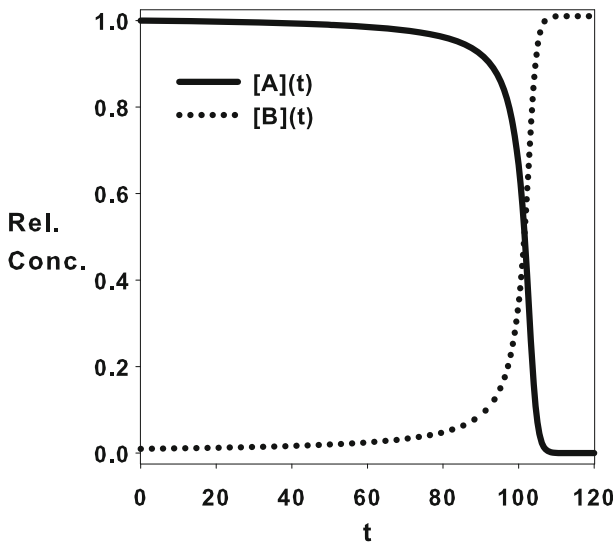

Fig. 2 $[A](t)$ and $[B](t)$ for simple cubic autocatalysis ($[A]_0 = 1.00$, $[B]_0 = 0.01$, $k_A = 1$, Ref. [17]) determined from Eqs. (9) and (10). The plot gives $t_{ind} = 101.60237$, which agrees with Eq. (12)

6 Conclusion

The results presented above show that for a third order rate law first order in one reactant and second order in another, where one of the reactants is limiting, it is possible to find expressions for the concentration of each component represented directly as dependent functions of time. The solutions presented here rely on the result that a special function ($g(t)$ in Eq. 4) represented in terms of the Lambert function $W[x]$ with argument $x(t) = \alpha \exp(\alpha - \beta t)$ solves a differential equation related to these types of rate laws. A solution for the important case of simple cubic autocatalysis also results from this approach. Given that the mechanisms associated with the general case and simple cubic autocatalysis appear to occur in many chemical systems, the availability of these solutions should aid in the investigation of their kinetics.

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