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Short communication

Elliptic integral solutions for the kinetics of autocatalytic termolecular reactions with reactive intermediate species

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Abstract

The kinetics of an autocatalytic termolecular reaction with overall stoichiometry of $A+B\rightarrow C+D$ was investigated. It is assumed that each of the three components A, B and C dissociate into reactive intermediate species, with equilibrium always established in all three cases. The rate-limiting step is then assumed to be the reaction between the intermediates formed from A and B, respectively, catalyzed by the reactive intermediate formed from product C. Integration of the differential equation describing the chemical kinetics of this process was performed for various special cases of initial reactant concentrations—stoichiometric and non-stoichiometric. The analytical solution in the latter case incorporates incomplete elliptic integrals of the first kind. Numerical values of reaction times may then be readily computed with the aid of various extensive compilations of elliptic integrals. © 1997 Elsevier Science S.A.

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1. Introduction

We consider here the case of a nominally bimolecular reaction with the following overall stoichiometry:

$$A+B\rightarrow C+D \qquad (1)$$

Each of the three materials A, B and C is assumed to dissociate into reactive intermediate species, with equilibrium always established in all three cases. It is further supposed that the rate-limiting step is the reaction between the intermediates formed from A and B, respectively, catalyzed by the reactive intermediate formed from product C. Integration of the differential equation describing the chemical kinetics of this process is then performed for various special cases of initial reactant concentrations—stoichiometric and non-stoichiometric. It is found in the latter case that the integrated rate expression incorporates incomplete elliptic integrals of the first kind.

2. Reaction mechanism

The initial reactants A and B are assumed to dissociate into the intermediate reactive species I_1 and I_2, respectively, in the following fashion:

$$A \overset{K_1}{\leftrightarrow} 2I_1 \qquad (2)$$

$$B \overset{K_2}{\leftrightarrow} 2I_2 \qquad (3)$$

wherein K_1 and K_2 denote the equilibrium constants for these two respective dissociation reactions, and would have the units of concentration. Product C is also assumed to dissociate into a reactive intermediate species I_3 as follows:

$$C \overset{K_3}{\leftrightarrow} 2I_3 \qquad (4)$$

with a dissociation equilibrium constant of K_3.

It is further assumed that the concentration of each one of these intermediate species is always much less than that of its precursor, that is, $[I_1]\ll[A]$, $[I_2]\ll[B]$, and $[I_3]\ll[C]$. With these assumptions, it follows that the concentrations of these three reactive intermediates are given by the subsequent three equations:

$$[I_1]=\sqrt{K_1[A]} \qquad (5)$$

$$[I_2]=\sqrt{K_2[B]} \qquad (6)$$

$$[I_3]=\sqrt{K_3[C]} \qquad (7)$$

where concentrations are denoted by brackets, e.g., $[I_1]$.

The formation of products C and D is then postulated to occur via the elementary termolecular reaction between I_1 and I_2, catalyzed by species I_3, or:

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$$I_1+I_2 \xrightarrow{k_1[I_3]} C+D \tag{8}$$

The rate of the above autocatalytic reaction is assumed to be linearly proportional to the concentration of species I_3, and thus the rate of appearance of product D, for example, is given by:

$$\frac{d[D]}{dt}=k_1[I_1][I_2][I_3]=k_1\sqrt{K_1K_2K_3[A][B][C]} \tag{9}$$

where k_1 is the reaction rate constant for this process, with the dimensions of $(\text{concentration})^{-2}(\text{time})^{-1}$ corresponding to a third-order process.

We introduce now the conventional concept of a reaction extent $\xi=[A]_0-[A]$ $(=[B]_0-[B])$, where the subscript 0 denotes initial conditions (at time $t=0$). From the stoichiometry of the overall process, it is also clear that $[C]=[C]_0+\xi$ and $[D]=[D]_0+\xi$. Hence, Eq. (9) may be written as:

$$\frac{d\xi}{dt}=K\sqrt{([A]_0-\xi)([B]_0-\xi)([C]_0+\xi)} \tag{10}$$

where:

$$K\equiv k_1\sqrt{K_1K_2K_3} \tag{11}$$

and would have the units of $(\text{concentration})^{-1/2}(\text{time})^{-1}$.

3. Analytical solutions

The reaction rate expression of Eq. (10), in the non-stoichiometric case of $[A]_0\neq[B]_0$, may be compared with the representation of a general elliptic integral [1]:

$$I=\int R(x,y)\,dx \tag{12}$$

where R is a rational function of x and y, and y is a cubic or quartic polynomial in x whose zeroes are all different. Thus, the integrated solution to this differential equation in the non-stoichiometric case may be expected to include elliptic integrals.

We consider first the non-stoichiometric case wherein A is the limiting reactant, or $[A]_0<[B]_0$. After appealing to the appropriate mathematical transformations given in various handbooks on the subject [2,3], the integration of Eq. (10) in this particular case yields:

$$t=\frac{2}{K\sqrt{[B]_0+[C]_0}}[F(\phi_1,k_1)-F(\phi_2,k_2)] \tag{13}$$

as the reaction time required to achieve a reaction extent of ξ. It is important at this point to note that the following constraints must be observed in the development of Eq. (13): $[B]_0>[A_0]\geq\xi>-[C]_0$. Also in Eq. (13), the $F(\phi_i,k_i)$ $(i=1, 2)$ represent incomplete elliptic integrals of the first kind, defined as:

$$F(\phi,k)\equiv\int_0^{\phi}\frac{d\theta}{\sqrt{1-k^2\sin^2\theta}} \tag{14}$$

The two arguments of these integrals are denoted as the amplitude (ϕ_i) and the modulus (k_i). For this case of $[A]_0<[B]_0$, we have for the modulus at either limit of integration:

$$k_i=\sqrt{\frac{[A]_0+[C]_0}{[B]_0+[C]_0}} \tag{15}$$

that is, for either $i=1$ or $i=2$. The amplitude at the beginning of integration $(t=0,\ \xi=0)$ is:

$$\phi_2=\sin^{-1}\sqrt{\frac{[C]_0}{[A]_0+[C]_0}} \tag{16}$$

Similarly, for the upper limit of integration, the amplitude of the incomplete elliptic integral is:

$$\phi_1=\sin^{-1}\sqrt{\frac{[C]_0+\xi}{[A]_0+[C]_0}} \tag{17}$$

Numerical values of elliptic integrals may be found in a number of mathematical handbooks [4,5].

The other non-stoichiometric case occurs when $[B]_0<[A]_0$, or component B is the limiting reactant. Mathematically, this case is handled by merely interchanging $[A]_0$ with $[B]_0$ in Eq. (13) for the reaction time, as well as in Eq. (15) for the moduli at both integration limits and in Eqs. (16) and (17) for the two amplitudes of the incomplete elliptic integrals.

4. Special cases

Two special cases of this reaction system may be addressed. The stoichiometric case wherein $[A]_0=[B]_0$ does not result in the appearance of elliptic integrals. The rate expression of Eq. (10) in this case may be rewritten as:

$$\frac{d\xi}{dt}=K([A]_0-\xi)\sqrt{([C]_0+\xi)} \tag{18}$$

which may be integrated to yield for the reaction time:

$$t=\frac{1}{K\sqrt{[A]_0+[C]_0}}\left(\ln_e\left(\frac{\sqrt{[C]_0+\xi}+\sqrt{[A]_0+[C]_0}}{\sqrt{[C]_0+\xi}-\sqrt{[A]_0+[C]_0}}\right)-\ln_e\left(\frac{\sqrt{[C]_0}+\sqrt{[A]_0+[C]_0}}{\sqrt{[C]_0}-\sqrt{[A]_0+[C]_0}}\right)\right) \tag{19}$$

This latter expression may be rearranged by taking advantage of the properties of logarithms, but it does not appear to be amenable to significant simplification.

Secondly, we consider the case of a termolecular reaction, not autocatalytic but between three reactants which first dissociate into reactive intermediates as described by Eqs. (2)–(4). It should be clear in this case that, insofar as the differential equation describing this termolecular process would be similar to that of Eq. (10) ($[C]_0 - \xi$) rather than ($[C]_0 + \xi$) appearing in the radicand], elliptic integrals should also appear in the integrated solution when the initial reactant ratios are not stoichiometric.

5. Numeric calculation

We illustrate the usage of elliptic integrals in the calculation of the reaction time for this autocatalytic termolecular reaction system with a simple example. The following values for the reaction equilibria and rate constants will be taken:
$K_1 = 2\times10^{-10}$ gmol l^{-1}
$K_2 = 4\times10^{-12}$ gmol l^{-1}
$K_3 = 1\times10^{-8}$ gmol l^{-1}
$k_1 = 5\times10^{10}$ l^2 gmol^{-2} s^{-1}

The value of the lumped constant K as defined in Eq. (11) is then equal to 1.414×10^{-4} $l^{1/2}$ gmol$^{-1/2}$ s^{-1}. The following values of initial concentrations will be assumed here:
$[A]_0 = 0.8$ gmol l^{-1}
$[B]_0 = 1.2$ gmol l^{-1}
$[C]_0 = 0.01$ gmol l^{-1}
which is clearly non-stoichiometric, and hence Eq. (13) is applicable. We pose the problem of determining the reaction time required to achieve 80% conversion of the limiting reactant (A) or, equivalently, to attain a reaction extent of $\xi = (0.8)(0.8) = 0.64$ gmol l^{-1}.

From Eq. (15) the moduli k_i for this case are evaluated as 0.818. The amplitude at the lower limit of integration (ϕ_2) is equal to 0.111 from Eq. (16), while that at the upper limit (ϕ_1) is found from Eq. (17) as 1.110. The two required elliptic integrals, at the upper and lower limits of integration, are then evaluated [4] as 1.2828 and 0.1117, respectively. Finally, from Eq. (13), the reaction time required for 80% conversion of the limiting reactant A is 15 060 s, or 4.18 h. The course of this autocatalytic termolecular reaction system, with the reaction parameters and initial concentrations of the above example, is plotted in Fig. 1 in coordinates of the percentage conversion of the limiting reactant A as a function of the reaction time. The S-shaped curve presented therein is a classical characteristic of the behavior of autocatalytic reaction systems [6].

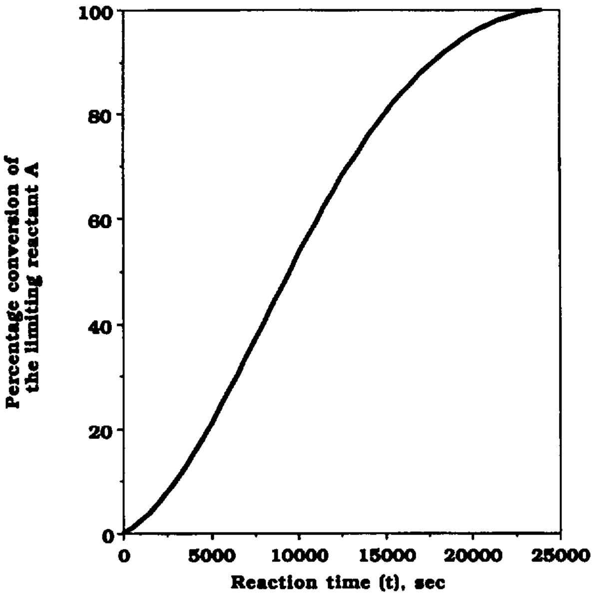

Fig. 1. Percentage conversion of the limiting reactant A as a function of the reaction time (t) for an autocatalytic termolecular reaction with reactive intermediates. Reaction equilibria and rate constants: $K_1 = 2\times10^{-10}$ gmol l^{-1}, $K_2 = 4\times10^{-12}$ gmol l^{-1}, $K_3 = 1\times10^{-8}$ gmol l^{-1}, $k_1 = 5\times10^{10}$ l^2 gmol^{-2} s^{-1}. Initial concentrations: $[A]_0 = 0.8$ gmol l^{-1}; $[B]_0 = 1.2$ gmol l^{-1}; $[C]_0 = 0.01$ gmol l^{-1}.

6. Conclusions

Analytical solutions have been developed for the differential equation describing the reaction kinetics of a nominally bimolecular reaction, catalyzed by one of the reaction products, and with the rate-limiting reaction step actually occurring between reactive intermediates of low concentrations. When the reactants are initially present in stoichiometric proportions, this differential equation may be integrated in conventional fashion to obtain an explicit expression for the reaction time as a function of the reaction extent. If the reactants are not initially present in a stoichiometric ratio, then the integrated expression for the reaction time incorporates elliptic integrals involving the reaction extent, specifically, incomplete elliptic integrals of the first kind. An example calculation for this latter case is also presented.

Appendix A. Nomenclature

[A]	concentration of reactant A
[B]	concentration of reactant B
[C]	concentration of catalytic product C
$F(\phi,k)$	incomplete elliptic integral of the first kind
I	general elliptic integral of the function $R(x,y)$
$[I_j]$	concentration of intermediate reactive species j (where $j = 1, 2, 3$)
K_j	equilibrium constant for the chemical reaction forming I_j ($j = 1, 2, 3$)
K	defined as the product of $\sqrt{K_1K_2K_3}$ and k_1
k	modulus of incomplete elliptic integrals
k_1	third-order rate constant for the autocatalytic reaction
R	rational function of x and y
t	reaction time
x	integration variable in the general elliptic integral
y	cubic or quartic function of the variable x
ϕ	amplitude of incomplete integral of the first kind
θ	integration variable in elliptic integrals of the first kind
ξ	extent of a chemical reaction

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