



Coupled autocatalytic reactions: Interconversion and extinction of species



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ARTICLE INFO

Keywords:

Autocatalytic reactions
Bifurcation Theory
Singularity theory
Species interconversion
Extinction

ABSTRACT

An autocatalytic reaction involves a species catalyzing its own formation and can be viewed as a mechanism to explain self-replication. This class of chemical reactions can be used to model phenomena across a wide cross-section of disciplines, i.e. chemical reaction engineering, biology, ecology, social sciences and economics. Here, we study a system of two species undergoing autocatalysis. Each species participates in the autocatalysis of the other. The autocatalytic reactions can represent interconversion of two social groups or isomers into each other. The two autocatalytic steps are assumed to be elementary and follow cubic and quadratic laws. We examine the behavior of this coupled autocatalytic system at steady state. Specifically, singularity theory and bifurcation theory are applied to classify the bifurcation behavior of the system. The focus of the work is to obtain the conditions for extinction or complete conversion of one of the species. We analyze the system for all combinations of generation and decay reactions. We find the common features and dominant factors in the different combinations analyzed.

1. Introduction

Autocatalysis or self-replication arises across various disciplines like chemistry, ecology (*animal reproduction*), economics (*sustained growth of goods and services*), biology (*DNA replication, RNA polymerization*). Autocatalytic systems due to the positive feedback inherent in them, show interesting non linear behavior like multiple steady states and oscillations. In the context of chemical reaction engineering, the dynamics of autocatalytic reactions were studied in Gray and Scott (1983, 1984).

In Gray and Scott (1983, 1984), the bifurcation behavior of the cubic ($A + 2B \rightarrow 3B$) and quadratic ($A + B \rightarrow 2B$) autocatalytic reactions in an open system was discussed. In Merkin et al. (1987a), the bifurcation behavior of the cubic autocatalator in a closed system under the pooled chemical approximation was studied. Further, in Merkin et al. (1987b) and Gray et al. (1989) the effect of additional reactions like uncatalyzed generation ($A \rightarrow B$) and quadratic autocatalysis ($A + B \rightarrow 2B$), substrate decay reaction ($A \rightarrow C$) on the system behavior was studied. In Balakotaiah (1987), the steady state behavior of a reversible autocatalytic reaction was analyzed. Spatial pattern formation in these systems was analyzed in subsequent years Kay and Scott (1988).

Other important coupled autocatalytic model systems studied extensively include the Brusselator (Prigogine and Lefever, 1968) and the Oregonator (Field and Noyes, 1974) which exhibit temporal oscillations. Coupled systems in which two species are produced

autocatalytically are also found in the literature. In ecology, the classical Lotka-Volterra predator-prey equations can be viewed as arising from an autocatalytic reaction (Lotka, 1910; Goel et al., 1971). Mutualism or co-operation in species can also be modeled by a coupled autocatalytic system. Complementary metabolism is discussed in Meyer et al. (1975); here, each species produces substances which catalyze the autocatalysis of the other species. Hypercycles (Manfred, 1971; Manfred and Peter, 2012) are another example of systems, where two species directly catalyze the autocatalysis of the other. This can be represented by



In this paper, we analyze another coupled autocatalytic system (2) where each species catalyzes the autocatalysis of the other species. This kind of coupling hasn't been studied so far. Here, each species acts as a substrate and gets consumed in the autocatalysis. This is distinct from a hypercycle, where the species catalyze the autocatalysis without getting consumed (i.e. in (1), B and A are not consumed in the two reactions respectively). The system we propose here is comprised of two species A and B both undergoing autocatalysis. One undergoes cubic autocatalysis while the other quadratic autocatalysis. Further, the system is coupled as each species participates in the autocatalysis of the other. Such systems can arise in the interconversion of two species. The asymmetry in this interconversion is introduced by the different orders of the autocatalysis. While both conversions need only one molecule of

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species B , the conversion to A needs two molecules of A and the conversion to B needs only one molecule of A .



This kind of interconversion can arise when the two chemical species are isomers. It can be a possible mechanism to obtain one enantiomer from another and hence, can be useful to convert a racemic mixture to a pure enantiomer. Enantiomers are known to undergo autocatalytic reactions. Their property of asymmetric autocatalysis is exploited to obtain the desired enantiomer by introducing it in excess in the system. Asymmetric autocatalysis was proposed by Frank (1953) and was experimentally proved 40 years later in the form of Soai reaction (Shibata 1996).

However, our proposed model is different from asymmetric autocatalysis in the literature. In asymmetric autocatalysis, the presence of an enantiomer (E) drives the substrates (S) to replicate that particular enantiomer ($S + E \rightarrow 2E$). This property can be exploited to obtain a solution containing a pure desired enantiomer, by introducing it in the solution. In contrast to asymmetric autocatalysis, where the substrate forms a particular enantiomer; in our reaction scheme (2), there is no substrate. Here, instead of a substrate, an enantiomeric species (E') in the presence of its optical isomer (E) gets converted into its optical isomer (3) and vice versa (4).



The model (2) proposed here has not been studied in the context of chemical reaction engineering. Realizing such a reaction scheme experimentally could help obtain a pure enantiomer from a racemic mixture. In this work, the autocatalytic species play the role of optical isomers. We specifically focus on the operating conditions under which we obtain a single species, that is a pure enantiomer as product.

The reactions in (2) can also represent an interaction between social or religious groups. The reaction system can be regarded as a basic model which captures the two way interconversion of these groups. Turchin (2003) discusses a threshold model which captures the interconversion of two groups- core (C) and periphery (P) ethnies. It is known as a threshold model, as the conversion into C occurs only when the concentration of C exceeds a threshold C_o . This system behavior is captured by (5). This model has been used to capture 'invasion', the case when a small group of invaders (P) captures a large ethnically diverse group (C). Here, the direction of conversion is dependent on the net population of the diverse group. This is analogous to our system (2), in the sense that it can be viewed as being made of a cubic and quadratic autocatalysis. Here, we can view C and P as undergoing cubic and quadratic autocatalysis respectively. Turchin analyzed the spatiotemporal behavior of the autocatalytic model in this context. The context of social groups is mentioned to highlight the versatility of the system. In this work, we focus only on the behavior of the species as isomers.



In addition to the two reactions in (2), uncatalyzed generation and decay of these species are included. This makes the system more realistic. We capture the non linear behavior of this system by applying Singularity theory and Bifurcation theory. An important question to ask is in a system where both species exist under what conditions will only one of the species remain. In a system of enantiomers reacting autocatalytically, this corresponds to conversion of a racemic mixture to a pure enantiomer. The analysis in this work will help understand the operating conditions to obtain a desired enantiomer from an undesired enantiomer. It would also help in the development of new technologies based on the proposed model. The effect of the generation and decay reactions on the system is analyzed in particular.

The outline of the paper is as follows: In Section 2, we discuss the model and present the rate equations. In Section 3, the critical surfaces in parameter space are determined across which the bifurcation diagrams change. In Section 4, the bifurcation diagrams obtained for a particular set of parameters are discussed. In Section 5, we find the conditions where at steady state only one species is obtained from a mixture of two species (formation of pure product). In Section 6, we summarize the key results obtained.

2. System

In this work, we consider two species which undergo a quadratic and cubic autocatalytic reaction in an isothermal closed system. The species denoted by A and B , are produced by precursors P_1 and P_2 respectively according to reactions (6) and (7). Reactions (6) and (7) are assumed to follow simple first order kinetics, with rate constants k_{pa} and k_{pb} respectively. The concentration of P_1 and P_2 is assumed to be in excess and the rate of their decay is very slow. Hence, they are assumed to be constant over the time of study (pooled chemical approximation).



Species A grows following a cubic autocatalysis while species B grows following a quadratic autocatalysis. The autocatalysis of both species is coupled as seen in reactions (8) and (9).



Additionally, reactants A and B undergo decay reactions to form inert species D_1 and D_2 . These follow first order kinetics.



The evolution of concentration of species A and B with time T is governed by the following equations,

$$\frac{dA}{dT} = k_{pa}P_1 + k_{ga}A^2B - k_{gb}AB - k_{da}A \quad (12)$$

$$\frac{dB}{dT} = k_{pb}P_2 - k_{ga}A^2B + k_{gb}AB - k_{db}B \quad (13)$$

We make the above evolution equations dimensionless by using the scaling

$$\begin{aligned} a &= \frac{k_{ga}}{k_{gb}}A, \quad b = \frac{k_{ga}}{k_{gb}}B, \quad p_a = \frac{k_{ga}^2}{k_{gb}^3}k_{pa}P_1, \quad p_b = \frac{k_{ga}^2}{k_{gb}^3}k_{pb}P_2, \quad d_a = \frac{k_{ga}}{k_{gb}^2}k_{da}, \\ d_b &= \frac{k_{ga}}{k_{gb}^2}k_{db}, \quad t = \frac{k_{gb}^2}{k_{ga}}T \end{aligned}$$

The dimensionless concentration of A i.e. a can also be viewed as the ratio of the autocatalytic formation rate of A to that of B because $a = \frac{k_{ga}A^2B}{k_{gb}AB}$. The dimensionless concentration of B i.e. b is the product of relative autocatalytic rate and relative amount of B compared to A , as $b = \frac{k_{ga}A^2B}{k_{gb}AB}$. The above scaling subsumes the reaction rate constants of autocatalytic reactions (k_{ga} , k_{gb}) in the dimensionless variables. We have modified the scaling used in Merkin et al. (1987b) where the motivation was to ensure validity of pooled chemical approximation by keeping the product ' $k_{pa}P_1$ ' together. There, the reaction rates of cubic autocatalysis and decay reaction were subsumed. In our modified scaling also, the pooled chemical approximation is valid. Also, the other dimensionless variables- p_a , p_b , d_a , d_b represent the magnitude of rate of generation and decay reactions.

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