CHEMICAL AMPLIFICATION THROUGH COMPETITIVE AUTOCATALYSIS

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Abstract. Linear stability analysis shows that in a theoretical system, which consists of two first order and two autocatalytic reactions, symmetry breaking takes place under certain circumstances. Total separation can be achieved if the stabilizing first order reactions are omitted from the mechanism.

1. Introduction

My goal has been to develop a model in which an asymmetrical outcome is produced from entirely symmetrical original conditions. The problem has come up mainly in studies on the origin of chemical chirality [1–4]. An autocatalytic model has been proposed by Calvin [3] under the influence of Havinga's experimental results [2] which suggested that optical activity might have developed spontaneously. Autocatalytic processes, in which a substance catalyses its own production, have been of great interest recently. The general conclusion, drawn from experiments [5, 6], computations [7] and theory [8–13], is that autocatalysis plays an important role in the development of spatial and temporal structures.

In Calvin's system the substance of interest, B, evolves from A: the left-handed lB from lA, the right-handed dB from dA. The rate of racemization between dA and lA, which are present initially in equal amounts, is infinitely fast. The rate constants for the reactions of the same kind are also equal. The mechanism consists of two first order and two autocatalytic steps.

$$\begin{aligned} & lA \overset{K}{\rightleftharpoons} dA \\ & lA \xrightarrow{k'} lB \\ & dA \xrightarrow{k'} dB \\ & lA + lB \xrightarrow{k^*} 2\,lB \\ & dA + dB \xrightarrow{k^*} 2\,dB. \end{aligned} \tag{1}$$

Since the racemization between the two forms of A is infinitely fast, fluctuations propagate freely between the d and l sides. As a result, Calvin stated, the first fluctuation will drive the total amount of A into either pure dB or pure lB, because the fluctuation is amplified by the two autocatalytic reactions.

Hochstim has provided a detailed critique [4] of the model, which under these conditions will always produce a 50–50% mixture of dB and lB. Total separation could be achieved only if a very large disproportion were present at the beginning; that, however, would sidetrack the original idea of symmetry breaking. A more sophisticated approach, the so-called 'assisted bifurcation', has been initiated by Prigogine *et al.* [12].

In this article a simple mechanism is described which satisfies both the requirement for perfect symmetry at the beginning and that the symmetry is broken by an infinitesimal fluctuation which is amplified by the nonlinearities of the system.

2. The Model

The model is a closed system, which consists of only two species, X and Y. At $t = 0$ X and Y are present in equal concentrations, $x = y = a/2$. The two substances are converted into each other in regular first order and autocatalytic third order reactions. The rate constants for the reactions of the same kind are equal.

$$\begin{aligned} &X \xrightarrow{k_1} Y \\ &Y \xrightarrow{k_1} X \\ &2X + Y \xrightarrow{k_2} 3X \\ &2Y + X \xrightarrow{k_2} 3Y. \end{aligned} \tag{2}$$

Considering that $x + y = a$ at all times, the rate of the reaction is

$$\mathrm{d}x/\mathrm{d}t = k_2(a - x)x^2 - k_2x(a - x)^2 + k_1(a - x) - k_1x.$$

A new time scale is introduced which is related to the original one with a $2k_2$ multiplier, and from now on $k = k_1/k_2$ will be used in the calculations. The rate equation acquires the following form:

$$\mathrm{d}x/\mathrm{d}t = -x^3 + 1.5ax^2 - (a^2/2 + k)x + ak/2. \tag{3}$$

First the steady states have to be located; the solution of (3) for $\mathrm{d}x/\mathrm{d}t = 0$ is

$$x_{ss} = a/2 \quad \text{if} \quad a^2/4 \leq k, \tag{4}$$

$$(x_{ss})_1 = a/2, \qquad (x_{ss})_{2,3} = a/2 \pm (a^2/4 - k)^{1/2} \quad \text{if} \quad a^2/4 > k.$$

An infinitesimal perturbation $\mu = \mu_0 \exp(\Theta t)$ is applied to the steady states in order to determine their stability [9]. The general result is

$$\Theta = 3x_{ss}(a - x_{ss}) - a^2/2 - k. \tag{5}$$

If the steady state is stable Θ is negative, if the steady state is unstable Θ is positive. We know from (4) that if $k > a^2/4$ there is only one steady state at $x_{ss} = a/2$. Substituting into (5)

$$\Theta = a^2/4 - k < 0,$$

that is, the steady state is always stable. Under these circumstances symmetry breaking does not take place and the original 50–50% mixture of X and Y will resist change; as a matter of fact, even if the initial composition were unevenly devided between X and Y, the system would evolve into this steady state.

It should be noted, that if $a^2/4 = k$, $\Theta = 0$, and the steady state is marginally stable.

The situation becomes dramatically different if $a^2/4 > k$. The steady state at $a/2$ loses its stability, since

$$\Theta = a^2/4 - k > 0.$$

At the same time, the two other steady states at $a/2 \pm (a^2/4 - k)^{1/2}$ are both stable:

$$\Theta = 2k - a^2/2 < 0.$$

Under these conditions the system which has equal concentrations of X and Y will evolve toward one of the stable steady states, depending on which direction the fluctuations move the system from the unstable steady state.

3. Conclusion

A symmetry breaking model has been proposed in which chemical amplification takes place as the result of a competition between two autocatalytic reactions. The two stable steady states are located at equal distance from $a/2$. The distance depends only on the ratio between the first order and the autocatalytic rate constants. Complete separation is achieved if $k \to 0$.

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