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Chemical Reactions as Dynamical Systems on the Interval

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We consider the most general chemical reaction of the type

$$n_1 A_1 + \cdots + n_N A_N \rightleftharpoons m_1 B_1 + \cdots + m_M B_M$$

where N, $M \geqslant 1$, $n_1, \ldots, n_N$ and $m_1, \ldots, m_M$ are positive integers defining the stoichiometry, and $A_1, \ldots, A_N$ and $B_1, \ldots, B_M$ are the names of chemicals or ions. We assume that $\sum_{i=1}^N n_i = \sum_{j=1}^M m_j$. The time evolution of the concentrations is given by the law of mass action and leads to a dynamical system (with discrete or continuous time) which is governed by a polynomial map of the interval $[B, C]$, where $B \geqslant 0$ and $C \leqslant 1$. We define the physically meaningful range for the parameters of the map, and we show that, within such a range, the map has a unique fixed point, which is stable and a global attractor, with the exception of one particular case, where bifurcation is observed.

KEY WORDS: Boltzmann; chemical kinetics; stability; chaos; entropy.

1. INTRODUCTION

The study of the evolution of complex chemical reactions constitutes a large field of research which is still the subject of some dispute.(1) Not everyone agrees as to the cause of the chaotic behavior seen experimentally. Even the chaos sometimes found in numerical simulations might be more a result of the approximations than a property of the original dynamical system. We take the view that these questions are best tackled by an exact analysis of models, and this paper is the first of a series in which models of increasing complexity are studied.

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In ref. 2 a general method is described for constructing "stochastic models" of chemical reactions, of the form

$$n_1 A_1 + \cdots + n_N A_N \rightleftharpoons m_1 B_1 + \cdots + m_M B_M$$

The process is regarded as "stirred," that is, the state is described by the concentrations $p_{A_1},..., p_{A_N}$ and $q_{B_1},..., q_{B_M}$. In the stochastic model, $p_{A_j} = p_j$ and $q_{B_k} = q_k$ are regarded as the (relative) probabilities that a particle, randomly fished out, will be, respectively, of type $A_1,..., B_M$. Here, we do not consider the case where some of the A's and B's are the same chemical, called the autocatalytic case, as this will be the subject of a future paper.

For the nonautocatalytic case, which we investigate here, i.e., for the case when no A is equal to any B, the law of mass action gives the rate equations

$$\begin{aligned} \frac{dp_j}{dt} &= n_j \lambda (q_1^{m_1} \cdots q_M^{m_M} - p_1^{n_1} \cdots p_N^{n_N}), \qquad j = 1,..., N \\ \frac{dq_k}{dt} &= -m_k \lambda (q_1^{m_1} \cdots q_M^{m_M} - p_1^{n_1} \cdots p_N^{n_N}), \qquad k = 1,..., M \end{aligned} \tag{1}$$

where $\lambda > 0$ is the rate constant. These generalize the equations of refs. 3 and 4.

If $n_1 + \cdots + n_N = m_1 + \cdots + m_M$, we say the system is "balanced." In that case$^{(2)}$ we can express the discrete form

$$\begin{aligned} p_j^* &= p_j + n_j \mu (q_1^{m_1} \cdots q_M^{m_M} - p_1^{n_1} \cdots p_N^{n_N}), \qquad j = 1,.., N \\ q_k^* &= q_k - m_k \mu (q_1^{m_1} \cdots q_M^{m_M} - p_1^{n_1} \cdots p_N^{n_N}), \qquad k = 1,..., M \end{aligned} \tag{2}$$

as a Boltzmann map on a probability space and this guarantees that (p^*, q^*) is a probability (p_i, q_j lie in $[0, 1]$ and $\sum p_i + \sum q_j = 1$) and that entropy is a nondecreasing function along the map, for a range of $\mu > 0$. The fact that (2) looks like a discretization of (1) will be discussed in a future paper.

The "stochastic models" require the equations to be balanced. Thus, the total number of particles is conserved. Classical probability cannot describe models in which the number of particles changes; a second-quantized theory would be needed if the particles appear and disappear. (There is no difficulty in classically describing particles that change identity.) The interaction is described by a bistochastic matrix T, whose entries are limited by the Markov condition. Within this class, the Boltzmann map must take probability measures to probability measures, since it is given by the composition of maps:

$$p \mapsto \underbrace{p \otimes p \otimes \cdots \otimes p}_{n \text{ times}} \mapsto T\left(\bigotimes_{1}^{n} p\right) \xmapsto{E} \tau p \tag{3}$$

where the last map E is conditional expectation onto the first factor, $n = \sum_1^N n_i$, and T is a bistochastic matrix of size $(N+M)^n \times (N+M)^n$.[2]

It is for this class of models that we here prove the existence and uniqueness of the fixed points and convergence to them. Equations (1) and (2) involve $N+M$ unknowns $p_1,..., q_M$, and $N+M-1$ relations given by $\sum p_i + \sum q_j = 1$ and the conserved quantities of the equations, of which there are $N+M-2$ further independent ones. Thus the dynamics reduces to a nonlinear map $[B, C] \mapsto [B, C]$ for the remaining single variable, where the nonnegativity of the probabilities implies that $B \geqslant 0$ and $C \leqslant 1$. In Section 2 we give some examples of chaotic maps. In Section 3 we study the detailed case $nA \rightleftharpoons mB + lC$, some of the results of which are useful in Section 3.1, which "generalizes" this to $nA \rightleftharpoons m_1 B_1 + \cdots + m_M B_M$. In Sections 4 and 5 we treat the remaining cases. For technical reasons, the cases in Sections 3 and 5 cannot be treated as special cases of those in Section 4. Section 6 is devoted to the study of the stability of the fixed points and to questions concerning the entropy of the systems.

If the couplings μ in τ become large, we see the usual phenomena of bifurcation and chaos. However, there is an upper bound, μ_0, for μ beyond which the matrix T is not bistochastic. We call $[0, \mu_0]$ the "bistochasticity" range for μ, which is also the physically meaningful range. We find that the lower bound for μ such that chaos occurs is larger than μ_0; therefore this phenomenon is not allowed in this theory except for values of the parameter which make no physical sense (e.g., corresponding to negative cross sections). The most complex behavior we observe, within the physical limits, is the emergence of limit cycles of period two, which will be discussed in Section 5.

2. CHAOS FROM CHEMICAL REACTIONS

Let us look at some particular autocatalytic and nonautocatalytic maps.

Example 1. $2A \rightleftharpoons A + B$. In this case we have

$$\tau(p) \equiv p' = (1+\mu)\, p - 2\mu p^2$$

Defining $p=\alpha y+\beta$ with $\alpha=(\mu^2-1)/8\mu$ and $\beta=(1+\mu)/4\mu$, and substituting in the expression for p', we get $y'=1-\nu y^2$, the logistic map,$^{(5)}$ where $\nu=(\mu^2-1)/4$. As the range $\nu\in[3/4, 3/2]$ contains all the values for which the map undergoes bifurcations and eventually chaos, we will see the same patterns arise for $\tau^n(p)$, $n=1, 2,\ldots$, by letting μ vary in $[2, \sqrt{7}]$, and choosing an initial condition $p\in[\beta-\alpha, \beta+\alpha]\subset[0, 1]$.

Example 2. $2A\rightleftharpoons B+C$. Similarly to Example 1, we can transform

$$\tau(p)\equiv p'=p-2\mu(p^2-q_1q_2)$$

into $y'=1-\nu y^2$, by letting $y=\alpha p+\beta$ with $\alpha=6\mu/[\mu^2(4-3c^2)-1]$, $\beta=2(\mu-1)/[\mu^2(4-3c^2)-1]$, and $\nu=[\mu^2(4-3c^2)-1]/4$, where $c=q_1-q_2$ depends on the initial conditions. It can be shown that there exists a subset $[a, b]\subset[0, 1]$ from which a p can be picked up such that c and μ can be adjusted to make ν take all the possible values in $[3/4, 3/2]$, for a fixed y in a subinterval of $[-1, 1]$. Therefore, also this map can give rise to chaotic behavior.

Example 3. $A+B\rightleftharpoons C+D$. Here we can see that

$$\tau(p_1)\equiv p'=p_1-\mu(p_1p_2-q_1q_2)$$

$$\tau^2(p_1)\equiv p''=p_1-\mu'(p_1p_2-q_1q_2)$$

where $\mu'=2\mu-\mu^2$. So, for a given μ we can write $\tau_\mu^{(n)}(p_1)=p_1-\mu^{(n-1)}(p_1p_2-q_1q_2)$, and the dynamics can be thrown from the space of probability measures into the dual space—the space of the maps τ_μ—i.e., we can write $\tau_\mu\mapsto\tau'_\mu=\tau_{\mu'}$. Now, if we let $\mu=y+1$, we can transform the map for μ into $y'=-y^2$, from which we deduce that:

(i) $\mu\in(0, 2)$ implies $\mu^{(n)}\to 1$ as $n\to\infty$.
(ii) $\mu=0$, 2 implies $\mu^{(n)}=0$ for every $n\in\mathbb{N}$.
(iii) $\mu>2$ implies $\mu^{(n)}\to-\infty$ as $n\to\infty$.

More general examples can be given, like $(n+1)A\rightleftharpoons nA+B$, for which $p'=\mu p^n(2p-1)$ and the only nonzero fixed point is $\hat{p}=1/2$. It is easy to see that $\hat{p}$ becomes unstable for $\mu>2^n$; and so on.

On the other hand, if we want to study our reactions within the limits that make physical sense, we must observe the following. Given a chemical reaction of the form presented in Section 1, there is a bistochastic matrix T whose entries $T_{i_1,\ldots,i_n;j_1,\ldots,j_n}$ represent the scattering probabilities for the process $C_{i_1} + \cdots + C_{i_n} \to C_{j_1} + \cdots + C_{j_n}$, where C_{i_k} is one of the A's or of the B's, according to a fixed ordering, e.g., $C_i = A_i$ for $i = 1,..., N$ and $C_{i+N} = B_i$ for $i = 1,..., M$. In order to have $T_{i_1,..., i_n; j_1,..., j_n} \geqslant 0$, we must have

$$\mu \leqslant (n-1)!/\max\{n_1! \cdots n_N!; m_1! \cdots m_M!\}$$

This defines the bistochasticity range. Therefore, the physically meaningful range turns out to be out of the range where instabilities and chaos occur, for the examples previously described. Furthermore, if we aim to approximate the solution of (1) by (2), we are interested in small values of μ, and we fall into the bistochasticity range. Therefore, spurious chaos can be "discovered" in the dynamical system (1) simply by approximating it by (2), with too large a time step, i.e., too large μ.

3. A DETAILED CASE

We consider all the reactions of the form

$$nA \rightleftharpoons mB + lC$$

with $l, m, n \in \mathbb{N}$ and $n = l + m$, so the system is balanced. The method has three stages. We first identify an invariant compact set under the map. Then we show that the iterated map drives any initial state into this set. Finally we show that the map is a proper contraction on this set, and so converges to a unique fixed point from any initial state.(6,7)

The sample space we have is $\Omega = \{A, B, C\}$; then the set of probability measures on it, $\mathscr{Q} = \{P\}$, is made of triples $P = (p_A, p_B, p_C) \in \mathbb{R}^3$ such that $0 \leqslant p_A, p_B, p_C \leqslant 1$, and $\sum_{i=A}^{C} p_i = 1$. The discrete map $\tau\colon \mathscr{Q} \to \mathscr{Q}$ that takes P at the instant t to P' at the instant $t+1$ is defined by the following set of equations:

$$\begin{aligned} p'_A &= p_A - n\mu(p^n_B p^l_C) = p_A - n\mu D, \quad \text{say} \\ p'_B &= p_B + m\mu D \qquad (4) \\ p'_C &= p_C + l\mu D \end{aligned}$$

where $\mu > 0$. D is called the disequilibrium parameter.

We see that the map τ preserves $p_A + p_B + p_C = 1$ and the quantity $q = mp_A + np_B$. That $p'_A, p'_B, p'_C \geqslant 0$ follows from the general result,(2) provided that the system comes from a bistochastic process. The condition for this is $\mu \leqslant 1/n$. Then, the nonnegativity of p_B and p_C implies $p_A \leqslant q/m$ and $p_A \leqslant (n-q)/l$, and eliminating p_B and p_C, we get a map $p'_A = p_A - n\mu D(p_A)$ from $[0, C]$ to itself, where $C = \min\{1, q/m, (n-q)/l\}$, which we also denote by τ. Our first lemma identifies $[0, 1/2]$ as an invariant subset, for the cases in which $C \geqslant 1/2$.

Lemma 1. If $C \geqslant 1/2$ and $\mu \leqslant 1/n$, the interval $[0, 1/2]$ is invariant under τ; otherwise it is $[0, C]$ that is invariant.

Proof. If $C \leqslant 1/2$, the preservation of the probabilities under τ trivially makes $[0, C]$ invariant. Therefore, let us take $C > 1/2$ and $x = p_A \in [0, 1/2]$. If $D \geqslant 0$, then $x' = x - \mu n D(x) \leqslant x$, so $x' \in [0, 1/2]$. So we may assume $D(x) < 0$. Then $x' \leqslant x - D(x) = x - x^n + p_B^m p_C^l$. Let $\gamma = 1 - x$. The maximum of $p_B^m p_C^l$, subject to $p_B + p_C = \gamma$, occurs where its logarithm is a maximum. But $m \log y + l \log(\gamma - y)$ has its maximum at y such that $m/y = l/(\gamma - y)$, i.e., $y = \gamma(m/n)$, $\gamma - y = \gamma(l/n)$. So, putting $p_B = y$ and $p_C = \gamma - y$, we get, for $D < 0$,

$$x' \leqslant x - x^n + \left(\frac{m}{n}\right)^m \left(\frac{l}{n}\right)^l (1 - x)^n = f(x) \quad \text{say} \tag{5}$$

For $n = 2$ and $l = 1 = m$ the right-hand side is $x - x^2 + (1 - x)^2/4$, which takes its maximum value, 1/3, at $x = 1/3$, giving $x' \leqslant 1/3 \in [0, 1/2]$. For $n = 3$, $l = 1$, $m = 2$ (or vice versa) we get $f(x) = x - x^3 + 4(1 - x)^3/27$, which has its maximum at $x = (8 + \sqrt{684})/62 \approx 0.55$ and its minimum at $x = (8 - \sqrt{684})/62 < 0$. Hence f is monotonic increasing in $[0, 1/2]$ and $f(x) \leqslant f(1/2) < 1/2$. Hence $x' \in [0, 1/2]$.

Finally, for $n \geqslant 4$, as m and l vary, $m + l = n$,

$$\log[(m/n)^m (l/n)^l] = m \log(m/n) + l \log(l/n)$$

the negative entropy function, has its minimum at $l = m$, and is concave, so takes its maximum at the endpoints $l = 1$, $m = n - 1$ (or vice versa). Hence we get

$$x' \leqslant x - x^n + \left(\frac{n-1}{n}\right)^{n-1} \frac{1}{n} (1 - x)^n < x - x^n + \frac{1}{n} (1 - x)^n = f_1(x) \tag{6}$$

If $x \leqslant 1/4$, $x' < 1/4 + 1/n \leqslant 1/2$, so we may limit the discussion to $x \in [1/4, 1/2]$. Now, f_1 is an increasing function in this range, as, for $n \geqslant 4$,

$$f_1'(x) = 1 - n x^{n-1} - (1 - x)^{n-1} \geqslant 1 - 4(1/2)^3 - (3/4)^3 > 0 \tag{7}$$

So

$$f_1(x) \leqslant f_1\left(\frac{1}{2}\right) = \frac{1}{2} - \left(\frac{1}{2}\right)^n + \frac{1}{n}\left(\frac{1}{2}\right)^n < \frac{1}{2}$$

This proves $x' \in [0, 1/2]$ for $n \geqslant 4$, too. ■

We note that by Brouwer's fixed-point theorem,$^{(7)}$ τ has a fixed point in $[0, 1/2]$. We now show that the set $[0, 1/2]$ is a global attractor.

Lemma 2. If $C > 1/2$ and $x \in [1/2, C]$, then $\tau^k x \in [0, 1/2]$ for all $k \geqslant 2^{n-1}/\mu(n-1)$.

Proof. If $x \in [1/2, C]$, $1 - x = \gamma \leqslant 1/2$, and we have

$$\begin{aligned} x - x' &= n\mu(x^n - p_B^m p_C^l) \\ &\geqslant n\mu\left\{\left(\frac{1}{2}\right)^n - \max_{0 \leqslant y \leqslant \gamma} [y^m(\gamma - y)^l]\right\} \\ &= n\mu\left[\left(\frac{1}{2}\right)^n - \left(\frac{m}{n}\right)^m \left(\frac{l}{n}\right)^l \gamma^n\right] \\ &\geqslant n\mu\left[\left(\frac{1}{2}\right)^n - \left(\frac{n-1}{n}\right)^{n-1} \frac{1}{n}\left(\frac{1}{2}\right)^n\right] \\ &> n\mu\left(\frac{1}{2}\right)^n \left(1 - \frac{1}{n}\right) = \varepsilon \end{aligned} \tag{8}$$

So a step left of size $> \varepsilon$ occurs as long as $x \geqslant 1/2$, so we reach $1/2$ in at most $1/(2\varepsilon) = 2^{n-1}/\mu(n-1)$ steps. ■

We note that the conserved quantity q lies between 0 and n. If $q = 0$, then $p_A = 0 = p_B$ and if $q = n$, $p_A = 0 = p_C$ and the reaction does not take place, i.e., we are at a fixed point. If $0 < q < n$, the motion, inside $\mathcal{Q}$, is confined to a line not intersecting these fixed points. The motion therefore lies at a distance $\geqslant \delta > 0$ from these fixed points. We now show that the map τ is a contraction with norm uniformly less than 1 in $[0, a]$, where $a = \min(C, 1/2)$.

Lemma 3. If $0 < q < n$, and $\mu \leqslant 1/n$, then τ is a contraction on $[0, a]$.

Proof. As $a \leqslant 1/2$, it is safe to study τ in $[0, 1/2]$. We show that $\sup_{x \in [0,1/2]} |(d/dx)\,\tau(x)| < 1$. Note that $p_B = (q - mx)/n$ and $p_C = (n - q - lx)/n$. Then

$$\begin{aligned} \frac{d\tau}{dx} &= 1 - n^2\mu x^{n-1} - m^2\mu(q - mx)^{m-1} \frac{p_C^l}{n^{m-1}} \\ &\quad - l^2\mu p_B^m \frac{(n - q - lx)^{l-1}}{n^{l-1}} \\ &= 1 - n^2\mu x^{n-1} - m^2\mu p_B^{m-1} p_C^l - l^2\mu p_B^m p_C^{l-1} \\ &= 1 - F(x) \quad \text{say} \end{aligned} \tag{9}$$

Since $F(x)>0$ and continuous on a compact set, we have

$$\inf_{x\in[0,1/2]} F(x)>0 \qquad \text{so} \qquad \frac{d\tau}{dx}<1-\varepsilon, \qquad x\in[0,1/2]$$

for some $\varepsilon>0$. So it remains to show $F(x)<2-\varepsilon$.

If $n=2$, $l=1$, and $m=1$,

$$F(x)=\mu(4x+p_B+p_C)=\mu(3x+1)\leqslant\frac{1}{2}\left(\frac{3}{2}+1\right)<2$$

as required.

If $n\geqslant 3$ and $m=1$, $l=n-1$, then, as $\mu\leqslant 1/n$, put $y=p_B$, and

$$F(x)\leqslant\frac{1}{n}\,[n^2x^{n-1}+(1-y)^{n-1}+(n-1)^2\,y(1-y)^{n-2}]$$

The maximum of $H=(1-y)^{n-1}+(n-1)^2\,y(1-y)^{n-2}$ in $0\leqslant y\leqslant 1$ occurs at $y=1/n$. Hence

$$\begin{aligned}F(x)&\leqslant\frac{1}{n}\left[n^2x^{n-1}+H\left(\frac{1}{n}\right)\right]\\&=\frac{1}{n}\left[n^2x^{n-1}+\left(1-\frac{1}{n}\right)^{n-2}(n-1)\right]\\&\leqslant n\left(\frac{1}{2}\right)^{n-1}+\left(\frac{n-1}{n}\right)^{n-1}<3\cdot\frac{1}{4}+1<2\end{aligned}\tag{10}$$

Finally, if $l\geqslant 2$, $m\geqslant 2$, and $n\geqslant 4$, we have

$$F(x)\leqslant\frac{1}{n}\,\{n^2x^{n-1}+y^{m-1}(1-y)^{l-1}\,[m^2(1-y)+l^2y]\}, \qquad 0\leqslant y\leqslant 1 \tag{11}$$

The maximum of $y^{m-1}(1-y)^{l-1}$ occurs at

$$y=\frac{m-1}{n-2}, \qquad 1-y=\frac{l-1}{n-2}$$

and is $(m-1)^{m-1}\,(l-1)^{l-1}/(n-2)^{n-2}$. The maximum of $m^2(1-y)+l^2y$ is $\max(l^2, m^2)$.

As we vary l and m with $l+m=n$ fixed, the maxima of $(m-1)^{m-1}\,(l-1)^{l-1}$ occur at the endpoints $m=2$, $l=n-2$ or vice versa. So

$$\begin{aligned}F(x)&\leqslant\frac{1}{n}\left[n^2x^{n-1}+\frac{(n-3)^{n-3}}{(n-2)^{n-2}}(n-2)^2\right]\\&\leqslant n\left(\frac{1}{2}\right)^{n-1}+\frac{(n-3)^{n-3}}{n(n-2)^{n-4}}<2\end{aligned}\tag{12}$$

3.1. A Generalization

We can now treat the case

$$nA \rightleftharpoons m_1 B_1 + \cdots + m_M B_M$$

with $M \geqslant 3$, which implies $n = \sum_{j=1}^{M} m_j \geqslant 3$. Here we have

$$p'_A = p_A - n\mu(p_A^n - q_1^{m_1} \cdots q_M^{m_M}) = p_A - n\mu D \tag{13}$$

and

$$m_j p_A + nq_j = K_j, \qquad j = 1,\dots, M \tag{14}$$

Before we prove the three lemmas given above for the present case, we need to observe that the maximum of $q_1^{m_1} \cdots q_M^{m_M}$ is achieved at the same place as its logarithm

$$L = m_1 \log q_1 + m_2 \log q_2 + \cdots + m_M \log q_M$$

Let $\sum_i p_i = (p_A \text{ in the present case}) = \gamma$, $\sum_j q_j = (1-\gamma)$ be fixed. Then using a Lagrange multiplier, we get the maximum of L at

$$q_1 = \frac{m_1}{n}\gamma, \dots, \quad q_M = \frac{m_M}{n}\gamma \tag{15}$$

Furthermore,

$$m_1^{m_1} m_2^{m_2} \cdots m_M^{m_M} \leqslant (n - M + 1)^{n-M+1} \tag{16}$$

if $m_1 + m_2 + \cdots + m_M = n$. This can be shown easily in several different ways; e.g., by induction; one needs to check that the statement is true for $M = 1$, and then the general result for $M = N + 1$ is implied by the case for $M = N$ as a consequence of the fact that

$$(K+1)^{K+1} x^x \leqslant (K+x)^{K+x} \qquad \forall x \geqslant 1$$

With this result in our hands, we can prove that

$$\begin{aligned} p'_A &\leqslant p_A - p_A^n + \frac{m_1^{m_1} m_2^{m_2} \cdots m_M^{m_M}}{n^n}(1-p_A)^n \\ &\leqslant p_A - p_A^n + \frac{(n-2)^{n-2}}{n^n}(1-p_A)^n \\ &\leqslant p_A - p_A^n + \frac{1}{n^2}(1-p_A)^n \end{aligned} \tag{17}$$

Let $C = \min[1, \min_j(K_j/m_j)]$ and repeat now, *mutatis mutandis*, the same argument developed for the proof of Lemma 1, to get the same result:

Lemma 1′. If $C \geqslant 1/2$, and $\mu \leqslant 1/n$, the interval $[0, 1/2]$ is invariant under τ; otherwise it is $[0, C]$ that is invariant.

The reasoning used to prove Lemma 2 will lead here to the following:

Lemma 2′. If $C > 1/2$ and $p_A \in [1/2, C]$, then $\tau^k p_A \in [0, 1/2]$ for all $k \geqslant n2^{n-1}/\mu(n^2-1)$.

Finally, we can repeat the proof of Lemma 3, splitting it in two parts: $n = 3$ and $n \geqslant 4$, to get a very similar result for the present case:

Lemma 3′. If $K_j \neq 0$ for $j = 1,..., M$, and $\mu \leqslant 1/n$, then τ is a contraction on $[0, a]$, where $a = \min(C, 1/2)$.

4. THE HIGHER NONAUTOCATALYTIC REACTIONS

We consider

$$n_1 A_1 + \cdots + n_N A_N \rightleftharpoons m_1 B_1 + \cdots + m_M B_M, \qquad M, N \geqslant 2$$

where the chemical types $A_1,..., B_M$ are all different. (If one A_i and one B_j are the same, the reaction is called autocatalytic.) Let n_1 be (one of) the largest coefficients $n_1,..., m_M$. We assume that the reaction is balanced and let $n_1 + \cdots + n_N = m_1 + \cdots + m_M = n$. We have the conserved quantities, in terms of the probabilities $p_1,..., p_n$ of $A_1,..., A_N$ and $q_1,..., q_M$ of $B_1,..., B_M$:

$$\begin{aligned} n_1 q_j + m_j p_1 &= K_j, \qquad j = 1,..., M \\ n_1 p_i - n_i p_1 &= L_i, \qquad i = 2,..., N \end{aligned} \tag{18}$$

The values of the constants of the motion $L_2,..., K_M$ are determined by the initial conditions, and it follows from them that $p_1 \geqslant B = \max[0, \max_{i=2,...,N}(-L_i/n_i)]$ and $p_1 \leqslant C = \min[1, \min_{j=1,...,M}(K_j/m_j)]$. The relations (18) ensure also that $p_2,..., q_M$ are linear functions of p_1, and the motion then becomes a mapping of $[B, C]$ to itself:

$$p'_1 = p_1 - n_1 \mu (p_1^{n_1} \cdots p_N^{n_N} - q_1^{m_1} \cdots q_M^{m_M}) = p_1 - F(p_1) \tag{19}$$

We show that, away from the fixed points on the boundary, $0 < \sup_{p_1} dF/dp_1 < 2$, provided that μ is smaller than the bistochasticity limit. The reaction does not proceed if one of the p_i is zero *and* one of the q_j is zero. Otherwise it does. So a sufficient condition for a fixed point is: K_j vanishes for one value of $j \in \{1,..., M\}$. This deals with p_1 as the special variable. There are other constants of the motion (linear combinations of our K_j, L_i) that correspond to other choices, namely all those of the form $c_{ij}=n_iq_j+m_jp_i$, and if one of them vanishes, the reaction does not proceed. Let $N_0=\min(N, M)$. Then we can prove the following:

Lemma 4. (a) If $c_{ij}\neq 0$ $\forall i, j$, then τ is a contraction on the interval $[B, C]$, provided that N, $M\geqslant 3$ and $\mu<2(n-1)^{N_0-2}/n$. (b) If $M=2$, $N\geqslant 3$, and $c_{ij}\neq 0$ $\forall i, j$, then τ is a contraction on the interval $[B, C]$, if $\mu\leqslant 1/\max(m_j)$. (c) If $N=2$ and $c_{ij}\neq 0$ $\forall i, j$, τ is a contraction on $[B, C]$ whenever $\mu\leqslant 1/n_1$.

Proof. Suppose that all the c_{ij} for $i=1,\ldots, N$ and $j=1,\ldots, M$ are different from zero. Then the reaction proceeds, and the constants of the motion remain the same, so the motion lies on a compact set

$$\mathscr{X}=\{K_j=\text{const}, L_i=\text{const}\}\cap\mathscr{Q}$$

where $\mathscr{Q}$ is the simplex $\{0\leqslant p_i, q_j\leqslant\sum_i p_i+\sum_j q_j=1\}$. This motion remains bounded away from the fixed points we mentioned above, and continuous functions achieve their maxima on $\mathscr{X}$. Now

$$\frac{dF}{dp_1}=\mu\left(\sum_{i=1}^{N} n_i^2p_1^{n_1}\cdots p_i^{n_i-1}\cdots p_N^{n_N}\right.$$
$$\left.+\sum_{j=1}^{M} m_j^2q_1^{m_1}\cdots q_j^{m_j-1}\cdots q_M^{m_M}\right)>0 \tag{20}$$

Hence $\inf_{p_1} F'>0$, and it is bounded away from zero. We now show $\sup_{p_1} F'<2$.

If $n=2$, $F'=\mu(p_1+p_2+q_1+q_2)=\mu\leqslant 1$, and we are done. (Note that the bistochasicity range is $[0, 1]$ in this case.) So we may consider $n\geqslant 3$. By Eqs. (15) we know that the maximum of $p_1^{n_1}\cdots p_{n_i}^{n_i-1}\cdots p_N^{n_N}$ is achieved at

$$p_1=\frac{n_1}{n-1}\gamma,\ldots,\qquad p_i=\frac{n_i-1}{n-1}\gamma,\ldots,\qquad p_N=\frac{n_N}{n-1}\gamma$$

where $\sum_i p_i=\gamma$, $\sum_j q_j=(1-\gamma)$ are fixed. Hence

$$F'\leqslant\mu\left\{\sum_i n_i^2\left(\frac{n_1}{n-1}\right)^{n_1}\cdots\left(\frac{n_i-1}{n-1}\right)^{n_i-1}\cdots\left(\frac{n_N}{n-1}\right)^{n_N}\gamma^{n-1}\right.$$
$$+\sum_j m_j^2\left(\frac{m_1}{n-1}\right)^{m_1}\cdots\left(\frac{m_j-1}{n-1}\right)^{m_j-1}$$
$$\left.\times\cdots\left(\frac{m_M}{n-1}\right)^{m_M}(1-\gamma)^{n-1}\right\} \tag{21}$$

Now use $n_i(n_i-1)^{n_i-1}\leqslant n_i^{n_i}$ and $\sum_i n_i=n=\sum_j m_j$, to get

$$F'\leqslant \mu n\left(\frac{1}{n-1}\right)^{n-1}[n_1^{n_1}\cdots n_N^{n_N}\gamma^{n-1}+m_1^{m_1}\cdots m_M^{m_M}(1-\gamma)^{n-1}] \tag{22}$$

Thus, we can write

$$F'\leqslant d_1\gamma^{n-1}+d_2(1-\gamma)^{n-1}$$

where

$$d_1=\mu n\left(\frac{1}{n-1}\right)^{n-1}(n_1^{n_1}\cdots n_N^{n_N})$$

$$d_2=\mu n\left(\frac{1}{n-1}\right)^{n-1}(m_1^{m_1}\cdots m_M^{m_M})$$

subject to $n_1+\cdots+n_N=n=m_1+\cdots+m_M$. Clearly, we have $F'\leqslant\max(d_1,d_2)$. Consider d_1 first. If $N=2$, suppose $n=2n_1$. Then $n\geqslant 4$ and

$$\begin{aligned} d_1&=\frac{n}{n_1}\left(\frac{1}{n-1}\right)^{n-1}\left(\frac{n}{2}\right)^{n/2}\left(\frac{n}{2}\right)^{n/2}\\ &=2\left(\frac{3n/4}{n-1}\right)^{n-1}\left(\frac{n}{2}\right)\left(\frac{2}{3}\right)^{n-1}\\ &\leqslant n\left(\frac{2}{3}\right)^{n-1}\leqslant\frac{32}{27}<2 \end{aligned} \tag{23}$$

If $N=2$ and $n_1>n/2$

$$d_1=\frac{n}{n_1}\frac{1}{(n-1)^{n-1}}n_1^{n_1}n_2^{n_2}\leqslant\frac{n}{n_1}\frac{1}{(n-1)^{n-1}}(n-1)^{n-1}<2 \tag{24}$$

Now, let $N\geqslant 3$. Using Eq. (16), we get

$$d_1\leqslant\mu n\left(\frac{1}{n-1}\right)^{n-1}(n-N+1)^{n-N+1}\leqslant\mu n\left(\frac{1}{n-1}\right)^{N-2} \tag{25}$$

and then d_1 is smaller than 2 if $\mu<2(n-1)^{N-2}/n$. Similarly, for $M=2$ one gets $d_2<2$ if $\mu\leqslant 1/\max(m_i)$, and d_2 is smaller than 2 for $M\geqslant 3$ if $\mu<2(n-1)^{M-2}/n$. Recalling that $n_1=\max(n_i,m_j)$, we obtain the result. ■

It follows that $\tau^k(p_1)$ converges exponentially to a fixed point as $k\to\infty$, for all the cases in this section. On the other hand, these cases do not exhaust all the physically meaningful ones, because a part of the bistochasticity range has not been covered for a number of reactions. In Section 6 we will prove that convergence to the unique fixed point determined by the initial conditions holds true for all the remaining cases, although we have less explicit control of the convergence in these cases. However, it is worth noting that the interest falls mainly on the small values of μ, which have already been dealt with, when one wants to approximate the solution of (1) by (2).

5. DIFFUSION AND TRANSMUTATIONS

By "transmutations" we mean all the reactions of the form

$$nA \rightleftharpoons nB, \qquad n \geqslant 1, \quad A \neq B$$

because these reactions describe the transformation that takes the substance A into the substance B, and vice versa, without interactions with other substances. We may as well call this kind of reaction "diffusion," as we may interpret A as a certain substance in the volume element V_i and B as the same substance in the volume element V_{i+1} contiguous to V_i. Then the reaction consists of the diffusion of that substance from V_i to V_{i+1} and vice versa. In particular, if $n=1$, the discrete scheme that describes the time evolution of the system under τ coincides with the very well known central difference approximation of the classical diffusion operator $-\Delta$. The time evolution will be described by

$$\begin{aligned} p'_A &= p_A - n\mu(p_A^n - p_B^n) \\ p'_B &= p_B + n\mu(p_A^n - p_B^n) \end{aligned} \tag{26}$$

where the bistochasticity range is $\mu \in [0, 1/n]$ and $p_B = 1 - p_A$. Therefore we have a map of $[0, 1]$ onto itself:

$$p'_A = p_A + n\mu[(1-p_A)^n - p_A^n] = \tau(p_A) \tag{27}$$

Clearly, τ has a unique fixed point: $\overline{p_A} = 1/2$. We are going to prove the following:

Lemma 5. $\lim_{k\to\infty} \tau^k(p_A) = \overline{p_A}$ $\forall p_A \in [0, 1]$ and $\forall n \in \mathbb{N}$ iff $0 < \mu < 1/n$.

Proof. Because of the fact that $p_B = 1 - p_A$, we can limit ourselves to the case $p_A < 1/2$, as the case $p_A > 1/2$ can be treated in the same way by considering p_B as our variable. Then, assuming $p_A < 1/2$, we have

$\tau(p_A) > p_A$ and there are two possible cases: (i) $\tau(p_A) \leqslant 1/2$ and (ii) $\tau(p_A) > 1/2$. Clearly, $|\tau(p_A) - 1/2| < |p_A - 1/2|$, in the first case. So we only need to check what may happen in the second case. Let us consider $n = 1$ first. Then

$$\tau(p_A) - \tfrac{1}{2} = p_A + \mu[(1 - p_A) - p_A] - \tfrac{1}{2} < \tfrac{1}{2} - p_A \tag{28}$$

if and only if $\mu < 1$. Then consider $n \geqslant 2$ and observe that

$$(1 - p_A)^{n+1} - p_A^{n+1} \leqslant (1 - p_A)^n - p_A^n \tag{29}$$

for $p_A < 1/2$. Therefore we have

$$\begin{aligned} p'_A - \tfrac{1}{2} &= p_A + n\mu[(1 - p_A)^n - p_A^n] - \tfrac{1}{2} < p_A + (1 - p_A)^n - p_A^n - \tfrac{1}{2} \\ &\leqslant p_A + (1 - p_A) - p_A - \tfrac{1}{2} = \tfrac{1}{2} - p_A \end{aligned} \tag{30}$$

iff $\mu < 1/n$. Finally, we combine (i) and (ii) and we get $|\tau(p_A) - 1/2| < |p_A - 1/2|$ in the case that $\mu < 1/n$. The convergence follows.

If, instead, $\mu = 1/n$, then we may choose $p_A = 0$ and get

$$\tau(p_A) = 0 + (1 - 0)^n - 0 = 1$$
$$\tau^2(p_A) = 1 + (1 - 1)^n - 1 = 0$$

from which it is clear that the process does not converge to the fixed point. Since this is the limiting case, the occurrence of this bifurcation does not give rise to chaotic evolution. The lemma is proved. ■

We can finally discuss in deeper detail the case $\mu = 1/n$. Here the result is:

Lemma 6. If $n \geqslant 3$ and $\mu = 1/n$, then $\lim_{k \to \infty} \tau^k(p_A) = \overline{p_A}\ \forall p_A \in (0, 1)$. If $n = 1$ or $n = 2$ and $\mu = 1/n$, then τ is a permutation.

Proof. If $n = 1$ or $n = 2$ and $\mu = 1/n$, we have

$$p'_A = p_A + 1 - 2p_A = 1 - p_A = p_B$$

Therefore the map τ is a permutation.

If $n \geqslant 3$ and $0 < p_A < 1/2$, then $\tau(p_A) > p_A$ and again we have two possible cases: (i) $\tau(p_A) \leqslant 1/2$ and (ii) $\tau(p_A) > 1/2$. Case (i) yields $|\tau(p_A) - 1/2| < |p_A - 1/2|$. For case (ii) and $n = 3$, we have

$$\tau(p_A) = p_A + 3\mu(1 - 3p_A + 3p_A^2 - 2p_A^3) \tag{31}$$

Therefore $\tau(p_A) - 1/2 < 1/2 - p_A$ for $p_A \in (0, 1/2)$. Hence, recalling Eq. (29), we can conclude that

$$|\tau(p_A) - \tfrac{1}{2}| < |p_A - \tfrac{1}{2}|$$

for every map τ relating to $\mu = 1/n$ for $n \geqslant 3$. This proves the lemma. ■

6. STABILITY OF THE FIXED POINTS AND ENTROPY INCREASE

As we have seen, given any balanced nonautocatalytic reaction, the iterations of the corresponding map τ will drive the system to a well-determined fixed point. Such a fixed point satisfies

$$p_1^{n_1} \cdots p_N^{n_N} - q_1^{m_1} \cdots q_M^{m_M} = 0 \tag{32}$$

which describes a smooth $(N+M-1)$-dimensional manifold in $\mathbb{R}^{N+M}$, and it satisfies the $N+M-1$ equations (18). Note that the system (32) + (18) has a unique solution in the simplex of probability measures $\mathscr{Q}$. As one of the constants of the motion is not independent of the others, because $\sum p_i + \sum q_j = 1$ is fixed, we get that the set of fixed points of τ is an $(N+M-2)$-parameter family. One element is singled out of this set whenever one set of constants of motion (hyperplanes of the motion) is given. The intersection of the hyperplanes of the motion is a 1-dimensional subspace (the line of the motion) of $\mathbb{R}^{N+M}$; therefore, many different initial conditions correspond to the same set of constants of motion.

Concerning the stability of the fixed points of a given τ, we observe that the case of transmutations shows one fixed point only which is trivially stable, and it is an attractor for every point in $[0, 1]$ if $\mu < 1/n$. For all the other reactions, we use the fact that the zeros of a real polynomial are continuous functions of the coefficients of the polynomial itself, and the fact that the constants of motion imply

$$\begin{aligned} p_1^{n_1} \cdots p_N^{n_N} - q_1^{m_1} \cdots q_M^{m_M} &= p_1^{n_1} \left[\frac{1}{n_1} (L_2 + n_2 p_1) \right]^{n_2} \cdots \left[\frac{1}{n_1} (L_N + n_N p_1) \right]^{n_N} \\ &\quad - \left[\frac{1}{n_1} (K_1 - m_1 p_1) \right]^{m_1} \cdots \left[\frac{1}{n_1} (K_M - m_M p_1) \right]^{m_M} \end{aligned} \tag{33}$$

which is a polynomial whose coefficients depend continuously on the initial conditions. Moreover, the lines of the motion of all possible initial conditions are all parallel. Then the stability of all the fixed points of τ follows from this, from the fact that all the nontrivial fixed points attract every initial condition in their line of the motion, and from the fact that the line of the motion of a trivial fixed point P intersects the simplex $\mathcal{Q}$ in P only. Here, by trivial fixed points we mean those that correspond to one p_i and one q_j equal to zero.

Finally, we note that the fixed point p_1' corresponding to a given choice of the initial conditions maximizes the entropy $S(p_1)$ along the line of the motion, as the map is entropy nondecreasing and every initial condition along such a line converges to p_1', under its iterations, for certain values of the parameter. Furthermore,

$$S(p_1) = -\sum p_i(p_1) \log p_i(p_1) - \sum q_j(p_1) \log q_j(p_1)$$

and

$$\frac{dS}{dp_1} = 0 \qquad \text{if and only if} \qquad p_1 = p_1'$$

We conclude that $S(p_1) < S(p_1')$ unless $p_1 = p_1'$, but more can be proven.

Consider the general balanced reaction

$$n_1 A_1 + \cdots + n_N A_N \rightleftharpoons m_1 B_1 + \cdots + m_M B_M$$

where this time some of the A's may equal some of the B's. Let N_a be the number of autocatalytic elements, and $n = \sum_i n_i$. Every entry of the associated $(N+M-N_a)^n \times (N+M-N_a)^n$ bistochastic matrix T represents the scattering probability for a given channel $C_{i_1} + \cdots + C_{i_n} \rightarrow C_{j_1} + \cdots + C_{j_n}$, and will be written as $T_{i_1 \cdots i_n; j_1 \cdots j_n}$. Here we take $C_i = A_i$ for $i = 1,\ldots, N$ and $C_{i+N} = B_i$ for $i = 1,\ldots, M - N_a$. The remaining B's coincide with some of the A's. For simplicity we choose the same scattering probability for this channel as for the channel $\pi_k(C_{i_1},\ldots, C_{i_n}) \rightarrow \pi_l(C_{j_1},\ldots, C_{j_n})$ where π_k and π_l are any two permutations. Therefore, we can introduce an Abelian group $(G, \cdot)$, with generators $C_1,\ldots, C_{N+M-N_a}$, and call ω_i its words of length n. These constitute a set of $K = (N+M-N_a)^n$ elements. Then we can write $T_{i_1 \cdots i_n; j_1 \cdots j_n} = T_{\omega_i; \omega_j}$. As we assume the principle of microscopic reversibility, we have $T_{\omega_j; \omega_i} = T_{\omega_i; \omega_j}$. Also, $T_{\omega_i; \omega_j}$ is vanishing for those processes $\omega_i \rightarrow \omega_j$ that are not allowed. Now, let $\omega_1 = A_1^{n_1} \cdots A_N^{n_N}$ and $\omega_2 = B_1^{m_1} \cdots B_M^{m_M}$. Then

$$T_{\omega_i; \omega_i} > 0 \qquad \text{for} \quad i = 1, 2 \quad \text{and} \quad T_{\omega_1; \omega_2} > 0$$

provided that the rate constant of the reaction is neither zero nor equal to the upper bound of the bistochasticity range. Also, one gets $T_{\omega_1; \omega_k} = 0$ if

$k \neq 1, 2$. Then, because of the bistochasticity of T, we have $\sum_{\pi,k} T_{\omega_i;\,\pi(\omega_k)} = 1$, which, for $i = 1, 2$, becomes

$$\sum_{\pi} T_{\omega_i;\,\pi(\omega_i)} + \sum_{\pi} T_{\omega_i;\,\pi(\omega_j)} = 1 \qquad \text{for} \quad i \neq j = 1, 2$$

where π has been used to stress that all the permutations must be taken. By the symmetry of T we have thus isolated a bistochastic block in it, $T' = [T_{\pi_k(\omega_i);\pi_l(\omega_j)}]_{i,j=1,2}$, whose elements are all positive. Therefore, $(T')^2_{i,j} > 0$ for every i and j, which implies that the corresponding Boltzmann map τ increases the entropy, unless the input probability is a fixed point.$^{(2)}$ Then, by Theorem 3 in ref. 2 the convergence to the unique fixed point determined by the initial conditions follows.

We have thus proven the following result.

Theorem. Consider a balanced, nonautocatalytic reaction τ that comes from a bistochastic process. If the coupling constant μ belongs to $(0, \mu_0)$, where μ_0 is the upper limit of the bistochasticity range, then:

(a) All the fixed points of τ are stable and constitute an $(N + M - 2)$-parameter family.

(b) Every choice of the initial conditions different from a fixed point converges to the corresponding fixed point.

(c) The entropy S is a strict Liapunov function for τ.

If $\mu = \mu_0$ and the iterations of $P(0)$ under τ converge to the corresponding fixed point, then the entropy is nondecreasing and there is a $k \in \mathbb{N}$ such that $S(\tau^k(P(0))) > S(P(0))$, unless $P(0)$ is a fixed point.

7. CONCLUSIONS

We have studied the dynamics of the general chemical reaction

$$n_1 A_1 + \cdots + n_N A_N \rightleftharpoons m_1 B_1 + \cdots + m_M B_M$$

with any number of chemicals and stoichiometry, as given by the law of mass action for stirred systems. We have identified the obvious fixed points, and apart from these, the system converges from any initial conditions to the unique equilibrium point, which is therefore a global attractor, whenever the coupling constant μ lies in the appropriate range. We show that the fixed points are all stable, as a consequence of the smoothness of the manifold to which they belong, and that they are characterized as states of maximum entropy, given the conserved quantities as constraints.

The reactions we have considered are all balanced. However, many reactions that appear in the specialized literature do not appear to be balanced. Such reactions can be treated within the theory that we have developed via the introduction of extra particles, e.g., photons, that carry away part of the energy of the reacting species. In this way we can balance any given reaction; for example, we can transform

$$O_2 + 2H_2 \rightleftharpoons 2H_2O$$

by adding one photon γ, in order to get the balanced reaction

$$O_2 + 2H_2 \rightleftharpoons 2H_2O + \gamma$$

This makes perfect sense in classical probability theory provided that the energy of the γ is positive. The occurrence of such γ's provides us also with a tool for modeling the rate constants of those reactions that proceed mostly in one direction. In our example, the reaction proceeds mostly from the left to the right provided that $p_\gamma(0)$ is small. The opposite occurs if $p_\gamma(0)$ is big. This may be interpreted as a temperature dependence of the rate constants. Apart from these considerations, there is also the fact that to every balanced reaction we can associate a bistochastic matrix, which is known to be the only class of linear operators that do not decrease the entropy, in general.(8)

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