

**A STOCHASTIC TREATMENT OF REACTION AND DIFFUSION**

Lamberto Rondoni

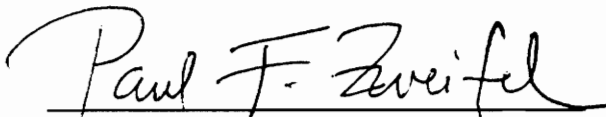
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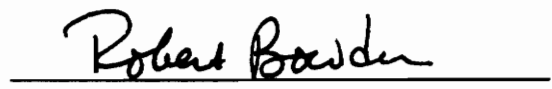
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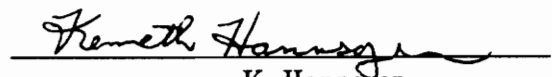
  
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# A STOCHASTIC TREATMENT OF REACTION AND DIFFUSION

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## ABSTRACT

We develop a theory for the analysis of chemical reactions in “isolated” containers. The main tool for this analysis consists of Boltzmann maps, which are discrete time dynamical systems that describe the time evolution of the normalized concentrations of the chemicals in the reactions. Moreover, the use of these maps allows us to draw conclusions about the continuous dynamical systems that the law of mass action associates with the different reactions.

The theorems we prove show that entropy is a strict Liapunov function and that no complex evolution is expected out of the discrete dynamical systems. In fact, we prove convergence to a fixed point for most of the possible cases, and we give solid arguments for the convergence of the remaining ones. The analysis of the continuous systems is more complicated, and fewer results have been proven. However, the conclusions we draw are similar to those relative to the Boltzmann maps. Therefore, we suggest that no chaos is to be found in systems that do not exchange energy nor matter with the outer environment, both for the discrete and for the continuous cases. Such a phenomenon is more likely to occur in “closed” or in “open” reactors.

Finally, we argue that the discrete dynamical systems have more physical content than the continuous ones, and that Boltzmann maps may be useful in the analysis of the non chaotic regions of many other kinds of finite dimensional maps.

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## CHAPTER I: INTRODUCTION

### **I.1 Are Chemical Reactions Chaotic ?**

About three decades ago a Russian Chemist, Boris Belousov, unexpectedly found that mixing certain amounts of sulphuric acid potassium bromate, cerium sulphate and malonic acid, produced visible oscillations in the concentrations of bromide and cerium. In fact, rather sharp and periodic changes in the colour of the mixture indicated that the concentrations of such chemicals were, in turn, changing periodically. It was not easy at all to convince other chemists that what had been observed was a genuine phenomenon and not just the result of an improperly run experiment. As a matter of fact, the first two papers in which Belousov described his discovery were rejected, and so he decided not to pursue that research any more, apart from publishing a short report in the proceedings of a conference on radiation medicine. Some years later, Anatol Zhabotinskii, another Russian chemist, performed a thorough analysis of Belousov's experiments, and was able to convince the rest of the scientific community that something extremely interesting had been discovered. Today reactions of that type are called "Clock" reactions and they have been the starting point for the study of those intriguing chemical reactions that, in the current literature, are listed as "Chaotic" reactions.

The Belousov-Zhabotinskii reaction, though the most famous, historically is not the first recorded chemical clock. In 1921, William Bray, a chemist at the University of Berkeley, had accidentally found that the iodate-hydrogen peroxide reaction presents an almost periodic behavior, as far as the color of the mixture and the bursts of oxygen bubbles produced by the reaction are concerned. But almost no one took his experiment seriously. During the following half century, most of the specialized literature aimed to prove that



Bray's experiment was influenced by the presence of perturbing causes like dust and bad experimental apparatuses.

These two examples describe in part the skepticism that accompanied the discovery of complex dynamics in chemical reactions. Probably, this was due to the belief that those experiments were a violation of the second law of thermodynamics: sort of perpetual motion machines. This would have been, though, a wrong opinion, as it resulted from an application of equilibrium thermodynamics to phenomena very far from thermodynamical equilibrium. Today, it is widely accepted that the conclusions of classical thermodynamics apply to near equilibrium processes, and in fact no oscillations have been observed in such systems, but there is strong evidence that dramatically different laws describe the evolution of systems held far from thermodynamical equilibrium.

In the past decade, the study of chemical oscillations and connected nonlinear dynamical systems has made remarkable progress. The original skepticism, that had affected both the experimental research and the theoretical analysis, has turned into a great positive effort aimed to fully understand this particular problem. Many questions have been answered. Important new results in chemical kinetics, insights into the interactions between the nonlinearities inherent in the chemistry and diffusion and transport phenomena, and some new understanding of the complexity of two or more oscillators when they are linked together, constitute part of the relevant progress that has been made.

The evidence that chaotic patterns appear in experiments of the Belousov-Zhabotinskii type now appears to be incontrovertible. Strange attractors have been found as well as period doublings, even to the point of experimentally modelling the one-dimensional dynamics of famous maps of the interval.

Therefore, the study of complex chemical reactions has gained a position of primary importance among the uncountably many different fields that deal with nonlinear systems, both as an experimental science and as a forge of interesting theoretical models. Most

of the features that are now observed in population dynamics, biology, transport theory, mechanics etc., are found in chemical reactions as well. On the other hand, it is easier to control the conditions of the experiment for a chemical reaction than in many other cases.

Despite these successes, the study of the evolution of complex chemical reactions is still the subject of some dispute. In particular, questions arise as to whether present experiments are really perfectly controlled or not. It is not clear what role is played by spatial inhomogeneities and thermal fluctuations, neither is it known what are the effects of unavoidable noise, dust, cosmic rays, gravity etc.. Stochastic effects on a macroscopic scale have just begun to be investigated. A very intriguing problem is posed by certain experiments that do not appear to be chaotic but yield different results each time, as if very strong instabilities produce dramatically different evolutions under the effect of extremely small and uncontrollable disturbances.

One of the most important open questions –at least as far as chemistry is concerned– is probably the following. Does chaos arise solely from the chemistry, or is it the interplay of chemistry and transport processes which triggers it?

Even if we take a purely theoretical standpoint, we find that the situation is similar. The laws that are supposed to govern such processes have been known for more than a century; nonetheless many questions still remain. In particular, it is a difficult task to study the behaviour of the solutions of those differential equations that are meant to describe the evolution of complex chemical reactions. In fact, such equations are highly nonlinear, and the geometries involved may be rather complicated. The advent of modern super-computers has shown that numerical simulations can match remarkably well certain features of experimental outcomes. On the other hand, there is no universal agreement on what value should be attributed to these calculations.

If all these many questions could be answered for the relatively simple systems that are studied in chemistry, a big step forward would have been taken, and many more complicated

problems, like those relevant to biological systems, could be tackled with much greater confidence. Further details about the points discussed in this section can be found in [1] - [8].

## I.2 A Possible Approach

Some authors [1] describe the debate about the problems outlined in section I.1 as very hot. In particular, the controversy is made even more disturbing by the fact that different groups, that run numerical simulations of the Belousov-Zhabotinskii reaction, get completely different results when they re-run each other's programs. Therefore, an exact analysis of models is required, so that some order may be put in the present rather confused situation.

The point of view of this thesis is that of constructing a theory which aims to provide the tools necessary to a rigorous analysis of the already existing models. Furthermore, new models will be generated using these same tools. In particular, the law of mass action will be shown to fit into a stochastic process, which will be used to describe the most general kind of chemical reaction. Such a project will be pursued through the study of models of increasing complexity which belong to a special class: the bistochastic maps [9]. The resulting physical model is one that obeys the principle of microscopic reversibility at all times. This, in turn, implies that the rate of the process that transforms certain chemicals into others is equal to the rate of the inverse process. As this disagrees with the experimental evidence –i.e. many reactions proceed faster in one direction than in the other– we will explain this fact and show that it doesn't constitute a difficulty. Because of this, the name “law of mass action” will be used throughout this thesis, although it properly applies to the more general case of reactions with unequal backward and forward rates. The necessary generalizations beyond the theory here developed will be identified, and the restrictions under which this

study helps to draw rigorous conclusions from the general theory of chemical reactions will be outlined.

In the next section we discuss how the law of mass action –that rests on good experimental foundations– can be derived from basic physical principles. In section I.6 we will see how the resulting dynamical system can be cast into the framework of a bistochastic process, for a special case.

### **I.3 The Law of Mass Action**

In order to give a molecular description of chemical reactions, it is usually assumed that collisions among the molecules of the reacting substances are the basic causes for the reactions to take place. In this context, an elementary process is defined to be a molecular event that produces a well-defined change in the extensive variables that somehow describe the system, in particular in the total amount of each chemical [10]. This is very similar to the basic process that is hypothesized for the construction of the fundamental equation of kinetic theory: the Boltzmann equation. The difference is mainly that collisions in a rarefied and non-reacting gas are supposed to produce changes in momentum space, while collisions of reacting molecules produce changes in the concentrations of the substances involved. Moreover, in most applications of the Boltzmann equation, like neutron transport theory, the collision term is linear due to the fact that the neutrons do not collide with each other, given the extremely low ratio of the neutron density to the host particle density. On the contrary, the fact that chemical collisions are nonlinear in nature implies that nonlinear laws are required.

Let us take a look at the way the rate equation for the concentrations of the chemicals in a given reaction is usually constructed. This will give some insight on our understanding of elementary processes. We will follow the approach given in [11].

The rate at which molecules undergo chemical reactions cannot be taken to be the number of collisions that take place in unit time. If this were the case, reactions would be much faster than what is experimentally observed. This means that a fraction of the collisions in question do not trigger any chemical reaction. Therefore it is usually assumed that a reaction actually proceeds in three steps:

- a) the reactants collide at a certain relative kinetic energy
- b) part of that energy is used to form a “metastable” (intermediate) compound
- c) the intermediate compound decays into the final reaction products.

Therefore, a given kinetic energy is required of the colliding molecules, so that the threshold for the formation of the metastable state is exceeded. For instance, let us consider the process  $A + B \rightarrow C + D$ , by which we mean the reaction that  $A$  and  $B$  undergo, when mixed together, that produces the chemicals  $C$  and  $D$ . Then, if we let  $\epsilon$  be the activation energy of the intermediate state, we must have  $\mu v^2/2 > \epsilon$  where  $\mu$  is the reduced mass of  $A$  and  $B$  and  $v$  is the relative speed. It follows that the rate at which reactions between  $A$  and  $B$  can take place is the product of the collision frequency,  $\nu$ , by the probability that their relative speed is big enough for the reaction to take place. This probability is usually calculated under the assumption that the velocities of the reacting molecules obey the Maxwell-Boltzmann distribution. The result is that such a probability is an exponentially falling function of the activation energy. Concerning the collision frequency, it is assumed that the molecules are rigid spheres and that their velocities obey the Maxwell-Boltzmann distribution. This leads to an expression for  $\nu$  that is proportional to the product of the number,  $n_A$ , of particles  $A$  times the number,  $n_B$ , of particles  $B$  per unit volume, i.e.

$$\nu = n_A n_B \pi \left( \frac{d_A + d_B}{2} \right)^2 \left( \frac{8k_B T}{\pi \mu} \right)^{1/2}, \quad (\text{I.1})$$

where  $d_A$  and  $d_B$  are respectively the radii of molecules  $A$  and  $B$ ,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature of the mixture.

Therefore, we can write the following rate equations for the number of particles of the different species that are present at the time  $t$  in a “well stirred” (i.e. spatially homogeneous) medium:

$$\frac{dN_A}{dt} = -kN_A N_B = \frac{dN_B}{dt} = -\frac{dN_C}{dt} = -\frac{dN_D}{dt} \quad (\text{I.2})$$

where  $N_i$  represents the number of particles of species  $i$ , and  $k$  is a parameter that encompasses the microscopic dynamics of the reaction. In particular,  $k$  depends on the temperature and on the activation energy.

The reaction we have considered here is very special, as it involves four chemicals; it proceeds in one direction only (i.e.  $A$  and  $B$  are used to produce  $C$  and  $D$ , but not viceversa) and it is simply quadratic. As we will see, (I.1) and (I.2) can be generalized to include reactions of any order, where an arbitrarily large number of particles interact, and that proceed in both directions, i.e. the products of the reaction may also react back and produce the reactants. Equation (I.1) and its generalizations express the content of the law of mass action, for nonequilibrium processes.

Although the derivation of the law of mass action outlined above relies on strong simplifying assumptions, it provides a reasonable picture of the microscopic phenomena that determine the law itself. More accurate models would certainly be welcome, especially if they include quantum mechanics [12], but it is not clear what good alternatives might be. Thus, as it appears that the law of mass action gives a good description of the evolution of chemical reactions, it is universally accepted, so far.

#### I.4 Models of Real Chemical Reactions

The discussion developed in the previous section helps to understand how a theoretical description of a single chemical reaction can be given, starting from the knowledge of certain microscopic data. Nonetheless, most of the reactions that are under experimen-

tal investigation are more complex. Usually –and especially in chaotic systems– different kinds of reactions take place at the same time in the reactor vessels. In order to model such real processes, it is not enough to know how to describe each single reaction, something must also be said about how to combine the different partial contributions. In the effort of providing suitable theoretical descriptions, researchers throughout the world have invented many different models, all based on the law of mass action, and on some commonly accepted assumptions on how the contributions of the different single reactions should be put together. In this section we want to examine some of the models that have made the recent history of chemical kinetics.

EXAMPLE 1: The simplest model for complex chemical reactions is probably the Schlögl model, [11],[13]. The reaction scheme is the following:



and the dynamical system associated with this set of reactions is

$$\begin{aligned} \frac{dN_X}{dt} &= k_1 N_A N_X^2 - k_2 N_X^3 - k_3 N_X + k_4 N_B \\ \frac{dN_A}{dt} &= -k_1 N_A N_X^2 + k_2 N_X^3 \\ \frac{dN_B}{dt} &= k_3 N_X - k_4 N_B \end{aligned} \quad (\text{I.4})$$

where  $k_1$  and  $k_2$  are respectively the rate constants for the processes that go from left to right and from right to left, in the first reaction; while  $k_3$  and  $k_4$  have the same meaning, for the second reaction.

The thermodynamical equilibrium is defined by

$$\begin{aligned} k_1 N_A N_X^2 &= k_2 N_X^3 \\ k_3 N_X &= k_4 N_B. \end{aligned} \quad (\text{I.5})$$

But we may prepare an experiment in which  $N_A$  and  $N_B$  are fixed at some value that does not respect eq.s (I.5), and let  $N_X$  vary. Under these circumstances, this model becomes

very interesting, in fact it exhibits a phase transition and hysteresis behaviour, when  $N_A$  and  $N_B$  are fixed at a value far from thermodynamic equilibrium. If this is done, the steady states of the system, characterized by the vanishing of the time derivative of  $N_X$ , change in a discontinuous way with the parameter  $b = k_4 N_B / k_2$ ; and this is the cause for phase transition and hysteresis to occur. A modified version of this model, that has two stationary points, has been discussed in [14].

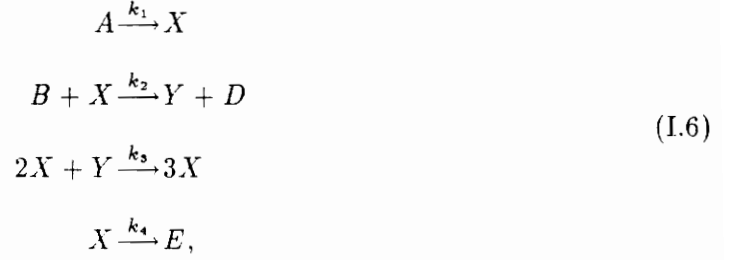
EXAMPLE 2: The Gray-Scott model, [2],[3], draws a strong analogy between the very simple reaction  $A \rightarrow B$  and the two autocatalytic ones  $A + B \rightarrow 2B$  and  $A + 2B \rightarrow 3B$ . Note that the term autocatalytic is commonly used in the specialized literature to mean a reaction in which some chemicals appear both as reactants and as products.

In this model, which assumes that the chemical  $A$  is continuously supplied at a given rate, these three elementary processes are supposed to make up the real reaction. In this way the opposite procedure to the usual is followed, as usually complex reactions are broken into simpler elementary processes. The competition between input of  $A$  from the flow and consumption of  $A$  by the chemical reaction gives a balance between  $A$  and  $B$  at the steady state. The supply of  $A$  is represented by a linear term while the production is represented by a cubic term, which presents a point of inflection. Therefore, the equation for the steady states, which is the intersection of these two functions, may contain up to three points. If the input flow is adjusted to one of the values that allow for three steady states, it is found that one of them is unstable while the other two are stable. This phenomenon is called bistability (i.e. there are two stable states between which the system can be flipped by suitable perturbations). In a case like this, the initial conditions will determine the convergence to either one of the two stable steady states. This is also another model in which phase transitions and hysteresis occur.

EXAMPLE 3: The Schlögl and the Gray-Scott models are interesting, but they do not al-

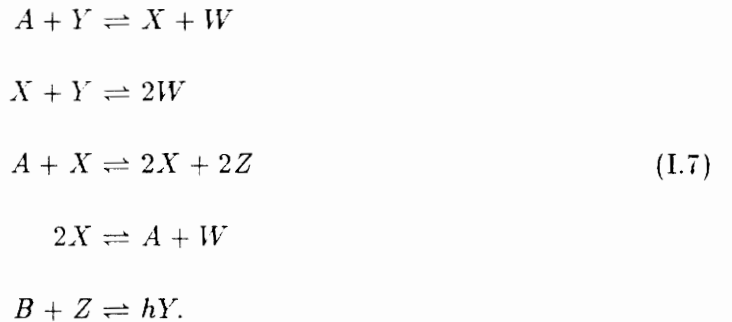


low phenomena like periodic behaviour and bifurcations, which are the basic ingredients for chaos to be produced. One classical model, in which oscillations are observed, is the “Brussellator”, [15], that draws its name from the University of Bruxelles where it was developed. This is one of the simplest models that describe clock reactions. The reaction scheme is the following:



where it is assumed that the concentrations of  $A$  and  $B$  are fixed, and the first and the last reactions can be viewed as a flow of  $X$ . If we introduce the two parameters  $a = N_A(k_1^2 k_3/k_4^3)^{1/2}$  and  $b = N_B k_2/k_4$ , we can see that the unique steady state for this reaction is given by  $X = a$  and  $Y = b/a$ . A simple stability analysis shows that such a steady state is stable for  $b < a^2 + 1 = b_c$ , it is unstable for  $b > b_c$ , and it admits periodic orbits for  $b = b_c$  [16]. A generalization of this model, in which the concentrations of  $A$  and  $B$  are not required to be fixed, is discussed in [17].

**EXAMPLE 4:** The most famous of all models is the so called “Oregonator”, that was developed by Field and Noyes at the University of Oregon, as a model of the Belousov-Zhabotinskii reaction [7],[18]. The following is the reaction scheme of the version called Reversible Oregonator.



Here the capital letters represent different chemicals, while  $h$  is a rather unusual stoichio-

metric coefficient, as it may vary between 0.5 and 1.4; moreover, by varying  $h$  appropriately, it is claimed that different complex dynamic evolutions are observed.

The features that this model is asked to reproduce are startling. Sustained temporal oscillations, waves through thin unstirred layers, bistability, intermittent bursts of regular oscillations followed by periods of quiescence, and quasi-periodic and chaotic oscillations are some of the most important experimental patterns for the description of which the oregonator was invented. It is remarkable that numerical simulations based on this model have reproduced a good deal of these features, for both batch and flow reactors. Nonetheless, even those authors who support the “overwhelming” reasons to believe in chaos as a genuine characteristic of the Belousov-Zhabotinskii reaction, do acknowledge the fact that the theoretical analysis has not furnished convincing answers yet. In [3], Epstein says: *“While the existence of chaos in the BZ system appears undeniable, its origin is still a matter of dispute. No calculation based on a reasonable mechanism for the reaction gives convincing evidence of chaos resulting from the dynamics of the homogeneous reaction.”* Therefore, new models in which space inhomogeneities play a major role are now under study, and they might replace the Oregonator in the future.

EXAMPLE 5: Finally, let us take a look at a model which is not used to describe any chemical reaction, but which is intrinsically very close to those that we have presented in the previous examples: the Lotka-Volterra model [14]. Its reaction scheme is the following:



As this reaction is not dissipative, it is not a very good model for real chemical reactions; it is instead of great interest in population dynamics, as a model of predator-prey ecosystems. It is clear, anyway, that the same sort of analysis that is performed on chemical reactions may successfully be applied here. This is a very simple example of the connections that can

be found between chemistry and biology in the study of nonlinear evolution.

### I.5 The Need for a Systematic Analysis

The models presented in the previous section and many others (either closely or not so much) related to the dynamics of chemical reactions have been the object of a lot of research work. To enumerate all the papers that have been published on the subject is practically impossible. Even to provide a list of all the different approaches that have been adopted is too hard a task. Our impression is that the experimental work is very difficult and still a lot needs to be done, but one thing seems now to be certain: it is possible to simulate complex dynamics and chaos in chemical reactions by running the experiments in the appropriate ways [6],[19].

From the point of view of theoretical analysis, our opinion is that the complexity of the mathematical models used to describe these systems has forced the researchers to accept some compromise. Some old studies have concentrated on extremely simplified models, as in [20], where a stochastic approach to the coupled reactions  $A_i \rightleftharpoons B_j$ , for all the chemicals in the set  $\{A_1, \dots, A_n, B_1, \dots, B_m\}$ , had been used. Here the contribution was to show that the nonequilibrium thermodynamics of those chemical reactions and, in particular, the entropy production can be modelled within the framework of a stochastic process. Other important examples of this trend can be found in [21], [22] and many other places.

A different approach has been made possible by the advent of the modern computers, see [7],[23],[24] for instance. Here the models that have been used are supposed to be more realistic, and very spectacular results have been obtained, but we have already seen how much disagreement there is on those calculations. The complexity of the problems is such that no sure conclusions can be drawn, despite the very hard analytical and numerical analysis being performed. The upshot is that it is not possible even to conclude whether

the models under investigation are truly “realistic” or not, because there is no rigorous proof of many of the properties they are supposed to have, and that appear in numerical simulations.

Other studies start with very hard mathematical problems, and proceed by proving step by step all the claims that have been announced. [25] is a good example of this approach, where an asymptotic analysis has been performed on the very general problem

$$\frac{\partial u}{\partial t} = \epsilon \Delta u - \epsilon^{-1} f(u) , \quad x \in \Omega, \quad (1.9)$$

where  $\Omega$  is a domain in  $\mathbb{R}^n$ ,  $u \in \mathbb{R}^m$ ,  $f$  is a function that vanishes on a given manifold, and the asymptotic analysis of  $u$  is performed in the limit of small  $\epsilon$ . The results are that  $u$  tends rapidly to the connected manifold  $M$  of the stable equilibrium points, being driven by the reaction  $f$ , and subsequently it evolves slowly inside  $M$ , being driven by the diffusion process. In the end,  $u$  converges to a harmonic map of  $\Omega$  into  $M$ . Although these results are rigorous, some simplifying hypothesis were needed, like assuming that  $M$  has no boundary, or that  $f(u)$  can be expressed as the gradient of a smooth scalar potential that is spherically symmetric. We will see that usually these hypothesis are not satisfied by an  $f$  that stems from the law of mass action. Furthermore, no conclusions can be drawn about the positivity of the solutions, which is a fundamental question as far as the concentrations of chemicals in a reaction are considered.

Among the recent studies on the famous models that we have presented in the previous section, it is worth quoting also [17],[26] and [27]. These three papers constitute indeed a thorough analysis of complex reactions, in which the concentrations of a number of substances is kept fixed and therefore they can be eliminated from the rate equations. The same thing is shown to be possible when some of the elementary processes of the reaction are much faster than the others, and the two cases are shown to be equivalent, in the sense that the elimination of fast variables works for both. There are many examples in which

the above approximations are reasonable, even if some restrictions must be imposed.

This discussion, far from being a criticism of the enormous amount of work devoted at various levels to the study of complex reactions, attempts to show some of the problems encountered in the construction and rigorous analysis of realistic models. Clearly, a program capable of providing a systematic way of proceeding is highly desirable.

### I.6 A Stochastic Process for the Reaction $2A \rightleftharpoons A + B$

In [28] a general method is described for constructing nonlinear “Boltzmann maps”, which are discrete time stochastic processes that imitate the classical Boltzmann equation. The similarity lies at least in two points. Both the maps and the equation assume the *Stosszahlansatz*, which implies no correlations between the particles before a collision, and the maps look like discretized versions of the equation, within certain limits. In this thesis we show that, under some assumptions, Boltzmann maps can be given as models of the dynamical systems associated with chemical reactions. This will provide us with a powerful tool for the analysis of such dynamical systems, and for the construction of new ones. The details will be given in the next chapters; here we want to introduce some concepts and useful notation, with the aid of a special example.

Let us consider the simple autocatalytic reaction  $2A \rightleftharpoons A + B$ , in a well stirred reactor.

The law of mass action, in this case, is expressed by

$$\begin{aligned} \frac{dp}{dt} &= -\lambda(p^2 - pq) = -\lambda D \\ \frac{dq}{dt} &= \lambda D, \end{aligned} \tag{I.10}$$

where  $p$  and  $q$  are respectively the concentrations of  $A$  and  $B$ ,  $\lambda$  is the rate constant, and  $D = p^2 - pq$  is called the disequilibrium parameter. At the molecular level, we may think of this reaction as the process drawn in Figure I.1, where the forward and the backward processes are assumed to be equally probable, i.e. they proceed with equal rates.

Let  $p$  and  $q$  be the concentrations at time  $t = 0$ , and  $p^*$  and  $q^*$  those at  $t = 1$  (in some system of units). We can write a discrete version of (I.10) as

$$\begin{aligned} p^* &= p - \mu D \\ q^* &= q + \mu D, \end{aligned} \tag{I.11}$$

where  $\mu$  is a positive parameter appropriately chosen. As a matter of fact one can obtain (I.11) also from the following argument.

Let  $\Omega = \{A, B\}$  be a sample space and let  $\mathcal{Q}$  be the simplex of probability measures on  $\Omega$ . If the concentrations are normalized so that  $p+q = 1$ , we have that  $P = (p, q) \in \mathcal{Q} \subset \mathbb{R}^2$ , and we may interpret each component of  $P$  as the probability that a molecule  $A$  or a molecule  $B$  be fished out of the reactor at the time  $t = 0$ . Similarly, define  $\Omega_2 = \Omega \times \Omega$  and let  $\mathcal{Q}_2 \subset \mathbb{R}^4$  be the simplex of probability measures on  $\Omega_2$ . Then, each component  $p_{ij}$  of a  $P_2 \in \mathcal{Q}_2$  may be interpreted as the probability of pulling out a molecule  $i$  and a molecule  $j$  from the reactor at  $t = 0$ . The stosszahlansatz requires that  $P_2 = P \otimes P$ . Due to the evolution of the chemical system, at the instant  $t = 1$  it may or may not be that  $P$  and  $P_2$  can still be interpreted as at the time  $t = 0$ . In general, two other elements of  $P^* \in \mathcal{Q}$  and  $P_2^* \in \mathcal{Q}_2$  will represent the probabilities just described. Therefore, a map  $\tau : \mathcal{Q} \rightarrow \mathcal{Q}$  and a map  $T : \mathcal{Q}_2 \rightarrow \mathcal{Q}_2$ , can be defined by  $\tau(P) = P^*$  and  $T(P_2) = P_2^*$ , and  $\tau$  and  $T$  can be interpreted as time evolutions on  $\mathcal{Q}$  and  $\mathcal{Q}_2$ .

Now, for every element  $(i, j)$  in  $\Omega_2$ , consider the new sample space  $\Omega_3^{(i,j)} = (i, j) \times \Omega_2$  and the simplex  $\mathcal{Q}_3^{(i,j)} \subset \mathbb{R}^4$  of the probability measures on  $\Omega_3^{(i,j)}$ . Every  $P_3^{(i,j)} \in \mathcal{Q}_3^{(i,j)}$  can be viewed as a law that describes all the possible channels through which the particles  $i$  and  $j$  may react producing two other particles of  $\Omega$ . In fact each component  $P_{ij,kl}$  of  $P_3^{(i,j)}$  lies in  $[0, 1]$  and  $\sum_{(k,l)} P_{ij,kl} = 1$ , and so it may represent the scattering probability for the collision of the molecules  $i$  and  $j$  to produce the molecules  $k$  and  $l$  in the unit interval of time. Moreover, differently from the case of  $P$  and  $P_2$  that are supposed to vary with time, we assume that the scattering laws do not depend on time (e.g. hydrogen and oxygen

together were as likely to produce water yesterday as they are today). Thus, we assume that there is a unique  $P_3^{(i,j)} \in \mathcal{Q}_3^{(i,j)}$  that can be interpreted as the scattering law for the process under study, and that doesn't change with time. If such a law obeys the principle of microscopic reversibility, i.e. the scattering of  $i$  and  $j$  to produce  $k$  and  $l$  is equally probable as the scattering of  $k$  and  $l$  to produce  $i$  and  $j$ ,  $P_{ij,kl}$  must equal  $P_{kl,ij}$  for every  $k$  and  $l$ . Moreover, if the collision of  $i$  and  $j$  is the same as the collision of  $j$  and  $i$ ,  $P_{ij,kl}$  must equal  $P_{ji,kl}$  for every  $k$  and  $l$ . This hypothesis, that is not necessarily satisfied in classical probability, does not alter the physical content of the present theory, as shown in section II.5, and it is correct in quantum probability. Therefore, it will be adopted in the rest of this thesis, for the sake of simplicity.

Having interpreted  $P_3$  in this way, we are now bound to have

$$p_{ij}^* = \sum_{(k,l)} P_{ij,kl} p_{kl}, \quad (\text{I.12})$$

for the component  $(i, j)$  of  $P_2^*$  is the sum of the contributions of all the reactions that produce it from different elements plus the contribution of no reaction. Therefore we realize that the map  $T$  is linear and can be expressed as a  $4 \times 4$  bistochastic matrix, whose entry  $T_{ij,kl}$  equals  $P_{ij,kl}$  for all  $i, j, k, l$ . In our case, if we let  $T_{AA,AA} = 1 - 2\mu$ ;  $T_{AA,AB} = \mu$ ;  $T_{AA,BB} = 0$ ;  $T_{AB,AB} = (1 - \mu)/2$ ;  $T_{AB,BB} = 0$ ;  $T_{BB,BB} = 1$  we get

$$P_2^* = TP_2 = \begin{pmatrix} 1 - 2\mu & \mu & \mu & 0 \\ \mu & \frac{1-\mu}{2} & \frac{1-\mu}{2} & 0 \\ \mu & \frac{1-\mu}{2} & \frac{1-\mu}{2} & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} p^2 \\ pq \\ qp \\ q^2 \end{pmatrix} = \begin{pmatrix} (1 - 2\mu)p^2 + 2\mu pq \\ \mu p^2 + (1 - \mu)pq \\ \mu p^2 + (1 - \mu)pq \\ q^2 \end{pmatrix} = \begin{pmatrix} p_{AA}^* \\ p_{AB}^* \\ p_{BA}^* \\ p_{BB}^* \end{pmatrix} \quad (\text{I.13})$$

Then, if we let  $P^* = (p^*, q^*)^T$ ,  $p^* = p_{AA}^* + p_{AB}^*$  and  $q^* = p_{BA}^* + p_{BB}^*$  we get (I.11), considering that  $p + q = 1$ . Note that this last step defines a map  $E : \mathcal{Q}_2 \rightarrow \mathcal{Q}$ , which is the conditional expectation onto the first factor.

To sum up, a map  $\tau : \mathcal{Q} \rightarrow \mathcal{Q}$  has been constructed, that transforms  $P$  according to

$$P \xrightarrow{\sigma} P \otimes P \xrightarrow{T} T(P \otimes P) \xrightarrow{E} P^* = \tau(P), \quad (\text{I.14})$$

which shows how (I.11) can be made into a nonlinear stochastic process. Here  $\sigma$  is the so called “sampling map”, that forms the tensor product of copies of the input probability, thus implementing the stosszahlansatz. The map defined by (I.14) is called a quadratic Boltzmann map.

Note that we have implicitly assumed that the reaction  $2A \rightleftharpoons A + B$  exhausts all the physics of the problem of two particles of  $\Omega$ ; i.e.  $(i, j)$  is allowed to produce  $(A, A)$ ,  $(A, B)$ ,  $(B, A)$  and  $(B, B)$  only, and not  $(A, A, B)$  for instance. If this were not the case, other reactions should have been introduced. In chapter 4 we will show how this can be done.

## I.7 Plan of Part One

Besides the previous introduction, the study presented in Part One is organized as follows:

Chapter II introduces the basic definitions and theorems that will be used in the following chapters. Part of these are well known results, and can be found in standard books; another part is more recent, and it first appeared in [28]. Moreover, some of the material of section II.5 is original.

Chapter III studies the details of the stochastic processes introduced in Chapter II, for the case of single chemical reactions.

Chapter IV is devoted to the study of complex reactions, through the convex combinations of maps relative to single reactions.

Chapter V deals with the continuous dynamical systems that arise in the applications of the law of mass action. Furthermore, some hints are given on how to improve the theory of chemical kinetics.

Chapter VI completes the arguments developed in the preceding chapters, with some comments and an overview.



## CHAPTER II: STOCHASTIC PROCESSES, ENTROPY AND DYNAMICAL SYSTEMS

### II.1 Introduction

In this chapter the complete definitions of the terms and the exact statements of the theorems that will be used in the rest of the thesis are introduced. In section II.2 the generalities of bistochastic maps and their relation to entropy will be discussed. Section II.3 will introduce some notions necessary to the proof of existence and stability of the fixed points of nonlinear dynamical systems, as well as to the proof of convergence to such fixed points. Section II.4 will be particularly devoted to continuous time dynamical systems, with a view on the numerical analysis results that allow one to connect the discrete to the continuous systems. All the material presented in these sections is well known; nonetheless, an effort will be made to adapt it to the purpose of this thesis. Finally, section II.5 will show how to construct bistochastic processes for the most general single chemical reactions, along the lines of section I.6, and a new result will be presented.

### II.2 Stochastic and Bistochastic Maps on $\mathbb{R}^n$

In this section references [29],[30] and [31] are broadly used, for what concerns the classical results. [9] and [28], instead, are the source of the more recent results and of those relative to the Boltzmann maps. Let us denote  $\mathcal{B} = (\mathbb{R}^n, \|\cdot\|_1)$ , with  $\|\mathbf{a}\|_1 = |a_1| + \dots + |a_n|$  for every  $\mathbf{a} = (a_1, \dots, a_n) \in \mathbb{R}^n$ . An element  $\mathbf{a}$  of  $\mathcal{B}$  is said to be **positive** if all its components are non-negative real numbers. To indicate that  $\mathbf{a}$  is positive we write  $\mathbf{a} \geq 0$ . If all components of  $\mathbf{a}$  are positive, we say that  $\mathbf{a}$  is **strictly positive**. The notion of positivity establishes a partial ordering on  $\mathcal{B}$ ; in fact, it is possible to compare the two elements  $\mathbf{a}$  and

$\mathbf{b}$ , by writing  $\mathbf{a} \geq \mathbf{b}$  if and only if  $\mathbf{a} - \mathbf{b} \geq 0$ .

DEFINITION II.1. A linear map  $T : \mathcal{B} \rightarrow \mathcal{B}$  is said to be **Stochastic** if

- i.  $\mathbf{a} \geq 0$  implies  $T\mathbf{a} \geq 0$ , which is to say that  $T$  is positivity preserving.
- ii.  $\|T\mathbf{a}\|_1 = \|\mathbf{a}\|_1$  for all  $\mathbf{a} \geq 0$ .

$T$  is called **Bistochastic** if it is stochastic and it satisfies the following condition:

- iii.  $Te = \mathbf{e}$ , where  $\mathbf{e} = (1, \dots, 1)$ .

Note that many authors call doubly stochastic the maps that here have been defined as bistochastic. Moreover, there are many alternative definitions, which can be proven to be equivalent to Definition II.1. Here are summarized some of these, in the form of a theorem, where the map and its associated matrix are identified.

THEOREM II.1. (a) A nonnegative  $n \times n$  matrix is bistochastic if and only if each of its column and row sums is 1.

(b) A nonnegative  $n \times n$  matrix,  $T$ , is bistochastic if and only if  $TJ_n = J_nT = J_n$ , where  $J_n$  is the  $n \times n$  matrix whose entries are  $1/n$ .

(c) A linear map  $T : \mathcal{B} \rightarrow \mathcal{B}$  is bistochastic if and only if it is a convex linear combination of positivity preserving isometries.

Let  $\mathcal{S}^n$  be the set of all stochastic maps on  $\mathbb{R}^n$ , and  $\mathcal{D}^n$  the set of all the bistochastic maps. Then the following fundamental result holds:

THEOREM II.2. (a) If  $T \in \mathcal{S}^n$  then  $\|T\| = 1$ .

(b)  $\mathcal{S}^n$  and  $\mathcal{D}^n$  are two compact and convex subsets of  $\mathbb{M}_n$ , the set of  $n \times n$  real matrices.

(c) The product of two stochastic matrices is stochastic. The product of two bistochastic matrices is bistochastic.

(d) (Birkhoff's Theorem)  $T$  is extremal in  $\mathcal{D}^n$  if and only if  $T$  is a permutation.

The reason for which bistochastic maps are preferred to the others here, is that they are positivity preserving –thus guaranteeing a theory from which negative concentrations are

excluded— and because they are the unique linear operators on  $\mathbb{R}^n$  that do not decrease the entropy in general. This last property is the consequence of a set of other classical results that are outlined below. The definition of the entropy  $S$  of a system of reacting chemicals that we adopt is:

$$S(P) = - \sum_{i=1}^N p_i \log p_i, \quad (\text{II.1})$$

where it is assumed that there are  $N$  chemicals  $\{A_1, \dots, A_N\}$ ,  $p_i$  is the concentration of the element  $A_i$  in the reactor, and  $\sum_i p_i = 1$ .

**DEFINITION II.2.** For two elements  $\mathbf{a}, \mathbf{b} \in \mathcal{B}$  we say that  $\mathbf{a}$  is **More Chaotic than**  $\mathbf{b}$ , and we write  $\mathbf{a} \succ \mathbf{b}$ , if and only if there exists  $T \in \mathcal{D}^n$  such that  $\mathbf{b} = T\mathbf{a}$ .

This new relation on  $\mathcal{B}$  defines a partial pre-ordering only, because the implication  $\mathbf{a} \succ \mathbf{b}$  and  $\mathbf{b} \succ \mathbf{a} \implies \mathbf{a} = \mathbf{b}$  does not hold. The next important theorem, of which a short proof is given, follows

**THEOREM II.3.** Given a linear map  $T$  on  $\mathcal{B}$  such that  $T\mathbf{a} \succ \mathbf{a}$  for every  $\mathbf{a} \in \mathcal{B}$ , then  $T$  is bistochastic.

**PROOF:** For every  $\mathbf{a} \in \mathcal{B}$ , let  $\mathbf{b} = T\mathbf{a} \succ \mathbf{a}$ . If  $\mathbf{a} \geq 0$ , then  $\mathbf{b} \geq 0$ . In fact, the definition of more chaotic implies the existence of a map  $T' \in \mathcal{D}^n$  such that  $\mathbf{b} = T'\mathbf{a}$ . Then  $\|T\mathbf{a}\|_1 = \|\mathbf{b}\|_1 = \|\mathbf{a}\|_1$  and  $T\mathbf{a} \geq 0$ . Thus,  $T \in \mathcal{S}^n$ . Now, consider  $\mathbf{a} = \mathbf{e}$  then, as  $\mathbf{b} = T\mathbf{e} \succ \mathbf{e}$ , there exists  $T' \in \mathcal{D}^n$  such that  $\mathbf{b} = T'\mathbf{e}$  which, in turn, equals  $\mathbf{e}$ . Therefore,  $T\mathbf{e} = \mathbf{e}$ , i.e.  $T$  belongs to  $\mathcal{D}^n$ . ■

Consider now a function  $f : [0, \infty) \rightarrow \mathbb{R}$  such that  $f(0) = 0$ , and define  $S_f(\mathbf{a}) = \sum_{i=1}^n f(a_i)$  for all  $\mathbf{a} \geq 0$ , where  $a_i$  is the  $i$ -th component of  $\mathbf{a}$ . Moreover, let a real function  $f$  be called **concave** if  $-f$  is convex, i.e. let  $f$  be called concave if  $f((1-\lambda)\mathbf{x} + \lambda\mathbf{y}) \geq (1-\lambda)f(\mathbf{x}) + \lambda f(\mathbf{y})$ , for every  $\lambda \in (0, 1)$ . Then the following is true:

**THEOREM II.4.** Let  $I$  be an interval in  $\mathbb{R}$ , and assume that  $\mathbf{a}, \mathbf{b} \in I^n$ , where  $I^n$  is the

cartesian product of  $n$  copies of  $I$ . Then  $\mathbf{a} \succ \mathbf{b}$  if and only if  $S_f(\mathbf{a}) \geq S_f(\mathbf{b})$  for all concave functions  $f : I \rightarrow \mathbb{R}$ .

In particular, if  $f(x) = -x \log x$  for  $x \in [0, 1]$ , then  $S_f$  coincides with the definition of the entropy of a chemical system. Thus, this theorem states that the concepts of entropy non-decrease and of chaos enhancement –according to Definition II.2– are the same, for the time evolution of a chemical reaction. It follows that every linear theory in which entropy does not decrease –whatever the initial conditions are– and whose states are given by vectors in  $\mathbb{R}^n$ , comes from bistochastic maps. Furthermore, if a linear theory increases the entropy at every time step, the relative maps belong to a proper subset of  $\mathcal{D}^n$ .

In [28], Streater characterized a subset of the bistochastic maps that contains matrices whose application increases the entropy of a system, unless the system is at a fixed point of the map itself. The relevant results of that paper are summarized below.

Let  $\mathcal{Q}_m$  be the simplex of probability measures on  $\Omega^m = \{A_1, \dots, A_n\}^m$ . Let  $\sigma$  and  $E$  be the generalizations of the maps defined by (I.14) to  $\Omega^m$ , that is:  $\sigma(P) = \otimes_1^m P$  for every  $P \in \mathcal{Q}$ , and  $E : \mathcal{Q}_m \rightarrow \mathcal{Q}$  the conditional expectation onto the first factor. Then we define a Boltzmann map of order  $m$  as follows.

**DEFINITION II.3.** A **Boltzmann map** of order  $m$  is a map of the form  $\tau(P) = E(T(\sigma(P)))$ , i.e.

$$P \xrightarrow{\sigma} \otimes_1^m P \xrightarrow{T} T(\otimes_1^m P) \xrightarrow{E} P^* = \tau(P),$$

for every  $P \in \mathcal{Q}$ , where  $T \in \mathcal{D}^{n^m}$  is symmetric.

It follows that

**THEOREM II.5.** (a) A Boltzmann map of order  $m$  maps  $\mathcal{Q}$  into itself.

(b) The entropy  $S$  of a system of reacting chemicals does not decrease under the action of  $\tau$ ; i.e.  $S(\tau(P)) \geq S(P)$  for every  $P \in \mathcal{Q}$ .

and

**THEOREM II.6.** *If 1 is a simple eigenvalue of  $TT^*$  and  $P \in \mathcal{Q}$ , then  $\tau^k(P) \rightarrow e/n$  as  $k \rightarrow \infty$ .*

The proof of Theorem II.6 relies on the fact that the crucial step for the increase of the entropy determined by  $\tau$  is the application of  $T$ , and it is based on the following fundamental result from the same paper.

**THEOREM II.7.** *Let  $T$  be a bistochastic map on  $\mathbb{R}^N$  and let  $P = \{p_j\}_1^N$  be a semiprobability, i.e.  $1 \geq p_j \geq 0$ ,  $j = 1, \dots, N$ . Let the eigenvalue 1 of  $TT^*$  be simple, with a gap  $\Delta$  to the next largest eigenvalue. Let  $q_l = \sum_k T_{kl} p_k$ . Then*

$$\sum_k p_k \log p_k \geq \sum_j q_j \log q_j + \frac{1}{2} \Delta \|p - \hat{p}\|_2^2 \quad (\text{II.2})$$

where  $\hat{p} = \|P\|_1/N$ , and  $\|P\|_2 = \sqrt{|p_1|^2 + \dots + |p_N|^2}$ .

Therefore, whenever  $TT^*$  has a spectral gap  $\Delta$ , the entropy of the system increases a positive amount at every application of  $\tau$ , unless  $P$  is the uniform distribution. It follows that the entropy converges to a finite limit as it is a continuous function on a compact domain. At the same time, the sequence  $\{\tau^m P\}$  lies in the same compact set, and so it has a subsequence that converges to  $\hat{P}$  say. This observation allows the author to prove that  $S(\tau \hat{P}) = S(\hat{P})$ , and that  $\hat{P}$  is the limit of all the convergent subsequences of  $\{\tau^m P\}$ . Then  $\hat{P}$  must be the uniform probability distribution, otherwise Theorem II.7 would be violated.

A result that will be needed in chapter IV, for the estimate of the entropy of a convex combination of probability measures, is the so called Kulback's Lemma [9].

**LEMMA II.1. (Kulback's Lemma)** *Let  $P, Q$  be probability measures on  $\Omega$ . Then*

$$\sum_i p_i \log p_i \geq \sum_i p_i \log q_i + \frac{1}{2} \|P - Q\|_2^2.$$

*If we have semiprobabilities such that  $\sum p_i, \sum q_i < 1$ , the statement is also true.*

The problem of determining whether the  $T$  of a given reaction has a spectral gap or not is too difficult to be answered by direct methods; in fact even the size of  $T$  for a very simple

reaction like  $A + B \rightleftharpoons C + D$  is  $16 \times 16$  ! Nonetheless, such a problem can be successfully tackled thanks to the following results, due to Perron and Frobenius, as will be shown in Chapter III. Some definitions are needed first.

**DEFINITION II.4.** *A real matrix is called **nonnegative (positive)** if all its entries are non-negative (positive) numbers. An  $n \times n$  complex matrix  $A$  is called **irreducible** if there exists no permutation matrix  $P$  such that*

$$PAP^T = \begin{pmatrix} A_{1,1} & A_{1,2} \\ 0 & A_{2,2} \end{pmatrix},$$

where  $A_{1,1}$  is an  $r \times r$  submatrix and  $A_{2,2}$  is an  $(n-r) \times (n-r)$  submatrix, where  $1 \leq r < n$ . An irreducible nonnegative matrix is said to be **primitive** if it has one and only one eigenvalue whose modulus equals its spectral radius.

Then the following can be proved.

**THEOREM II.8.** (Perron - Frobenius) *Let  $A$  be an irreducible  $n \times n$  nonnegative matrix.*

*Then*

- i.  $A$  has a positive real eigenvalue equal to its spectral radius  $\rho(A)$ .*
- ii. To  $\rho(A)$  there corresponds a strictly positive eigenvector.*
- iii.  $\rho(A)$  increases when any entry of  $A$  increases.*
- iv.  $\rho(A)$  is a simple eigenvalue of  $A$ .*

and

**THEOREM II.9.** *Let  $A$  be a nonnegative  $n \times n$  matrix. Then  $A^m$  is positive for some  $m \in \mathbb{N}$  if and only if  $A$  is primitive.*

Therefore, if there exists a natural number  $r$  such that all the entries of  $T^{2r}$  are positive, then  $T^2 (= TT^*)$  is primitive, and as such it has a spectral gap between 1, its highest eigenvalue, and the next largest one. In section II.5 this result will be used to show that, given any single chemical reaction, the square of the associated bistochastic map  $T$  has a

spectral gap in one of its invariant subspaces, and so the entropy of the system is a strict Liapunov function for the discrete time dynamical system generated by  $\tau$ . Finally it is worth giving the explicit form of  $T$  for a couple of simple chemical reactions.

Example 1.  $2A \rightleftharpoons B + C$  The bistochastic matrix associated with this reaction is given by (II.3) below. There the capital letters have been used to better identify which process is represented by which matrix element.

$$\begin{array}{c}
 \begin{array}{c}
 AA \quad BC \quad CB \quad AB \quad BA \quad AC \quad CA \quad BB \quad CC \\
 AA \\
 BC \\
 CB \\
 AB \\
 BA \\
 AC \\
 CA \\
 BB \\
 CC
 \end{array}
 \begin{pmatrix}
 1 - 2\mu & \mu & \mu & 0 & 0 & 0 & 0 & 0 & 0 \\
 \mu & \frac{1-\mu}{2} & \frac{1-\mu}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
 \mu & \frac{1-\mu}{2} & \frac{1-\mu}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & .5 & .5 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & .5 & .5 & 0 & 0 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & .5 & .5 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & .5 & .5 & 0 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1
 \end{pmatrix}
 = T \quad (\text{II.3})
 \end{array}$$

Clearly,  $T$  acts like the identity on a part of the vector that is given as input. In fact,  $T$  is applied to vectors of the form  $P \otimes P$  only, and so the part relative to the components  $p_{AB}, p_{BA}, p_{AC}, p_{CA}, p_{BB}$  and  $p_{CC}$  is left unchanged.

On the other hand, the subspace relative to the components  $p_{AA}, p_{BC}$  and  $p_{CB}$  is invariant, but it is also "mixed" by the action of  $T$ . In fact, the submatrix of  $T^2$  that is relevant to such a subspace is positive, and so it has a spectral gap. As a consequence, the application of  $\tau$  increases the entropy until the input vector for  $T$  has  $p_{AA} = p_{BC} = p_{CB}$ , i.e.  $p_A^2 = p_{BPC}$ , which is exactly the equation for the stationary points of  $\tau$ .

Example 2.  $a + b \rightleftharpoons c + d$  The bistochastic matrix  $T$  associated with this reaction is given by (II.4). In this example the same basic features of Example 1. are found; the only difference being that entropy is increased until  $p_{APB} = p_{CPD}$ .

$$T = \begin{matrix} & ab & ba & cd & dc & ac & ca & ad & da & bc & cb & bd & db & aa & bb & cc & dd \\ \begin{matrix} ab \\ ba \\ cd \\ dc \\ ac \\ ca \\ ad \\ da \\ bc \\ cb \\ bd \\ db \\ aa \\ bb \\ cc \\ dd \end{matrix} & \left( \begin{array}{cccccccccccccccc} \frac{1-\mu}{2} & \frac{1-\mu}{2} & \frac{\mu}{2} & \frac{\mu}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{1-\mu}{2} & \frac{1-\mu}{2} & \frac{\mu}{2} & \frac{\mu}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{\mu}{2} & \frac{\mu}{2} & \frac{1-\mu}{2} & \frac{1-\mu}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{\mu}{2} & \frac{\mu}{2} & \frac{1-\mu}{2} & \frac{1-\mu}{2} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & .5 & .5 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & .5 & .5 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & .5 & .5 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & .5 & .5 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & .5 & .5 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & .5 & .5 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & .5 & .5 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{array} \right) \end{matrix} \quad (\text{II.4})$$



### II.3 Fixed Points of Dynamical Systems

Given a map  $G : D \rightarrow D$ ,  $D \subseteq \mathbb{R}^n$ , it is possible to construct a discrete and a continuous dynamical system as follows:

$$\mathbf{x}_{m+1} = \mathbf{x}_m + hG(\mathbf{x}_m), \quad \mathbf{x}_m \in D \quad (\text{II.5})$$

$$\frac{d\mathbf{x}}{dt} = G(\mathbf{x}), \quad \mathbf{x} \in D \quad (\text{II.6})$$

where  $h$  is a real constant different from zero. The points  $\mathbf{x} \in D$  such that  $G(\mathbf{x}) = 0$  are called Fixed Points (or stationary points, or equilibria, etc.) of (II.5) and (II.6), for obvious reasons. The question on whether there are any such points is easily answered by the following result, [32], for the class of maps relevant to chemical reactions.

**THEOREM II.10.** (The Brouwer Fixed Point Theorem) *Let  $D$  be a bounded closed convex subset of a finite dimensional normed vector space. If  $\tau$  is a continuous mapping of  $D$  into itself,  $\tau$  has a fixed point in  $D$ .*

Once a fixed point  $\hat{P} \in D$  for (II.5) and (II.6) has been found, it is important to study its stability, i.e. the kind of evolution that the solutions of (II.5) or (II.6) undergo for initial conditions close to  $\hat{P}$ . In the following this formal definition of stability is used [33]:

**DEFINITION II.5.** *A fixed point  $\hat{P}$  of a map  $\tau : D \rightarrow D$  (or of an ordinary differential equation  $P' = R(P)$ ,  $P \in D$ ) is said to be **Stable** if for every neighbourhood  $V$  of  $\hat{P}$  in  $D$  there exists a neighbourhood  $V_1 \subseteq V$  such that  $\tau^k(P) \in V$  for every  $P \in V_1$  and for every  $k \in \mathbb{N}$  (or the solution  $P(t)$  lies in  $V$  for every initial condition  $P(0) \in V_1$  and for all  $t > 0$ ). If, in addition,  $V_1$  can be chosen so that  $\tau^k(P) \rightarrow \hat{P}$  as  $k \rightarrow \infty$  (or  $P(t) \rightarrow \hat{P}$  as  $t \rightarrow \infty$ ) then  $\hat{P}$  is said to be **Asymptotically Stable**. A fixed point is called **Unstable** if it is not stable.*

Unfortunately, there are at least a couple of reasons for which the stability of the fixed points of the systems considered here cannot be analyzed by looking at the spectrum

of  $G'$ , the Fréchet derivative of  $G$ . In fact, even the very simple example  $2A \rightleftharpoons B + C$  has a  $G'$  with spectral radius equal to 1. Moreover, when the reaction involves many chemicals,  $G'$  can be so large that it is practically impossible to compute its eigenvalues. Nonetheless, there are cases in which it is possible to use Liapunov's stability theory, for the continuous dynamical system, while for every single reaction the contraction mapping principle and some elementary topology completely solve the problem. Putting together these two approaches, the most general case can be successfully tackled. In Chapters III, IV, V and VI the following definitions and theorems will be widely used [32].

**DEFINITION II.6.** Suppose that  $\mathcal{B}$  and  $\mathcal{C}$  are Banach spaces. Let  $D$  be an open subset of  $\mathcal{B}$ , and let  $\tau : D \rightarrow \mathcal{C}$  be a map.  $\tau$  is said to be **Fréchet Differentiable** at  $g \in D$  if there exists a linear operator  $\tau' : \mathcal{B} \rightarrow \mathcal{C}$  such that

$$\lim_{\|h\| \rightarrow 0} \frac{\|\tau(g+h) - \tau(g) - \tau'(h)\|}{\|h\|} = 0.$$

When  $\tau'$  exists it is called the **Fréchet Derivative** of  $\tau$  at  $g$ .

**DEFINITION II.7.** The map  $\tau$  is called a **Contraction** with Lipschitz constant  $q$  if  $\|\tau(f) - \tau(g)\| \leq q\|f - g\|$  and  $q < 1$ , for every  $f$  and  $g$  in its domain.

Then the following is true:

**THEOREM II.11.** (The Contraction Mapping Principle) Suppose that  $\tau$  maps the closed subset  $D$  of a Banach space  $\mathcal{B}$  into  $D$  and is a contraction with Lipschitz constant  $q$ . Then  $\tau$  has exactly one fixed point,  $\hat{P}$  say, in  $D$ . Moreover, for every  $P \in D$ ,

$$\|\tau^k(P) - \hat{P}\| \leq \frac{q^k}{1-q} \|\tau(P) - P\|, \quad \text{for every } k \in \mathbb{N}.$$

**THEOREM II.12.** Suppose that  $\mathcal{B}$  and  $\mathcal{C}$  are Banach spaces. Let  $D$  be a convex subset of  $\mathcal{B}$  and assume that  $\tau : D \rightarrow \mathcal{C}$  is Fréchet differentiable at every point of  $D$ . Then

$$\|\tau(f) - \tau(g)\| \leq \|f - g\| \sup_{h \in D} \|\tau'(h)\|,$$

i.e.  $\tau$  has a Lipschitz constant  $q = \sup_{h \in D} \|\tau'(h)\|$ .

Finally, let  $D \subseteq \mathbb{R}^n$  be an open set, and  $G : D \rightarrow \mathbb{R}^n$  be a map. Then [33]

**THEOREM II.13.** (First Liapunov's Stability Theorem) Let  $\hat{P} \in D$  be a fixed point for (II.6). Let  $V : U \rightarrow \mathbb{R}$  be a continuous function defined on a neighbourhood  $U \subset D$  of  $\hat{P}$ , differentiable on  $U \setminus \hat{P}$ , such that

(a)  $V(\hat{P}) = 0$  and  $V(P) > 0$  if  $P \neq \hat{P}$ ;

(b)  $\frac{dV}{dt} \leq 0$  in  $U \setminus \hat{P}$ .

Then  $\hat{P}$  is stable. Furthermore, if also

(c)  $\frac{dV}{dt} < 0$  in  $U \setminus \hat{P}$ ,

then  $\hat{P}$  is asymptotically stable.

## II.4 Ordinary Differential Equations and Euler's Method

In this section the basic theorems about existence and uniqueness of the solutions of an ordinary differential equation (O.D.E.), needed for the study of chemical reactions, are given following the approach of [33],[34] and [35]. Moreover, Euler's method for the numerical solution of such O.D.E.'s is presented from the viewpoint of [36].

Let  $U$  be a subset of a normed vector space  $E$ , and  $f : U \rightarrow E$  a smooth function. Then

$$\frac{dx}{dt} = f(x), \quad x \in U, \quad x(t_0) = x_0 \quad (\text{II.7})$$

is called an O.D.E. with initial condition  $x_0$ . A solution of (II.7) is a differentiable map  $\varphi : I \rightarrow U$ ,  $t_0 \in I = (a, b) \subseteq \mathbb{R}$ , such that for every  $s \in I$

$$\left( \frac{d\varphi}{dt} \right)_{t=s} = f(\varphi(s)) \quad \text{and} \quad \varphi(t_0) = x_0.$$

$f$  is called a vector field, and  $U$  is called the phase space of (II.7). These two fundamental results follow.

**THEOREM II.14.** *Let  $U$  be an open subset of a normed vector space  $E$ . Let  $f : W \rightarrow E$  be a continuously differentiable map, and  $x_0 \in W$ . Then there is some  $c > 0$  and a unique solution  $\varphi : (-c, c) \rightarrow W$  of (II.7).*

**THEOREM II.15.** *Let  $\varphi_1 : I_1 \rightarrow U$  and  $\varphi_2 : I_2 \rightarrow U$  be two solutions of (II.7), such that  $\varphi_1(t_0) = x_0 = \varphi_2(t_0)$ . Then there exists an interval  $I_3 \subset \mathbb{R}$  such that  $t_0 \in I_3$  and  $\varphi_1(t) = \varphi_2(t)$  for every  $t \in I_3$ .*

Clearly, by the two previous theorems, it is possible to find a maximal interval  $(\alpha, \beta)$  (possibly  $\alpha = -\infty$  or  $\beta = \infty$  or both) on which a solution of (II.7) is defined. Then the following can be proven.

**THEOREM II.16.** *Let  $U \subset E$  be open, and let  $f : U \rightarrow E$  be a continuously differentiable map. Let  $\varphi(t)$  be a solution of (II.7) on a maximal open interval  $J = (\alpha, \beta)$  with  $\beta < \infty$ . Then given any compact set  $K \subset U$ , there is some  $t \in (\alpha, \beta)$  with  $\varphi(t) \notin K$ .*

Therefore, if a solution  $\varphi$  of (II.7) cannot be extended beyond a certain finite time  $\beta$ , it means that  $\varphi(t)$  tends to the boundary of  $U$  or  $\|\varphi(t)\| \rightarrow \infty$  or both. It follows that (II.7) surely has a solution for all times if the complement of  $U$  is a “repeller” for the flow based at the interior points of  $U$ . That is to say, for  $\varphi$  to be defined for all  $t > t_0$  it is sufficient that the vector field does not allow the solution to reach the boundary of a compact subset of  $U$ .

Once it is known that (II.7) has a unique solution  $\varphi$  defined for  $t \in (\alpha, \beta)$ , the need arises for constructing such a solution, and most of the times nothing better than a numerical integration can be done. In such a case it is important to know how close the computer outputs are to the real solution. Among the many integration techniques, the Euler’s method is helpful in the analysis of the solutions of the equations of the law of mass action.

This method is based on the observation that

$$\frac{\varphi(t+h) - \varphi(t)}{h} \approx f(\varphi(t)) \quad (\text{II.8})$$

for small  $h$ , with  $t, t+h \in (\alpha, \beta)$ , and sufficiently smooth  $f$ . Then it is possible to approximately compute the values of  $\varphi$  at given times  $t_i = i \cdot h$ ,  $i = 0, 1, 2, \dots$  using the recursion formula

$$\varphi_{i+1}(h) = \varphi_i(h) + hf(\varphi_i(h)), \quad \varphi_0(h) = x_0. \quad (\text{II.9})$$

Assume that  $z_y$  is the solution of  $z' = f(z)$  with initial condition  $z(t) = y$  for every  $y \in U$ .

Define

$$F(t, y, h) = \begin{cases} \frac{z_y(t+h) - y}{h}, & \text{if } h \neq 0 \\ f(y), & \text{if } h = 0. \end{cases}$$

Then the theorem given below applies.

**THEOREM II.17.** Consider (II.7), having the unique solution  $\varphi : (\alpha, \beta) \rightarrow U$ . Let  $a, b \in \mathbb{R}$  be such that  $t_0 \in J = [a, b] \subset (\alpha, \beta)$ . Let  $f$  be Lipschitz continuous on  $U$  with constant  $M$ , and let there exist  $h_0, N \in \mathbb{R}^+$  such that  $\|F(t, \varphi(t), h) - f(\varphi(t))\| \leq N|h|^p$  for some  $p > 0$ , for every  $t$  in  $J$  and for  $|h| \leq h_0$ . Then

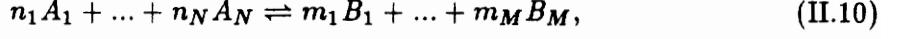
$$\|e(t, h_n)\| \leq |h_n|^p N \left( \frac{e^{-M|t-t_0|} - 1}{M} \right)$$

for every  $t \in [a, b]$  and  $h_n = (t - t_0)/n$ ,  $n \in \mathbb{N}$ , with  $|h_n| \leq h_0$ .

Here  $e(t, h)$  is called the global discretization error and is defined as  $e(t_i, h) = \varphi_i(h) - \varphi(t_0 + ih)$ , where  $\varphi(t)$  is the solution of (II.7) and  $\varphi_i(h)$  is computed as in (II.9). The method is called convergent if  $\lim_{n \rightarrow \infty} e(t, h_n) = 0$  for all  $t \in J$ . When this is the case, we say that the map defined by (II.9) converges in norm to the solution of (II.7) in  $J$ , meaning that the sequence of simple functions  $\{\psi_n\}$  that take the values  $\{\varphi_i(h_n)\}_i$  on the intervals  $\{(t_i, t_{i+1}]\}_i$  converge in norm to the solution of (II.7) in  $J$  as  $n \rightarrow \infty$ .

## II.5 Boltzmann Maps for Single Chemical Reactions

Consider the general single chemical reaction



which is called **autocatalytic** if some of the  $A$ 's equal some of the  $B$ 's, and it is called **non-autocatalytic** otherwise. In the case of autocatalytic reactions, every chemical that appears on both sides of the reaction is called autocatalytic. The law of mass action associates to (II.10) a dynamical system of the form

$$\frac{dp_i}{dt} = -r_i \lambda (p_1^{n_1} \cdots p_N^{n_N} - p_{N+1}^{m_1} \cdots p_{N+M}^{m_M}) = -r_i \lambda D, \quad i = 1, \dots, N + M - N_a, \quad (\text{II.11})$$

where  $N_a$  is the number of autocatalytic elements,  $\lambda$  is the rate constant and  $r_i$  is the difference between the stoichiometric coefficient of the chemical  $i$  that appears on the left hand side of the reaction minus the stoichiometric coefficient of the same chemical that appears on the right.  $D$  is called the **Disequilibrium Parameter**. Then, if (II.10) is non - autocatalytic, all the  $r$ 's relative to the  $A$ 's are positive, while all those relative to the  $B$ 's are negative, and equal the respective stoichiometric coefficients. From now it will be assumed that the chemicals are ordered in such a way that  $r_1 = \max\{r_1, \dots, r_{N+M-N_a}\}$ .

Following an argument parallel to that of section I.6, a discrete version of (II.11) can be constructed using bistochastic maps, if (II.10) is **balanced**, i.e. if  $\sum_i n_i = \sum_j m_j = n$ . In fact, let

$$p_i^* = p_i - r_i \mu D, \quad i = 1, \dots, N + M - N_a, \quad (\text{II.12})$$

be the discrete version, which looks like the Euler's scheme if we take  $\mu = \lambda \Delta t$ . Let  $\Omega = \{A_i, B_j\}_{i,j}$  be the sample space, which contains  $N + M - N_a$  elements. Let  $\mathcal{Q}$  be the simplex of probability measures on  $\Omega$  and let  $P = (p_1, \dots, p_{N+M-N_a}) \in \mathcal{Q}$  represent the set of the normalized concentrations of the chemicals in the reactor, at time  $t$ . Define the sampling map  $\sigma : \mathcal{Q} \rightarrow \mathcal{Q}_n$  as  $\sigma(P) = \otimes_1^n P$ , where  $\mathcal{Q}_n$  is the set of probabilities on  $\Omega^n$ ,

the cartesian product of  $n$  copies of the sample space. Then each component of  $\sigma(P)$  has the form of a product of  $n$  components of  $P$ ,  $p_{i_1} \cdots p_{i_n}$  say, and it can be interpreted as the probability of fishing out the molecules  $C_{i_1}, \dots, C_{i_n} \in \Omega$  from the reactor, at time  $t$ . This assumes that the particles are uncorrelated before they collide with each other, that is to say  $\sigma$  implements the *Stosszahlansatz*. Moreover, collisions of  $n$  particles only are considered here, as they are the only ones described by (II.10). Let us construct, now, a bistochastic map  $T : \mathcal{Q}_n \rightarrow \mathcal{Q}_n$  that describes the scattering process of  $n$  elements of  $\Omega$  to produce other  $n$  elements of  $\Omega$ . To every  $n$ -tuple in  $\Omega^n$ ,  $\omega_i = (C_{i_1}, \dots, C_{i_n})$  say, it is possible to associate a set of nonnegative numbers that represent the scattering probabilities for the collision of the elements of  $\omega_i$  to produce every  $n$ -tuple  $\omega_j$  of  $\Omega^n$ . Clearly, there are  $(N + M - N_a)^n$  such numbers, i.e. the number of samples with replacement of size  $n$  from a population of  $(N + M - N_a)$  elements [37]. Call  $P_{\omega_i, \omega_j}$  the scattering probability for the process  $\omega_i \rightarrow \omega_j$ . Then  $P_{\omega_i, \omega_j} \geq 0$  and  $\sum_j P_{\omega_i, \omega_j} = 1$ , because the collision of  $n$  particles of  $\Omega$  always produces one element of  $\Omega^n$ . Furthermore, following the argument given in section I.6, we assume for simplicity that  $P_{\omega_i, \omega_j}$  equals  $P_{\omega_i, \omega'_j}$ , for every permutation  $\omega'_j$  of  $\omega_j$ . That is to say, we consider equivalent for the scattering process  $n$ -tuples that contain the same elements, even if they are differently ordered.

Now, assume that  $x$  is the cumulative scattering probability for the process

$$\omega_1 = (A_1, \dots, A_1, \dots, A_N, \dots, A_N) \longrightarrow (B_1, \dots, B_1, \dots, B_M, \dots, B_M) = \omega_2, \quad \text{and}$$

$$\omega_1 \longrightarrow \pi_j(\omega_2),$$

for all the permutations of  $\pi_j(\omega_2)$  of  $\omega_2$ , where  $\omega_1$  contains  $n_i$  elements  $A_i$  for every  $i$ , and  $\omega_2$  contains  $m_j$  elements  $B_j$  for every  $j$ . Then

$$\begin{aligned} P_{\omega_1, \omega_1} &= P_{\omega_1, \pi(\omega_1)} = (1 - x) \frac{n_1! \cdots n_N!}{n!}, \\ P_{\omega_1, \omega_2} &= P_{\omega_1, \pi(\omega_2)} = x \frac{m_1! \cdots m_M!}{n!}, \end{aligned} \tag{II.13}$$

because there are  $n!/(n_1! \cdots n_N!)$  permutations of  $\omega_1$ , and  $n!/(m_1! \cdots m_M!)$  permutations of  $\omega_2$ . Moreover

$$P_{\omega_1, \omega_j} = 0, \quad \text{for every } \omega_j \in \Omega^n \setminus [\{\pi_k(\omega_1)\}_k \cup \{\pi_l(\omega_2)\}_l] = \Lambda, \quad (\text{II.14})$$

because  $\omega_1$  can produce either permutations of itself –by not reacting– or permutations of  $\omega_2$  –by reacting– and nothing else. Similarly, for  $\omega_2$  we get

$$P_{\omega_2, \omega_1} = P_{\omega_2, \pi(\omega_1)} = P_{\omega_1, \omega_2}, \quad (\text{II.15})$$

because we assume the principle of microscopic reversibility,

$$P_{\omega_2, \omega_2} = P_{\omega_2, \pi(\omega_2)} = \left(1 - x \frac{m_1! \cdots m_M!}{n_1! \cdots n_N!}\right) \cdot \frac{m_1! \cdots m_M!}{n!}, \quad (\text{II.16})$$

and

$$P_{\omega_2, \omega_j} = 0, \quad \text{for every } \omega_j \in \Lambda. \quad (\text{II.17})$$

Finally, for  $i \neq 1, 2$

$$P_{\omega_i, \omega_j} = 0, \quad \text{for every } \omega_j \notin \{\pi_k(\omega_i)\}_k \quad (\text{II.18})$$

and

$$P_{\omega_i, \pi(\omega_i)} = \frac{1}{\# \text{ of permutations of } \omega_i}, \quad (\text{II.19})$$

because only  $\omega_1$  and  $\omega_2$  can react according to (II.10).

These prescriptions are enough to construct the bistochastic  $(N + M - N_a)^n \times (N + M - N_a)^n$  matrix  $T$ , as a function of  $x$ , by taking  $T_{i,j} = P_{\omega_i, \omega_j}$ , as done in section I.6. It is clear that  $T$  turns out to be symmetric and with rows and columns sum equal to 1, by construction. Now, it only remains to compute  $x$ . This can be done by applying  $T$  to  $\sigma(P)$ , which produces a new probability measure  $P_n^*$  on  $\Omega^n$ , and then taking the conditional expectation onto the first factor  $E(P_n^*)$ , which produces a new probability,  $P^*$  say, on  $\Omega$ . Then  $x$  can be computed by requiring that the first component of  $P^*$ ,  $p_1^*$ , satisfies

$$p_1^* = p_1 - r_1 \mu D,$$



which is the desired form for the discretization of the law of mass action (II.12). This is done observing that  $p_1$  can be written as

$$p_1 = p_1 \cdot 1^{n-1} = p_1 \left( \sum_{j=1}^{N+M-N_a} p_j \right)^{n-1}$$

thus making  $p_1$  into a polynomial of degree  $n$ , which is needed for the fact that  $p_1^*$  is a polynomial of degree  $n$ . Then the remaining conditions imposed by the rest of (II.12) turn out to be automatically satisfied. In fact, the law of mass action (both discrete and continuous version) has  $N + M - N_a - 1$  constants of motion, and so it is enough to follow the evolution of  $p_1$  (see next chapter). Furthermore, these constants of motion can be used to subdivide  $T$  into smaller bistochastic blocks, that do not change the norm of the semiprobabilities on which they act, thus allowing  $\tau$  to have the same constants of motion as in the law of mass action. For the sake of clarity, we will consider the autocatalytic and the non-autocatalytic cases as separate. In fact, when  $E$  is applied to  $P_n^*$  it happens that elements from both  $\{\pi(\omega_1)\}$  and  $\{\pi(\omega_2)\}$  contribute to  $p_1^*$ , if  $A_1 = B_M$  for instance. On the contrary, if no  $B_i$  equals  $A_1$  the contribution to  $p_1^*$  comes from  $\{\pi(\omega_1)\}$  only. Then the equation for  $x$ , in the non-autocatalytic case, is the following

$$\begin{aligned} p_1^* &= \frac{(n-1)!}{(n_1-1)!n_2!\cdots n_N!} \left[ (1-x)p_1^{n_1}\cdots p_N^{n_N} + x p_{N+1}^{m_1}\cdots p_{N+M}^{m_M} \right] \\ &+ \sum_{\substack{i_2, \dots, i_n \\ (1, i_2, \dots, i_n) \notin \{\pi_k(\omega_1)\}}} p_1 p_{i_2} \cdots p_{i_n} \\ &= p_1 - x \frac{(n-1)!}{(n_1-1)!n_2!\cdots n_N!} \left( p_1^{n_1}\cdots p_N^{n_N} - p_{N+1}^{m_1}\cdots p_{N+M}^{m_M} \right), \end{aligned} \quad (\text{II.20})$$

because  $(n-1)!/((n_1-1)!n_2!\cdots n_N!)$  is the number of permutations of  $\omega_1$  when the first element is fixed to be  $A_1$ . Therefore, we get

$$x = \frac{(n_1-1)!n_2!\cdots n_N!}{(n-1)!} n_1 \mu = \frac{n_1!n_2!\cdots n_N!}{(n-1)!} \mu. \quad (\text{II.21})$$

Similarly, for the autocatalytic case ( $A_1 = B_M$ ) we have

$$\begin{aligned}
 p_1^* &= \frac{(n-1)!}{(n_1-1)!n_2!\cdots n_N!} \left[ (1-x)p_1^{n_1} \cdots p_N^{n_N} + x p_{N+1}^{m_1} \cdots p_{N+M}^{m_M} \right] + \sum_{\substack{i_2, \dots, i_n \\ (1, i_2, \dots, i_n) \in \Lambda}} p_1 p_{i_2} \cdots p_{i_n} \\
 &+ \frac{(n-1)!}{m_1! \cdots m_{M-1}!(m_M-1)!} \left[ x \frac{m_1! \cdots m_M!}{n_1! \cdots n_N!} p_1^{n_1} \cdots p_N^{n_N} \right. \\
 &\quad \left. + \left( 1 - x \frac{m_1! \cdots m_M!}{n_1! \cdots n_N!} \right) p_{N+1}^{m_1} \cdots p_{N+M}^{m_M} \right] \\
 &= p_1 - x \frac{(n-1)!}{(n_1-1)!n_2!\cdots n_N!} \left[ 1 - \frac{m_M}{n_1} \right] \left( p_1^{n_1} \cdots p_N^{n_N} - p_{N+1}^{m_1} \cdots p_{N+M}^{m_M} \right),
 \end{aligned} \tag{II.22}$$

and we get

$$x = \frac{n_1!n_2!\cdots n_N!}{(n-1)!} \mu,$$

as for the non-autocatalytic case.

It is now clear why taking  $P_{\omega_i, \omega_j} = P_{\omega_i, \omega'_j}$  does not alter the physical content of the theory, when compared to the most general assumption. In fact, in this last case we would have an equation for an higher number of unknowns, rather than (II.21), for  $x$ . This shows that an infinite number of stochastic processes fit the discrete law of mass action, and our choice is just the simplest one.

Note that  $T$  is bistochastic for  $x \in [0, \min\{1; (n_1! \cdots n_N!)/(m_1! \cdots m_M!)\}]$ . Therefore, the method described here yields a bistochastic matrix if  $\mu \in \mathcal{R}_B = [0, L_B]$  where

$$L_B = \frac{(n-1)!}{n_1! \cdots n_N!} \cdot \min \left\{ 1; \frac{n_1! \cdots n_N!}{m_1! \cdots m_M!} \right\} = \min \left\{ \frac{(n-1)!}{n_1! \cdots n_N!}; \frac{(n-1)!}{m_1! \cdots m_M!} \right\}. \tag{II.23}$$

We call  $\mathcal{R}_B$  the **Bistochasticity Range** of the reaction (II.10). Then we have  $\mathcal{R}_B = [0, 1/n]$  for  $\boxed{nA \rightleftharpoons m_1B_1 + \cdots + m_MB_M}$ ; while  $\mathcal{R}_B = [0, 1]$  for  $\boxed{A + B \rightleftharpoons C + D}$ ; and so on.

Finally, observe that every  $T$  constructed in the way presented here can be expressed as a direct sum  $T = T' \oplus M_1 \oplus \cdots \oplus M_m$ , with  $M_i = (1/t_i) \cdot J_{t_i}$ ,  $i = 1, \dots, m$ , where  $J_{t_i}$  is a  $t_i \times t_i$  matrix whose entries are all equal to 1, and  $T' = [P_{\pi_k(\omega_i), \pi_l(\omega_j)}]_{i,j=1,2}$ . Also,  $T'$  is a bistochastic matrix whenever  $\mu \in \mathcal{R}_B$ , and it is positive if  $\mu \in (0, L_B)$ . Then, because of Theorem II.8 and Theorem II.9, the following result holds.

**LEMMA II.2.** *Given a balanced chemical reaction, the associated bistochastic matrix  $T$  has a bistochastic block  $T'$  with a spectral gap  $\Delta > 0$  whenever  $\mu$  is strictly contained in the bistochasticity range.*

## CHAPTER III: SINGLE REACTIONS IN STIRRED TANKS

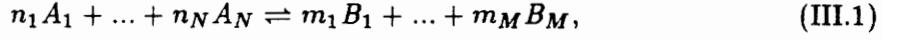
### III.1 Introduction

This chapter is devoted to the study of single chemical reactions that take place in so called “stirred” containers. This means that at every time the reacting chemicals are homogeneously distributed in the volume available to them, thus giving rise to space independent dynamical systems. Both the autocatalytic and non-autocatalytic cases are considered, for the most general balanced reactions that satisfy the principle of microscopic reversibility. For technical reasons, the two kinds of reactions must be studied separately, although a few results can be drawn jointly.

Here the discrete dynamical systems only are considered, as the continuous time problems will be addressed in chapter V. Section III.2 provides the setting for the description of non-autocatalytic reactions, which it will be dealt with through section III.6. In section III.3 we study the detailed case  $nA \rightleftharpoons mB + lC$ , some of the results of which are useful in III.3.1, which “generalizes” this to  $nA \rightleftharpoons m_1B_1 + \dots + m_MB_M$ . In section III.4 and III.5 we treat the remaining cases. For technical reasons, the cases in sections III.3 and III.5 cannot be treated as special cases of those in section III.4. Section III.6 deals with questions concerning the stability of the fixed points, the entropy of the systems and some problems on the convergence of the iterations. Section III.7 provides the setting for the autocatalytic cases, which will be the subject of the rest of this chapter. Section III.8 addresses the questions about convergence of the iterations, stability of the fixed points and increase of the entropy, for the autocatalytic case. Section III.9 concludes this chapter with some “completely solved” examples.

### III.2 The Non-Autocatalytic Reaction

In section II.5 a general method is described for constructing “stochastic models” of balanced chemical reactions, i.e. reactctons of the form



where  $n_1 + \dots + n_N = m_1 + \dots + m_M$ . The process is regarded as “stirred”, that is, the state is described by the concentrations  $p_{A_1}, \dots, p_{A_N}, q_{B_1}, \dots, q_{B_M}$ . If we normalize the sum of these concentrations to be  $\sum_i p_i + \sum_j q_j = 1$ , we can construct a probability theory in which  $\Omega = \{A_1, \dots, A_N, B_1, \dots, B_M\}$  is the sample space,  $P = (p_1, \dots, q_M)$  is a probability measure on  $\Omega$ , and  $\mathcal{Q} = \{P\} \subset \mathbb{R}^K$  is the simplex of probability measures on  $\Omega$ , where  $K = N + M$ . Then, 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  $A_1, \dots, B_M$ .

For the non-autocatalytic case, i.e. for the case when no  $A$  is equal to any  $B$ , the law of mass action gives the rate equations

$$\begin{aligned} \frac{dp_j}{dt} &= n_j \lambda (q_1^{m_1} \dots q_M^{m_M} - p_1^{n_1} \dots p_N^{n_N}), & j &= 1, \dots, N \\ \frac{dq_k}{dt} &= -m_k \lambda (q_1^{m_1} \dots q_M^{m_M} - p_1^{n_1} \dots p_N^{n_N}), & k &= 1, \dots, M \end{aligned} \quad (\text{III.2})$$

where  $\lambda > 0$  is the rate constant. These generalize the equations of [21],[22]. Such an O.D.E. describes the time evolution of the concentrations, which leads to a motion within  $\mathcal{Q}$ . The fact that (III.2) gives rise to a probability theory is easily seen by the observation that the boundaries of  $\mathcal{Q}$  repel the points approaching from inside, and so it is a consequence of Theorem II.16.

Because of the fact that (III.1) is balanced, we can express the discrete form

$$\begin{aligned} \dot{p}_j &= p_j + n_j \mu (q_1^{m_1} \dots q_M^{m_M} - p_1^{n_1} \dots p_N^{n_N}), & j &= 1, \dots, N \\ \dot{q}_k &= q_k - m_k \mu (q_1^{m_1} \dots q_M^{m_M} - p_1^{n_1} \dots p_N^{n_N}), & k &= 1, \dots, M \end{aligned} \quad (\text{III.3})$$

as a Boltzmann map  $\tau$  on a probability space [28], 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 non-decreasing function along the map, for a range of  $\mu > 0$ . The fact that (III.3) looks like a discretization of (III.2) will be discussed in chapter V.

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 [38]. (There is no difficulty in classically describing particles that change identity).

It is for this class of models that we here prove the existence and uniqueness of the fixed points and convergence to them. Equations (III.2) and (III.3) involve  $N + M$  unknowns  $p_1, \dots, q_M$ , 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. We can write these relations as  $n_i p_1 - n_1 p_i = K_i$  for  $i = 2, \dots, N$ , and  $m_j p_1 + n_1 q_j = L_j$  for  $j = 1, \dots, M$ , and we call them the **Hyperplanes of the Motion**. Their intersection is a straight line in  $\mathbb{R}^K$  that cuts through  $\mathcal{Q}$ , and we call **Line of the Motion** the portion of this line that lies in  $\mathcal{Q}$ . This line segment, denoted by  $\Gamma$  in this thesis, is uniquely determined by the initial conditions,  $P(0) \in \mathcal{Q}$ , and its name comes from the fact that the solutions to (III.2) and the itinerary described by (III.3) both lie in it. In particular,  $P \in \Gamma$  implies  $p_1 \in [B, C]$  where  $B \geq \max[0; K_2/n_2; \dots; K_N/n_N]$  and  $C \leq \min[1; L_1/m_1; \dots; L_M/m_M]$ . Thus the dynamics reduces to a non-linear map,  $[B, C] \mapsto [B, C]$  for the remaining single variable. Once  $P(0)$  has been chosen, the concentrations vary in such a way to obey

$$\frac{dp_i}{dp_1} = \frac{n_i}{n_1}, \quad \frac{dq_i}{dp_1} = -\frac{m_i}{n_1}, \quad (\text{III.4})$$

where all the concentrations are written as functions of  $p_1$ , which we use as the independent variable parametrizing  $\Gamma$ . Because of this, we will often write  $\tau(p_1)$  instead of  $\tau(P)$ , to

stress the fact that the iterations of certain initial conditions lie in a straight line.

### III.3 A Detailed Case

We consider all the reactions of the form



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 by Theorem II.11.

The sample space we have is  $\Omega = \{A, B, C\}$ ; then the set of probability measures on it,  $\mathcal{Q} = \{P\}$ , is made of triples  $P = (p_A, p_B, p_C) \in \mathbb{R}^3$  such that  $0 \leq p_A, p_B, p_C \leq 1$ , and  $\sum_{i=A}^C p_i = 1$ . The discrete map,  $\tau : \mathcal{Q} \rightarrow \mathcal{Q}$ , that takes  $P$ , at the instant  $t$ , to  $P^*$ , at the instant  $t + 1$ , is defined by the following set of equations that express the discrete form of the law of mass action:

$$\begin{aligned} p_A^* &= p_A - n\mu(p_A^n - p_B^m p_C^l) = p_A - n\mu D \quad \text{say} \\ p_B^* &= p_B + m\mu D \\ p_C^* &= p_C + l\mu D \end{aligned} \quad (\text{III.6})$$

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

We see that the two quantities that are conserved by the map  $\tau$  are  $p_A + p_B + p_C = 1$  and the quantity  $K = mp_A + np_B$ . Then  $p_A^*, p_B^*, p_C^* \geq 0$  follows from Theorem II.5, provided that the system comes from a bistochastic process. The condition for this is  $\mu \leq 1/n$ , as found by applying equation (II.23). Then, the non-negativity of  $p_B$  and  $p_C$  implies  $p_A \leq K/m$  and  $p_A \leq (n - K)/l$ , and eliminating  $p_B, p_C$  we get a map  $p_A^* = p_A - n\mu D(p_A)$  from  $[0, C]$  to itself, where  $C = \min\{1; K/m; (n - K)/l\}$ , which we also denote by  $\tau$ . Our first lemma identifies  $[0, 1/2]$  as an invariant subset, for the cases in which  $C \geq 1/2$ .

LEMMA III.1. If  $C \geq 1/2$ , and  $\mu \leq 1/n$ , the interval  $[0, 1/2]$  is invariant under  $\tau$ ; otherwise it is  $[0, C]$  that is invariant.

PROOF: If  $C \leq 1/2$ , the preservation of the probabilities under  $\tau$  trivially makes  $[0, C]$  invariant. Therefore, let us take  $C > 1/2$  and  $x = p_A \in [0, 1/2]$ . If  $D \geq 0$  then  $x^* = x - \mu n D(x) \leq x$ , so  $x^* \in [0, 1/2]$ . So we may assume  $D(x) < 0$ . Then  $x^* \leq x - D(x) = x - x^n + p_B^m p_C^l$ . 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  $\frac{m}{y} = \frac{l}{(\gamma - y)}$  i.e.  $y = \gamma \frac{m}{n}$ ,  $\gamma - y = \gamma \frac{l}{n}$ . So putting  $p_B = y$ ,  $p_C = \gamma - y$  we get for  $D < 0$

$$x^* \leq x - x^n + \left(\frac{m}{n}\right)^m \left(\frac{l}{n}\right)^l (1 - x)^n = f(x) \quad \text{say.} \quad (\text{III.7})$$

For  $n = 2$ ,  $l = 1 = m$  the right hand side is  $x - x^2 + (1 - x)^2/4$  which takes its maximum value,  $1/3$ , at  $x = 1/3$ , giving  $x^* \leq 1/3 \in [0, 1/2]$ . 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  $f(x) \leq f(1/2) < \frac{1}{2}$ . Hence  $x^* \in [0, 1/2]$ .

Finally, for  $n \geq 4$ , 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 convex, so takes its maximum at the end-points  $l = 1$ ,  $m = n - 1$  (or vice versa). Hence we get

$$x^* \leq x - x^n + \left(\frac{n-1}{n}\right)^{n-1} \frac{1}{n} (1-x)^n < x - x^n + \frac{1}{n} (1-x)^n = f_1(x). \quad (\text{III.8})$$

If  $x \leq \frac{1}{4}$ ,  $x^* < \frac{1}{4} + \frac{1}{n} \leq \frac{1}{2}$  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  $n \geq 4$ ,

$$f_1'(x) = 1 - nx^{n-1} - (1-x)^{n-1} \geq 1 - 4 \left(\frac{1}{2}\right)^3 - \left(\frac{3}{4}\right)^3 > 0. \quad (\text{III.9})$$

So  $f_1(x) \leq f_1(1/2) = \frac{1}{2} - \left(\frac{1}{2}\right)^n + \frac{1}{n} \left(\frac{1}{2}\right)^n < \frac{1}{2}$ . This proves  $x^* \in [0, 1/2]$  for  $n \geq 4$  too. ■



We note that by Brouwer's fixed point theorem (Theorem II.10),  $\tau$  has a fixed point in  $[0, 1/2]$ . We now show that the set  $[0, 1/2]$  is a global attractor.

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

PROOF: If  $x \in [1/2, C]$ ,  $1 - x = \gamma \leq 1/2$ , and we have

$$\begin{aligned} x - x^* &= n\mu(x^n - p_B^m p_C^l) \geq n\mu \left\{ \left(\frac{1}{2}\right)^n - \max_{0 \leq y \leq \gamma} [y^m(\gamma - y)^l] \right\} \\ &= n\mu \left[ \left(\frac{1}{2}\right)^n - \left(\frac{m}{n}\right)^m \left(\frac{l}{n}\right)^l \gamma^n \right] \geq n\mu \left[ \left(\frac{1}{2}\right)^n - \left(\frac{n-1}{n}\right)^{n-1} \frac{1}{n} \left(\frac{1}{2}\right)^n \right] \quad (\text{III.10}) \\ &> n\mu \left(\frac{1}{2}\right)^n \left(1 - \frac{1}{n}\right) = \epsilon. \end{aligned}$$

So a step left of size  $> \epsilon$  occurs as long as  $x \geq 1/2$ , so we reach  $[0, 1/2]$  in at most  $\frac{1}{2\epsilon} = \frac{2^{n-1}}{\mu(n-1)}$  steps.  $\blacksquare$

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

LEMMA III.3. *If  $0 < K < n$ , and  $\mu \leq 1/n$ , then  $\tau$  is a contraction on  $[0, a]$ .*

PROOF: As  $a \leq 1/2$ , it is safe to study  $\tau$  in  $[0, 1/2]$ . We show that  $\sup_{x \in [0, 1/2]} \left| \frac{d}{dx} \tau(x) \right| < 1$ .

Note that  $p_B = (K - mx)/n$  and  $p_C = (n - K - lx)/n$ . Then

$$\begin{aligned} \frac{d\tau}{dx} &= 1 - n^2 \mu x^{n-1} - m^2 \mu (K - mx)^{m-1} \frac{p_C^l}{n^{m-1}} - l^2 \mu p_B^m \frac{(n - K - lx)^{l-1}}{n^{l-1}} \\ &= 1 - n^2 \mu x^{n-1} - m^2 \mu p_B^{m-1} p_C^l - l^2 \mu p_B^m p_C^{l-1} = 1 - F(x) \quad \text{say.} \end{aligned} \quad (\text{III.11})$$

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

$$\inf_{x \in [0, 1/2]} F(x) > 0 \quad \text{so} \quad \frac{d\tau}{dx} < 1 - \epsilon, \quad x \in [0, 1/2] \quad (\text{III.12})$$

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

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

$$F(x) = \mu(4x + p_B + p_C) = \mu(3x + 1) \leq \frac{1}{2} \left( \frac{3}{2} + 1 \right) < 2 \quad (\text{III.13})$$

as required.

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

$$F(x) \leq \frac{1}{n} [n^2 x^{n-1} + (1-y)^{n-1} + (n-1)^2 y(1-y)^{n-2}]. \quad (\text{III.14})$$

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

Hence

$$\begin{aligned} F(x) &\leq \frac{1}{n} \left[ n^2 x^{n-1} + H \left( \frac{1}{n} \right) \right] = \frac{1}{n} \left[ n^2 x^{n-1} + \left( 1 - \frac{1}{n} \right)^{n-2} (n-1) \right] \\ &\leq n \left( \frac{1}{2} \right)^{n-1} + \left( \frac{n-1}{n} \right)^{n-1} < 3 \cdot \frac{1}{4} + 1 < 2. \end{aligned} \quad (\text{III.15})$$

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

$$F(x) \leq \frac{1}{n} \left\{ n^2 x^{n-1} + y^{m-1} (1-y)^{l-1} [m^2(1-y) + l^2 y] \right\}, \quad 0 \leq y \leq 1. \quad (\text{III.16})$$

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

$$y = \frac{m-1}{n-2}, \quad 1-y = \frac{l-1}{n-2} \quad (\text{III.17})$$

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

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

$$\begin{aligned} F(x) &\leq \frac{1}{n} \left[ n^2 x^{n-1} + \frac{(n-3)^{n-3}}{(n-2)^{n-2}} (n-2)^2 \right] \\ &\leq n \left( \frac{1}{2} \right)^{n-1} + \frac{(n-3)^{n-3}}{n(n-2)^{n-4}} < 2. \end{aligned} \quad (\text{III.18})$$

■

### III.3.1 A Generalization

We can now treat the case

$$nA \rightleftharpoons m_1 B_1 + \dots + m_M B_M \quad (\text{III.19})$$

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

$$p_A^* = p_A - n\mu (p_A^n - q_1^{m_1} \dots q_M^{m_M}) = p_A - n\mu D \quad (\text{III.20})$$

and

$$m_j p_A + n q_j = K_j, \quad j = 1, \dots, M. \quad (\text{III.21})$$

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

$$L = m_1 \log q_1 + m_2 \log q_2 + \dots + m_M \log q_M. \quad (\text{III.22})$$

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

$$q_1 = \frac{m_1}{n} \gamma, \dots, q_M = \frac{m_M}{n} \gamma. \quad (\text{III.23})$$

Furthermore,

$$m_1^{m_1} m_2^{m_2} \dots m_M^{m_M} \leq (n - M + 1)^{n-M+1} \quad (\text{III.24})$$

if  $m_1 + m_2 + \dots + m_M = n$ . 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

$$(K + 1)^{K+1} x^x \leq (K + x)^{K+x}, \quad \forall x \geq 1. \quad (\text{III.25})$$

With this result in hand, we can prove that

$$\begin{aligned} p_A^* &\leq p_A - p_A^n + \frac{m_1^{m_1} m_2^{m_2} \dots m_M^{m_M}}{n^n} (1 - p_A)^n \\ &\leq p_A - p_A^n + \frac{(n-2)^{n-2}}{n^n} (1 - p_A)^n \\ &\leq p_A - p_A^n + \frac{1}{n^2} (1 - p_A)^n. \end{aligned} \quad (\text{III.26})$$

Let  $C = \min[1; K_1/m_1; \dots; K_M/m_M]$  and repeat now, *mutatis mutandis*, the same argument developed for the proof of Lemma III.1, to get the same result:

**LEMMA III.1.1.** *If  $C \geq 1/2$ , and  $\mu \leq 1/n$ , the interval  $[0, 1/2]$  is invariant under  $\tau$ ; otherwise it is  $[0, C]$  that is invariant.*

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

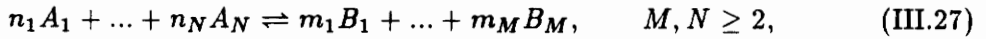
**LEMMA III.2.1.** *If  $C > 1/2$  and  $p_A \in [1/2, C]$ , then  $\tau^k p_A \in [0, 1/2]$  for all  $k \geq \frac{n2^{n-1}}{\mu(n^2 - 1)}$ .*

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

**LEMMA III.3.1.** *If  $K_j \neq 0$  for  $j = 1, \dots, M$ , and  $\mu \leq 1/n$ , then  $\tau$  is a contraction on  $[0, a]$ , where  $a = \min(C, 1/2)$ .*

### III.4 The Higher Non-Autocatalytic Reactions

We consider the reaction



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

$$\begin{aligned} n_1 p_i - n_i p_1 &= K_i, & i &= 2, \dots, N \\ n_1 q_j + m_j p_1 &= L_j, & j &= 1, \dots, M \end{aligned} \quad (\text{III.28})$$

The values of the constants of the motion  $L_2, \dots, K_M$  are determined by the initial conditions, and it follows from them that  $p_1 \geq B \geq \max[0; -K_2/n_2; \dots; -K_N/n_N]$  and  $p_1 \leq C \leq \min[1; L_1/m_1; \dots; L_M/m_M]$ . The relations (III.28) ensure also that  $p_2, \dots, q_M$

are linear functions of  $p_1$ , and the motion then becomes a mapping of  $[B, C]$  to itself:

$$\tau(p_1) = p_1^* = p_1 - n_1 \mu (p_1^{n_1} \cdots p_N^{n_N} - q_1^{m_1} \cdots q_M^{m_M}) = p_1 - F(p_1). \quad (\text{III.29})$$

We show that, away from the fixed points on the boundary,  $\sup_{p_1} \frac{dF}{dp_1} < 2$ , provided that  $\mu$  is smaller than the bistochasticity limit  $L_B$  as given by equation (II.23). 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:  $L_j$  vanishes for one value of  $j \in \{1, \dots, M\}$ . 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  $c_{ij} = n_i q_j + m_j p_i$ , and if one of them vanishes the reaction does not proceed. Let  $N_0 = \min(N, M)$ . Then we can prove the following

**LEMMA III.4.** (a) If  $c_{ij} \neq 0 \quad \forall i, j$  then  $\tau$  is a contraction on the interval  $[B, C]$ , provided that  $N, M \geq 3$  and  $\mu < 2(n-1)^{N_0-2}/n$ . (b) If  $M = 2, N \geq 3$ , and  $c_{ij} \neq 0 \quad \forall i, j$  then  $\tau$  is a contraction on the interval  $[B, C]$ , if  $\mu \leq 1/\max_j(m_j)$ . (c) If  $N = 2$  and  $c_{ij} \neq 0 \quad \forall i, j$ ,  $\tau$  is a contraction on  $[B, C]$  whenever  $\mu \leq 1/n_1$ .

**PROOF:** Suppose that all the  $c_{ij}$ , for  $i = 1, \dots, N, \quad j = 1, \dots, M$  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  $\Gamma = \{K_i = \text{const.}, \quad L_j = \text{const.}\} \cap \mathcal{Q}$ , where  $\mathcal{Q}$  is the simplex  $\{0 \leq p_i, q_j \leq \sum_i p_i + \sum_j q_j = 1\}$ . This motion remains bounded away from the fixed points we mentioned above, and continuous functions achieve their maxima on  $\Gamma$ . Now

$$\frac{dF}{dp_1} = \mu \left( \sum_{i=1}^N n_i^2 p_1^{n_1} \cdots p_i^{n_i-1} \cdots p_N^{n_N} + \sum_{j=1}^M m_j^2 q_1^{m_1} \cdots q_j^{m_j-1} \cdots q_M^{m_M} \right) > 0 \quad (\text{III.30})$$

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

If  $n = 2$ ,  $F' = \mu(p_1 + p_2 + q_1 + q_2) = \mu \leq 1$ , and we are done. (Note that the bistochasticity range is  $[0, 1]$  in this case). So we may consider  $n \geq 3$ . By eq. (III.23) 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

$$p_1 = \frac{n_1}{n-1}\gamma, \dots, p_i = \frac{n_i-1}{n-1}\gamma, \dots, p_N = \frac{n_N}{n-1}\gamma \quad (\text{III.31})$$

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

$$F' \leq \mu \left\{ \sum_i n_i^2 \left( \frac{n_1}{n-1} \right)^{n_1} \cdots \left( \frac{n_i-1}{n-1} \right)^{n_i-1} \cdots \left( \frac{n_N}{n-1} \right)^{n_N} \gamma^{n-1} \right. \\ \left. + \sum_j m_j^2 \left( \frac{m_1}{n-1} \right)^{m_1} \cdots \left( \frac{m_j-1}{n-1} \right)^{m_j-1} \cdots \left( \frac{m_M}{n-1} \right)^{m_M} (1-\gamma)^{n-1} \right\}. \quad (\text{III.32})$$

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

$$F' \leq \mu n \left( \frac{1}{n-1} \right)^{n-1} \left[ n_1^{n_1} \cdots n_N^{n_N} \gamma^{n-1} + m_1^{m_1} \cdots m_M^{m_M} (1-\gamma)^{n-1} \right]. \quad (\text{III.33})$$

Thus, we can write

$$F' \leq d_1 \gamma^{n-1} + d_2 (1-\gamma)^{n-1} \quad (\text{III.34})$$

where

$$d_1 = \mu n \left( \frac{1}{n-1} \right)^{n-1} (n_1^{n_1} \cdots n_N^{n_N}) \quad \text{and} \\ d_2 = \mu n \left( \frac{1}{n-1} \right)^{n-1} (m_1^{m_1} \cdots m_M^{m_M}) \quad (\text{III.35})$$

subject to  $n_1 + \cdots + n_N = n = m_1 + \cdots + m_M$ . Clearly, we have  $F' \leq \max(d_1, d_2)$ . Consider  $d_1$  first. If  $N = 2$ , suppose  $n = 2n_1$  and  $\mu \leq 1/n_1$ . Then  $n \geq 4$  and

$$d_1 \leq \frac{n}{n_1} \left( \frac{1}{n-1} \right)^{n-1} \left( \frac{n}{2} \right)^{n/2} \left( \frac{n}{2} \right)^{n/2} = 2 \left( \frac{3n/4}{n-1} \right)^{n-1} \left( \frac{n}{2} \right) \left( \frac{2}{3} \right)^{n-1} \\ \leq n \left( \frac{2}{3} \right)^{n-1} \leq \frac{32}{27} < 2. \quad (\text{III.36})$$

If  $N = 2$ ,  $\mu \leq 1/n_1$ , and  $n_1 > n/2$

$$d_1 \leq \frac{n}{n_1} \frac{1}{(n-1)^{n-1}} \cdot n_1^{n_1} n_2^{n_2} \leq \frac{n}{n_1} \frac{1}{(n-1)^{n-1}} (n-1)^{n-1} < 2. \quad (\text{III.37})$$

Now, let  $N \geq 3$ . Using eq. (III.24) we get

$$d_1 \leq \mu n \left( \frac{1}{n-1} \right)^{n-1} (n-N+1)^{n-N+1} \leq \mu n \left( \frac{1}{n-1} \right)^{N-2}, \quad (\text{III.38})$$

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  $\mu \leq 1/\max(m_i)$ , and  $d_2$  is smaller than 2 for  $M \geq 3$  if  $\mu < 2(n-1)^{M-2}/n$ . Recalling that  $n_1 = \max_{i,j}(n_i, m_j)$  we obtain the result. ■

It follows that  $\tau^k(p_1)$  converges exponentially to a fixed point as  $k \rightarrow \infty$ , 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 III.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  $\mu$ , which have already been dealt with, when one wants to approximate the solution of (III.2) by (III.3).

### III.5 Diffusion and Transmutations

By “transmutations” we mean all the reactions of the form



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  $\tau$  coincides with the very well known central difference approximation of the classical diffusion operator “ $-\Delta$ ”. The time evolution will be described by

$$\begin{aligned} p_A^{\tilde{}} &= p_A - n\mu(p_A^n - p_B^n) \\ p_B^{\tilde{}} &= p_B + n\mu(p_A^n - p_B^n) \end{aligned} \quad (\text{III.40})$$

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:

$$p_A^* = p_A + n\mu[(1 - p_A)^n - p_A^n] = \tau(p_A). \quad (\text{III.41})$$

Clearly,  $\tau$  has got a unique fixed point:  $\hat{p}_A = 1/2$ . We are going to prove the following:

LEMMA III.5.  $\lim_{k \rightarrow \infty} \tau^k(p_A) = \hat{p}_A \quad \forall p_A \in [0, 1]$  and  $\forall n \in \mathbb{N}$  if and only if  $0 < \mu < 1/n$ . If  $\mu = 1/n$  then  $\tau(0) = 1$  and  $\tau(1) = 0$ .

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*)  $\tau(p_A) \leq 1/2$  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

$$\tau(p_A) - \frac{1}{2} = p_A + \mu[(1 - p_A) - p_A] - \frac{1}{2} < \frac{1}{2} - p_A \quad (\text{III.42})$$

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

$$(1 - p_A)^{n+1} - p_A^{n+1} \leq (1 - p_A)^n - p_A^n \quad (\text{III.43})$$

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

$$\begin{aligned} p_A^* - \frac{1}{2} &= p_A + n\mu[(1 - p_A)^n - p_A^n] - \frac{1}{2} < p_A + (1 - p_A)^n - p_A^n - \frac{1}{2} \\ &\leq p_A + (1 - p_A) - p_A - \frac{1}{2} = \frac{1}{2} - p_A \end{aligned} \quad (\text{III.44})$$

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

$$\begin{aligned} \tau(p_A) &= 0 + (1 - 0)^n - 0^n = 1 \\ \tau^2(p_A) &= 1 + (1 - 1)^n - 1^n = 0 \end{aligned} \quad (\text{III.45})$$



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 III.6.** *If  $n \geq 3$  and  $\mu = 1/n$ , then  $\lim_{k \rightarrow \infty} \tau^k(p_A) = \hat{p}_A \quad \forall p_A \in (0, 1)$ . If  $n = 1$  or  $n = 2$  and  $\mu = 1/n$ , then  $\tau$  is a permutation.*

**PROOF:** If  $n = 1$  or  $n = 2$  and  $\mu = 1/n$ , we have

$$p_A^* = p_A + 1 - 2p_A = 1 - p_A = p_B \quad (\text{III.46})$$

therefore the map  $\tau$  is a permutation.

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

$$\tau(p_A) = p_A + 3\mu(1 - 3p_A + 3p_A^2 - 2p_A^3) \quad (\text{III.47})$$

therefore  $\tau(p_A) - 1/2 < 1/2 - p_A$  for  $p_A \in (0, 1/2)$ . Hence, recalling eq. (III.43), we can conclude that

$$\left| \tau(p_A) - \frac{1}{2} \right| < \left| p_A - \frac{1}{2} \right| \quad (\text{III.48})$$

for every map  $\tau$  relating to  $\mu = 1/n$  for  $n \geq 3$ . This proves the Lemma. ■

### III.6 Stability of the Fixed Points and Entropy Increase:

#### The Non-Autocatalytic Case

As we have seen, given any balanced non-autocatalytic reaction, the iterations of the corresponding map  $\tau$  will drive the system to a well determined fixed point, for certain

values of the parameter  $\mu$ . Such a fixed point satisfies

$$D(P) = p_1^{n_1} \cdots p_N^{n_N} - q_1^{m_1} \cdots q_M^{m_M} = 0, \quad (\text{III.49})$$

which describes a smooth  $(N + M - 1)$ -dimensional manifold in  $\mathbb{R}^{N+M}$ , and it satisfies the  $(N + M - 1)$  equations (III.28). Note that the system (III.28) + (III.49) has a unique solution in the line of the motion  $\Gamma$ . In fact the existence of one fixed point is ensured by Theorem II.10, and eqs. (III.4) say that the  $p$ 's increase with  $p_1$  while the  $q$ 's decrease with it. It follows that there cannot be more than one solution to (III.49) along  $\Gamma$ , as the  $p$ 's and the  $q$ 's are all nonnegative in it. 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  $\tau$  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. Clearly, all the points in a given  $\Gamma$  correspond to the same set of constants of motion, and so the questions about the convergence of the iterations based at different points along that line always concern the same fixed point.

Concerning the stability of the fixed points of a given  $\tau$ , 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

$$p_1^{n_1} \cdots p_N^{n_N} - q_1^{m_1} \cdots q_M^{m_M} = p_1^{n_1} \left[ \frac{1}{n_1} (L_2 + n_2 p_1) \right]^{n_2} \cdots \left[ \frac{1}{n_1} (L_N + n_N p_1) \right]^{n_N} - \left[ \frac{1}{n_1} (K_1 - m_1 p_1) \right]^{m_1} \cdots \left[ \frac{1}{n_1} (K_M - m_M p_1) \right]^{m_M}, \quad (\text{III.50})$$

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  $\tau$  follows from this, from the fact that all the non-trivial

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. In order to avoid repetition, further details about the stability of the fixed points will be given in section III.8, where the more complicated case of autocatalytic reactions is treated.

Now, we note that the fixed point,  $\hat{p}_1$ , 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 non-decreasing and every initial condition along such a line converges to  $\hat{p}_1$ , under its iterations, for certain values of the parameter  $\mu$ . Furthermore, we have

$$S(p_1) = - \sum p_i(p_1) \log p_i(p_1) - \sum q_j(p_1) \log q_j(p_1), \quad (\text{III.51})$$

which does not depend on  $\mu$ , and

$$\frac{dS}{dp_1} = 0 \quad \text{if and only if} \quad p_1 = \hat{p}_1. \quad (\text{III.52})$$

We conclude that  $S(p_1) < S(\hat{p}_1)$  unless  $p_1 = \hat{p}_1$ , but more can be proven.

Recall from section II.5 that the bistochastic matrix  $T$  associated with the reaction (III.1) can be expressed as  $T = T' \oplus M_1 \oplus \cdots \oplus M_t$ , where  $T'$  is a bistochastic block, which has a spectral gap  $\Delta > 0$  if  $\mu \in (0, L_B)$  (Lemma II.1). The remaining  $M_i$ 's are square matrices of the form

$$M_i = \frac{1}{t_i} \begin{pmatrix} 1 & 1 & \cdots & 1 \\ 1 & 1 & \cdots & 1 \\ \vdots & \vdots & \ddots & \vdots \\ 1 & 1 & \cdots & 1 \end{pmatrix}, \quad (\text{III.53})$$

and therefore they act like the identity on those components of the input vectors that concern their invariant subspaces. In fact, each  $M_i$  contains the elements of  $T$  that deal with a process of the form  $(A_{i_1}, \dots, A_{i_n}) \rightarrow (A_{i_1}, \dots, A_{i_n})$  and its permutations, where  $(A_{i_1}, \dots, A_{i_n}) \in \Lambda$  and  $\Lambda$  has been defined by eq. (II.14). Because of the fact that the components of the input vector,  $\otimes_1^n P$ , on which  $M_i$  acts are all equal to  $p_{i_1} \cdots p_{i_n}$ , they remain unchanged

under its application. Thus, we find that  $T$  is mixing on a certain subspace,  $\mathcal{M}$  say, due to the spectral gap of  $T'$ , and it acts like the identity on the vectors of  $\mathcal{M}^\perp$  that it receives as an input. Therefore, by Theorem II.6 and Theorem II.7 we can conclude that the iterations of every  $P \in \mathcal{Q}$  under  $\tau$  converge to the corresponding fixed point, whenever  $\mu$  lies in  $(0, L_B)$ .

To sum up, we have proven this result:

**THEOREM III.1.** *Consider a balanced, non-autocatalytic, reaction  $\tau$  that comes from a bistochastic process. If the coupling constant  $\mu$  belongs to  $(0, L_B)$ , where  $L_B$  is the upper limit of the bistochasticity range, then:*

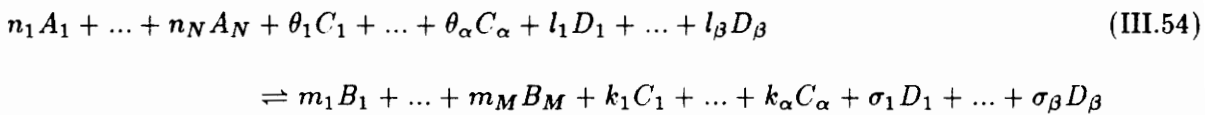
- (a) *All the fixed points of  $\tau$  are stable and constitute an  $(N + M - 2)$ -parameter family.*
- (b) *Every choice of the initial conditions different from a fixed point converges to the corresponding fixed point.*
- (c) *The entropy  $S$  is a strict Liapunov function for  $\tau$ .*

*If  $\mu = L_B$  and the iterations of  $P(0)$  under  $\tau$  converge to the corresponding fixed point, then the entropy is non decreasing 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.*

It is worth noting that there is at least one example in which  $\mu = L_B$  implies that no convergence can take place, namely the case of permutation maps studied in section III.5.

### III.7 The Autocatalytic Reaction

In the following sections the problem of autocatalytic reactions will be studied. In order to set an unambiguous notation we will refer to balanced reactions of the form



with the conventions  $N, M, \alpha, \beta \geq 0$ ,  $N + \alpha + \beta \geq 1$ ,  $M + \alpha + \beta \geq 1$  and  $\theta_i > k_i$ ,  $\sigma_j > l_j$  for every  $i$  and  $j$ . We then assume that the system is homogeneous in space, so that

the state is described by the concentrations  $p_{A_i} = p_i$ ,  $p_{C_i} = r_i$ ,  $p_{B_j} = q_j$  and  $p_{D_j} = s_j$ . Similarly to the non-autocatalytic case, if we normalize the sum of these concentrations to be  $\sum p_i + \sum r_i + \sum q_i + \sum s_i = 1$ , we can construct a probability theory in which  $\Omega = \{A_1, \dots, A_N, B_1, \dots, B_M, C_1, \dots, C_\alpha, D_1, \dots, D_\beta\}$  is the sample space,  $P = (p_1, \dots, s_\beta)$  is a probability measure on  $\Omega$  and  $\mathcal{Q} = \{P\} \subset \mathbb{R}^K$  is the simplex of all probability measures on  $\Omega$ , where  $K = N + \alpha + M + \beta$ .

Classically, one can set up a system of O.D.E's for (III.54), that represents the law of mass action for the present case, and that takes the form

$$\begin{aligned} \frac{dp_j}{dt} &= n_j \eta (q_1^{m_1} \cdots q_M^{m_M} r_1^{k_1} \cdots r_\alpha^{k_\alpha} s_1^{\sigma_1} \cdots s_\beta^{\sigma_\beta} - p_1^{n_1} \cdots p_N^{n_N} r_1^{\theta_1} \cdots r_\alpha^{\theta_\alpha} s_1^{l_1} \cdots s_\beta^{l_\beta}), \quad j = 1, \dots, N \\ \frac{dr_j}{dt} &= \nu_j \eta (q_1^{m_1} \cdots q_M^{m_M} r_1^{k_1} \cdots r_\alpha^{k_\alpha} s_1^{\sigma_1} \cdots s_\beta^{\sigma_\beta} - p_1^{n_1} \cdots p_N^{n_N} r_1^{\theta_1} \cdots r_\alpha^{\theta_\alpha} s_1^{l_1} \cdots s_\beta^{l_\beta}), \quad j = 1, \dots, \alpha \\ \frac{dq_j}{dt} &= -m_j \eta (q_1^{m_1} \cdots q_M^{m_M} r_1^{k_1} \cdots r_\alpha^{k_\alpha} s_1^{\sigma_1} \cdots s_\beta^{\sigma_\beta} - p_1^{n_1} \cdots p_N^{n_N} r_1^{\theta_1} \cdots r_\alpha^{\theta_\alpha} s_1^{l_1} \cdots s_\beta^{l_\beta}), \quad j = 1, \dots, M \\ \frac{ds_j}{dt} &= -\lambda_j \eta (q_1^{m_1} \cdots q_M^{m_M} r_1^{k_1} \cdots r_\alpha^{k_\alpha} s_1^{\sigma_1} \cdots s_\beta^{\sigma_\beta} - p_1^{n_1} \cdots p_N^{n_N} r_1^{\theta_1} \cdots r_\alpha^{\theta_\alpha} s_1^{l_1} \cdots s_\beta^{l_\beta}), \quad j = 1, \dots, \beta \end{aligned} \quad (\text{III.55})$$

where  $\eta > 0$  is the rate constant and  $\nu_i = \theta_i - k_i$ ,  $\lambda_i = \sigma_i - l_i$ . This system of differential equations describes the time evolution of the concentrations, which leads to a motion within  $\mathcal{Q}$ . Moreover, (III.55) gives rise to a probability theory because the boundaries of  $\mathcal{Q}$  repel the points approaching from inside.

Alternatively, one can construct a dynamical system with discrete time given by a Boltzmann map,  $\tau : \mathcal{Q} \rightarrow \mathcal{Q}$ , of order  $n = \sum_i n_i + \sum_i \theta_i + \sum_i l_i = \sum_j m_j + \sum_j k_j + \sum_j \sigma_j$ , which yields  $P^* = \tau(P)$  with

$$\begin{aligned} p_j^* &= p_j + n_j \mu (q_1^{m_1} \cdots q_M^{m_M} r_1^{k_1} \cdots r_\alpha^{k_\alpha} s_1^{\sigma_1} \cdots s_\beta^{\sigma_\beta} - p_1^{n_1} \cdots p_N^{n_N} r_1^{\theta_1} \cdots r_\alpha^{\theta_\alpha} s_1^{l_1} \cdots s_\beta^{l_\beta}), \quad j = 1, \dots, N \\ r_j^* &= r_j + \nu_j \mu (q_1^{m_1} \cdots q_M^{m_M} r_1^{k_1} \cdots r_\alpha^{k_\alpha} s_1^{\sigma_1} \cdots s_\beta^{\sigma_\beta} - p_1^{n_1} \cdots p_N^{n_N} r_1^{\theta_1} \cdots r_\alpha^{\theta_\alpha} s_1^{l_1} \cdots s_\beta^{l_\beta}), \quad j = 1, \dots, \alpha \\ q_j^* &= q_j - m_j \mu (q_1^{m_1} \cdots q_M^{m_M} r_1^{k_1} \cdots r_\alpha^{k_\alpha} s_1^{\sigma_1} \cdots s_\beta^{\sigma_\beta} - p_1^{n_1} \cdots p_N^{n_N} r_1^{\theta_1} \cdots r_\alpha^{\theta_\alpha} s_1^{l_1} \cdots s_\beta^{l_\beta}), \quad j = 1, \dots, M \\ s_j^* &= s_j - \lambda_j \mu (q_1^{m_1} \cdots q_M^{m_M} r_1^{k_1} \cdots r_\alpha^{k_\alpha} s_1^{\sigma_1} \cdots s_\beta^{\sigma_\beta} - p_1^{n_1} \cdots p_N^{n_N} r_1^{\theta_1} \cdots r_\alpha^{\theta_\alpha} s_1^{l_1} \cdots s_\beta^{l_\beta}), \quad j = 1, \dots, \beta, \end{aligned} \quad (\text{III.56})$$

and leads to a probability theory because of Theorem II.5. Note that from (III.55) and

(III.56) it turns out that the cases with  $\theta_i = k_i$  and  $\sigma_i = l_i$ , for some  $i$  and  $j$ , can be treated, because the corresponding concentrations do not change with time for both (III.55) and (III.56), so one can put them aside and normalize to 1 the sum of the remaining concentrations. Then the new system will have a new rate constant given by the product of either  $\eta$  or  $\mu$  times the initial values of the probabilities of those chemicals that were removed, raised to their stoichiometric coefficients.

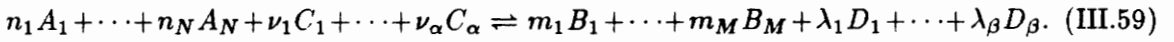
In the following we will not require  $n_1 = \text{maximum of the stoichiometric coefficients}$ , as we did in the study of the non-autocatalytic reactions. The term

$$p_1^{n_1} \dots p_N^{n_N} r_1^{\theta_1} \dots r_\alpha^{\theta_\alpha} s_1^{l_1} \dots s_\beta^{l_\beta} - q_1^{m_1} \dots q_M^{m_M} r_1^{k_1} \dots r_\alpha^{k_\alpha} s_1^{\sigma_1} \dots s_\beta^{\sigma_\beta} \quad (\text{III.57})$$

that appears on (III.55) and (III.56) can be written as  $D(P) \cdot r_1^{k_1} \dots r_\alpha^{k_\alpha} s_1^{l_1} \dots s_\beta^{l_\beta}$  where

$$D(P) = p_1^{n_1} \dots p_N^{n_N} r_1^{\nu_1} \dots r_\alpha^{\nu_\alpha} - q_1^{m_1} \dots q_M^{m_M} s_1^{\lambda_1} \dots s_\beta^{\lambda_\beta} \quad (\text{III.58})$$

is called the disequilibrium parameter of the **associated non-autocatalytic reaction**, which is



One should note now that a given reaction and its associated non-autocatalytic reaction have the same constants of motion ( hyperplanes of the motion ), which are

$$\begin{aligned} n_i p_1 - n_1 p_i &= K_i, & i &= 2, \dots, N \\ \nu_i p_1 - n_1 r_i &= L_i, & i &= 1, \dots, \alpha \\ m_i p_1 + n_1 q_i &= M_i, & i &= 1, \dots, M \\ \lambda_i p_1 + n_1 s_i &= N_i, & i &= 1, \dots, \beta \end{aligned} \quad (\text{III.60})$$

and from which all the other constants of motion can be recovered. These are  $N + \alpha + M + \beta - 1 = K - 1$  independent hyperplanes whose intersection is a straight line in  $\mathbb{R}^K$ . As for the non-autocatalytic case, we call the intersection of this line with  $\mathcal{Q}$  the “line of

the motion"  $\Gamma$ , and, as before, such a line segment is uniquely determined by the initial conditions,  $P(0) \in \mathcal{Q}$ . In particular,  $P \in \Gamma$  implies  $p_1 \in [B, C]$ , where this time  $B \geq \max_{i,j}[0; K_i/n_i; L_j/\nu_j]$  and  $C \leq \min_{i,j}[1; M_i/m_i; N_j/\lambda_j]$ . The concentrations vary in such a way to obey

$$\frac{dp_i}{dx} = \frac{n_i}{n_1}, \quad \frac{dr_i}{dx} = \frac{\nu_i}{n_1}, \quad \frac{dq_i}{dx} = -\frac{m_i}{n_1}, \quad \frac{ds_i}{dx} = -\frac{\lambda_i}{n_1}, \quad (\text{III.61})$$

when the initial condition  $P(0)$  have been fixed, if  $p_1$  is taken to be the independent variable parametrizing  $\Gamma$ . Similarly to the previous case, we will often write  $\tau(p_1)$  and  $D(p_1)$  instead of  $\tau(P)$  and  $D(P)$ , to stress the fact that the motion based at  $P(0)$  lies in a straight line. We also note that a reaction and its associated one share a common fixed point along  $\Gamma$ , the unique fixed point of the non-autocatalytic reaction. In the following  $\hat{p}_1$  will always denote the first component of such a fixed point  $\hat{P} \in \mathcal{Q}$ .

### III.8 Convergence to the Fixed Points of the Map:

#### The Autocatalytic Case

The entropy,  $S$ , of an autocatalytic system in the state described by the probability  $P = (p_1, \dots, s_\beta)$ , is given by

$$S(P) = - \sum p_i \log p_i - \sum q_i \log q_i - \sum r_i \log r_i - \sum s_i \log s_i, \quad (\text{III.62})$$

which generalizes (III.51). If the evolution of the system is governed by (III.56) and by a set of initial conditions,  $P(0)$ , then its entropy is a function of time, and the following can be proved:

**THEOREM III.2.** *Consider a balanced autocatalytic reaction described by a Boltzmann map  $\tau$  of some finite order, and let  $\mu \in (0, L_B)$ . Then the entropy of the system,  $S$ , is a strict Liapunov function for  $\tau$ . Moreover, if  $\mu = L_B$  and the iterations of certain initial conditions*

$P(0)$ , under  $\tau$ , converge to the fixed point  $\hat{P}$  of the associated non-autocatalytic reaction, there exists  $k \in \mathbb{N}$  such that  $S(\tau^k(P(0))) > S(P(0))$ , unless  $P(0)$  is  $\hat{P}$ .

PROOF: This fact is trivially true for the case  $P(0)$  is a fixed point. In the case that it is not, we need to observe that the expression of the entropy of our system coincides with that of the associated non-autocatalytic reaction. In fact, the sample and the probability space are the same, and the conserved quantities are also the same. Then the same argument developed in section III.6 for the proof of Theorem III.1 applies here and yields the result. ■

It is important now to give a description of the cases for which the convergence to  $\hat{P}$  can be proven. The result is the following

THEOREM III.3. Consider an autocatalytic reaction described by a Boltzmann map  $\tau$  of order  $n$ . The set of the fixed points of  $\tau$  consists of the  $(N + \alpha + M + \beta - 2)$ -parameter family of the fixed points of the associated non-autocatalytic reaction, together with the set of hyperplanes  $r_1 = 0, \dots, s_\beta = 0$ . Take every initial condition  $P(0) \in \mathcal{Q}$ , whose autocatalytic entries are all positive and let  $\Gamma$  be the corresponding line of the motion, with  $P_1$  and  $P_2$  as its end-points. Assume  $\mu \in (0, L_B)$  and call  $\hat{P}$  the unique fixed point of the associated non-autocatalytic reaction. Then we have

- (a)  $\tau^j(P(0))$  converges to  $\hat{P}$  as  $j \rightarrow \infty$ , if  $S(P_1) = S(P_2)$ .
- (b)  $\tau^j(P(0))$  converges to  $\hat{P}$  as  $j \rightarrow \infty$ , if  $P_i \in \Theta = \{P_1, P_2\}$  does not have any vanishing autocatalytic component, and  $P(0)$  lies in the subsegment of  $\Gamma$  that connects  $\hat{P}$  to  $P_k \in \Theta$  with  $i \neq k$ .
- (c)  $\tau^j(P(0))$  converges to  $\hat{P}$  as  $j \rightarrow \infty$ , if  $\mu < \min(L_B, L'_B)$ , where  $L'_B$  is the bistochasticity limit of the associated non-autocatalytic reaction.
- (d) There exists  $\mu_0 > 0$  such that  $\frac{d\tau}{dp_1} \geq 0$  for  $\mu \leq \mu_0$ , and such that  $\tau^j(P(0))$  converges monotonically to  $\hat{P}$  as  $j \rightarrow \infty$ , for every  $\mu \in (0, \mu_0]$ .

PROOF: Let us count how many fixed points are to be found in the line of the motion,  $\Gamma$ ,



that is determined by the choice of one set of initial conditions,  $P(0)$ . To do this let us write

$$\tau(p_1) = p_1 - n_1 \mu D(p_1) \cdot r_1^{k_1} \cdots r_\alpha^{k_\alpha} s_1^{l_1} \cdots s_\beta^{l_\beta} , \quad (\text{III.63})$$

then it is clear that the only possible fixed points are those due to the vanishing of the probability of at least one of the autocatalytic elements and the unique fixed point of the associated non-autocatalytic reaction, for which  $D(p_1) = 0$ . (Therefore the set of fixed points of  $\tau$  is that claimed in the theorem). Then there is at least one fixed point in  $\Gamma$ , the one of the associated non-autocatalytic reaction, and at most another fixed point at each end of the line segment  $\Gamma$ . So three fixed points along  $\Gamma$  is the most that we can expect. In fact, assume that there exists  $p_1 \in \Gamma$  such that  $r_i(p_1)$  or  $s_j(p_1)$  is equal to zero for some  $i$  or  $j$ . Then such a  $p_1$  must be one of the end points of  $\Gamma$ ; otherwise the conserved quantities

$$\nu_i p_1 - n_1 r_i = L_i , \quad \lambda_j p_1 + n_1 s_j = N_j \quad (\text{III.64})$$

would imply that negative values for  $r_i$  or  $s_j$  are allowed. As our theory is a probability theory, this is impossible. Therefore we have the following possible cases: i) the fixed point of the non-autocatalytic reaction is one end-point of  $\Gamma$ ; in which case there can be only one other fixed point, at the other end of  $\Gamma$ , due to the vanishing of some autocatalytic element. ii) The fixed point of the non-autocatalytic reaction lies in the interior of the line segment  $\Gamma$ ; then the possible vanishing of some autocatalytic element will allow two other fixed points at each end of  $\Gamma$ .

Consider part (d) now, and write (III.63) explicitly:

$$\tau(p_1) = p_1 - n_1 \mu p_1^{n_1} \cdots p_N^{n_N} r_1^{\theta_1} \cdots r_\alpha^{\theta_\alpha} s_1^{l_1} \cdots s_\beta^{l_\beta} + n_1 \mu q_1^{m_1} \cdots q_M^{m_M} r_1^{k_1} \cdots r_\alpha^{k_\alpha} s_1^{\sigma_1} \cdots s_\beta^{\sigma_\beta} . \quad (\text{III.65})$$

Then, using eq.s (III.60) and (III.61) we obtain

$$\begin{aligned} \frac{d\tau}{dp_1} \geq & 1 - \mu \left( \sum_{i=1}^N n_i^2 p_1^{n_i} \cdots p_i^{n_i-1} \cdots p_N^{n_N} r_1^{\theta_1} \cdots r_\alpha^{\theta_\alpha} \right. \\ & \left. + \sum_{i=1}^\alpha \theta_i \nu_i p_1^{n_1} \cdots p_N^{n_N} r_1^{\theta_1} \cdots r_i^{\theta_i-1} \cdots r_\alpha^{\theta_\alpha} \right) s_1^{l_1} \cdots s_\beta^{l_\beta} \\ & - \mu \left( \sum_{j=1}^M m_j^2 q_1^{m_j} \cdots q_j^{m_j-1} \cdots q_M^{m_M} s_1^{\sigma_1} \cdots s_\beta^{\sigma_\beta} \right. \\ & \left. + \sum_{j=1}^\beta \sigma_j \lambda_j q_1^{m_1} \cdots q_M^{m_M} s_1^{\sigma_1} \cdots s_j^{\sigma_j-1} \cdots s_\beta^{\sigma_\beta} \right) r_1^{k_1} \cdots r_\alpha^{k_\alpha} \geq \end{aligned} \quad (\text{III.66})$$

$$\geq 1 - \mu \left( \sum_{i=1}^N n_i^2 + \sum_{i=1}^\alpha \theta_i \nu_i + \sum_{j=1}^M m_j^2 + \sum_{j=1}^\beta \sigma_j \lambda_j \right) = 1 - \mu \Phi, \quad (\text{III.67})$$

and we have  $\frac{d\tau}{dp_1} \geq 1 - \mu \Phi \geq 0$  if  $\mu \leq \mu_0 = 1/\Phi$ , which is a positive number.

Let us see now what happens when the initial conditions  $P(0)$  do not involve vanishing probabilities of any autocatalytic element, and let us call  $\hat{p}_1$  the fixed point of the corresponding non-autocatalytic reaction. In the case that  $p_1(0) = \hat{p}_1$ , the analysis is trivial:  $\tau^j(p_1(0))$  is  $\hat{p}_1$  for all  $j$ 's. If  $p_1(0) \neq \hat{p}_1$  then the following happens

$$\tau(p_1(0)) > p_1(0) \quad \text{if} \quad p_1(0) < \hat{p}_1 \quad \text{or} \quad \tau(p_1(0)) < p_1(0) \quad \text{if} \quad p_1(0) > \hat{p}_1. \quad (\text{III.68})$$

In fact we have

$$\begin{aligned} p_1^{n_1} \cdots p_N^{n_N} r_1^{\nu_1} \cdots r_\alpha^{\nu_\alpha} &< q_1^{m_1} \cdots q_M^{m_M} s_1^{\lambda_1} \cdots s_\beta^{\lambda_\beta} \quad \text{if} \quad p_1 < \hat{p}_1, \quad \text{and} \\ p_1^{n_1} \cdots p_N^{n_N} r_1^{\nu_1} \cdots r_\alpha^{\nu_\alpha} &> q_1^{m_1} \cdots q_M^{m_M} s_1^{\lambda_1} \cdots s_\beta^{\lambda_\beta} \quad \text{if} \quad p_1 > \hat{p}_1 \end{aligned} \quad (\text{III.69})$$

because the conserved quantities imply that all the  $p_i$ 's and all the  $r_i$ 's increase with  $p_1$ , while the opposite happens to all the  $q_j$ 's and all the  $s_j$ 's and, of course, the two terms are equal when  $p_1 = \hat{p}_1$  only. Therefore  $D(p_1(0))$  is either positive or negative. Moreover, the product of the probabilities of the autocatalytic elements is a positive quantity in the interior of the segment  $\Gamma$ , as seen before.

Now, assume that  $\mu \in (0, \mu_0]$  so that  $\frac{d\tau}{dp_1} \geq 0$  over all its domain. We get

$$\begin{aligned} \tau(p_1(0)) &\leq \tau(\hat{p}_1) = \hat{p}_1 & \text{if } p_1(0) < \hat{p}_1, & \text{ or} \\ \tau(p_1(0)) &\geq \tau(\hat{p}_1) = \hat{p}_1 & \text{if } p_1(0) > \hat{p}_1. \end{aligned} \tag{III.70}$$

Combining (III.68) with (III.70), we have that  $\tau^j(p_1(0))$  converges to  $\hat{p}_1$  as  $j$  becomes large, in a monotonic way, whether  $\hat{p}_1$  is an end point of  $\Gamma$  or not. For suppose  $\tau^j(p_1(0)) \rightarrow p$ . Then, as  $\tau$  is continuous,  $\tau\tau^j(p_1(0)) \rightarrow \tau(p)$ . But  $\tau^{j+1}(p_1(0)) \rightarrow p$ , so  $p$  is a fixed point of  $\tau$  and eqs. (III.68) imply  $p = \hat{p}_1$ . This proves part (d).

For what concerns parts (a) and (b), consider the fact that the properties of the bistochastic matrix  $T$  associated with an autocatalytic reaction are the same as those that pertain to a matrix of a non-autocatalytic reaction. Now, let  $S(P_1) = S(P_2)$ . The fact that the map increases the entropy, unless the input probability is a fixed point implies that no initial condition  $P(0)$  whose autocatalytic entries are all positive can be driven to a limit point that has some vanishing autocatalytic component. In fact, equations (III.62) and (III.52) state that the entropy of the end points of  $\Gamma$ , which are the only ones at which some autocatalytic component may vanish, is less than that of any other point in  $\Gamma$ . If instead  $S(P_1) \neq S(P_2)$ , but  $P_1$  doesn't have any vanishing autocatalytic component, then it cannot be a fixed point unless it is  $\hat{P}$ . Therefore, every  $P$  contained in the part of  $\Gamma$  that lies between  $P_2$  and  $\hat{P}$  will converge to  $\hat{P}$  under the iterations of  $\tau$ —if it converges at all—because  $S(P) > S(P_2)$ , and so the limit cannot be  $P_2$ . Similarly for the case in which it is  $P_2$  that has no vanishing autocatalytic components. Apply now the same argument developed in section III.6, for the proof of Theorem III.1(b). Since we find that the iterations converge to some fixed point, we conclude that this in deed is  $\hat{P}$ .

For what concerns part (c), call  $\tau_0$  the map of the associated non-autocatalytic reaction, and observe that

$$\begin{aligned} \tau(p_1) &> \tau_0(p_1) & \text{if } p_1 < \hat{p}_1 & \text{ and} \\ \tau(p_1) &< \tau_0(p_1) & \text{if } p_1 > \hat{p}_1. \end{aligned} \tag{III.71}$$

In fact, as we assume that  $P(0)$  has no vanishing autocatalytic components, we have

$$|D(p_1)| \cdot r_1^{k_1} \cdots s_\beta^{l_\beta} < |D(p_1)|, \quad (\text{III.72})$$

unless  $r_1$  is the only autocatalytic component and  $r_1 = 1$ . Then, if this is the fixed point  $\hat{P}$ , we are done. Otherwise, the only case in which this would not be that fixed point is when the reaction has the form  $\theta_1 C_1 \rightleftharpoons k_1 C_1 + m_1 B_1 + \cdots + m_M + B_M$ , for which  $L_B = 1/\theta_1$  holds. Then, take  $r_1$  as the independent variable. We get

$$\begin{aligned} \tau(r_1) &= 1 - \nu_1 \mu (1 - 0) = 1 - \nu_1 \mu \geq 1 - \frac{\nu_1}{\theta_1} > 0 \\ \tau(q_j) &= 0 + m_j \mu (1 - 0) > 0, \quad j = 1, \dots, M. \end{aligned} \quad (\text{III.73})$$

At this point (III.72) applies to the present case, and thus eq. (III.71) is valid in general, as it can be seen by comparing eq. (III.63) and the corresponding equation for  $\tau_0$ , i.e.:  $\tau_0(p_1) = p_1 - n_1 \mu D(p_1)$ . Now, because of the fact that  $\tau_0(p_1)$  can at most equal  $P_1$  or  $P_2$ , we have that  $\tau(p_1)$  surely is not one of those points of  $\Gamma$ . Moreover,  $\tau(p_1)$  cannot approach more and more closely  $P_1$  or  $P_2$ , because of eqs. (III.68). Then, since  $\mu \in (0, L_B)$  by hypothesis, we have that the iterations converge, and there is no other choice than  $\hat{P}$  for the limit. ■

We conclude this section by proving a result on the stability of the fixed points of the maps considered here. Note that the same argument can be applied to the proof of Theorem III.1 (a), which was not developed in detail there to avoid repetition.

**THEOREM III.4.** *Consider an autocatalytic reaction described by a Boltzmann map  $\tau$  of order  $n$ , and let  $\mu \in (0, L_B)$ . Let  $\Gamma$  be the line of the motion corresponding to a given initial condition  $P(0) \in \mathcal{Q}$ . Then a fixed point in  $\Gamma$  is stable under small perturbations of the initial conditions if and only if it is a fixed point of the associated non-autocatalytic reaction; otherwise it is unstable.*

**PROOF:** First of all, observe that it is always possible to choose a segment  $V$  in  $\Gamma$  that contains  $\hat{P}$ , and so small that the entropy of the points in it is higher than that of  $P_1$

and  $P_2$ . Then the existence of the spectral gap in  $T'$ , and the fact that the entropy does not decrease, force the iterations to converge to  $\hat{P}$ . Consider now  $\hat{P}$ . The expression for  $\tau' = \frac{d\tau}{dp_1}$ , given by (9), can be put in the form

$$\frac{d\tau}{dp_1} = 1 - n_1\mu D(p_1) \left( r_1^{k_1} \cdots s_\beta^{l_\beta} \right)' - n_1\mu D'(p_1) \left( r_1^{k_1} \cdots s_\beta^{l_\beta} \right) \quad (\text{III.74})$$

where  $D$  is the disequilibrium parameter of the associated non-autocatalytic reaction. It is clear then, that the stability along  $\Gamma$  of the fixed point  $\hat{p}_1$ , which yields  $D = 0$ , is the same as for the non-autocatalytic case, unless such a fixed point corresponds to the vanishing of some autocatalytic element. In fact, if this is not the case, we get that  $\frac{d\tau}{dp_1}$  is positive, vanishing or negative whenever that happens for the derivative of the associated non-autocatalytic map. If, instead, the concentration of some autocatalytic element is zero, we get  $\frac{d\tau}{dp_1} = 1$ . In this case,  $\Gamma = \{\hat{p}_1\}$ . In fact, assume that  $r_i(\hat{p}_1) = 0$  for some  $i$ , then the motion is confined to  $p_1 \geq \hat{p}_1$ ; otherwise  $r_i(p_1)$  would become negative. Moreover,  $r_i(\hat{p}_1) = 0 = D(\hat{p}_1)$  implies  $q_j(\hat{p}_1) = 0$  or  $s_j(\hat{p}_1) = 0$  for some  $j$ , and then we must have  $p_1 \leq \hat{p}_1$ . The same result is obtained if one assumes that the vanishing autocatalytic element is  $s_j$ .

Now, assume that  $D(\hat{P}) = 0$ , for a  $\hat{P}$  either of the kind just discussed or not, and take an open ball  $\mathcal{B}(\hat{P}, \epsilon)$  of radius  $\epsilon > 0$  centered at  $\hat{P}$ . Denote  $\Gamma_P$  the line of the motion that contains  $P \in \mathcal{Q}$ , and consider the fact that all the lines of the motion are parallel to each other and that the manifold of the points  $P$  such that  $D(P) = 0$  is a continuous hypersurface in  $\mathbb{R}^K$ . Then it is possible to find  $\delta > 0$  so small that

$$\left( \bigcup_{P \in E_\delta} \hat{P}_P \right) \subseteq \mathcal{B}(\hat{P}, \epsilon), \quad \text{for } E_\delta = \mathcal{B}(\hat{P}, \delta) \cap \mathcal{Q}, \quad (\text{III.75})$$

where  $\hat{P}_P$  is the fixed point of the associated non-autocatalytic reaction along  $\Gamma_P$ . Then for every  $P \in E_\delta$  we have two possible cases:

- i)  $P \in E_\delta$  is a fixed point, in which case  $\tau^j(P) = P \in \mathcal{B}(\hat{P}, \epsilon)$  for all  $j$ 's.
- ii)  $P \in E_\delta$  is not a fixed point, in which case  $\tau^j(P) \rightarrow \hat{P}_P$ , with  $\hat{P}_P \in \mathcal{B}(\hat{P}, \epsilon)$ , and then  $\tau^j(P) \in \mathcal{B}(\hat{P}, \epsilon)$  for all  $j$ 's.

Note that (ii) depends also on the fact that the entropy is a strict Liapunov function for  $\tau$ . We conclude that, for every open ball  $\mathcal{B}$  around  $\hat{P}$  it is possible to find an open neighborhood  $\overset{\circ}{E}$  of  $\hat{P}$  such that  $\tau^j(P) \in \mathcal{B}$  for all  $j$ 's if  $P \in \overset{\circ}{E}$ ; i.e. the fixed point  $\hat{P}$  is stable.

On the other hand, small perturbations of those fixed points corresponding to the vanishing of some autocatalytic element, not coinciding with a non-autocatalytic fixed point  $\hat{P}$ , lead the system far away from the fixed point itself; therefore such fixed points are to be considered unstable. To see this, let us take as independent variable the concentration of the same autocatalytic element. There is no loss of generality to assume that such an element is  $C_1$ , and to consider the fixed point  $r_1 = 0$ , all the others greater than zero. Then a small neighborhood in  $\mathcal{Q}$  of  $\hat{P}$  contains points  $P$  with positive components, such that  $r_1 \approx 0$  and the values of the terms containing the  $p$ 's and the  $r$ 's in  $D(P)$  are smaller than those containing the  $q$ 's and the  $s$ 's. Therefore the point moves away from  $r_1 = 0$ , as  $\tau(r_1) = r_1 - \nu_1 \mu D \cdot r_1^{k_1} \cdots s_\beta^{l_\beta} > r_1$ , heading to the fixed point of the corresponding non-autocatalytic reaction, determined by this special choice of the initial conditions. This completes the proof of the Theorem. ■

### III.9 Completely Solved Examples

After the general method which has just been presented, we are going to consider some classes of autocatalytic reactions that include those present in some very popular models, like the Schlögl and the Brussellator models of complex reactions, [11],[17]. One characteristic of the reactions in these classes is that the derivative,  $\tau'_\mu$ , of  $\tau_\mu$  with respect to the reference variable  $p$ , is greater or equal to 0 in the range  $I = [0, \hat{p}]$ . Another feature is that  $\tau_\mu(p) = 0$  if and only if  $p = 0$ . Here we let  $\hat{p}$  be the unique fixed point of the corresponding non-autocatalytic reaction, while  $\bar{p}$  denotes the fixed point corresponding to the vanishing of  $p$  if it is an autocatalytic element, and we will see that there are no other

fixed points besides  $\hat{p}$  and  $\bar{p}$ . Note that the index  $\mu$  has been appended to  $\tau$  because, in some cases, the evolution of a given reaction will be studied for different values of  $\mu$ . Then, it will be important to know which are the values of that parameter, in order to compare the different results that one gets by using different choices for it.

The fact that those two conditions on  $\tau'_\mu$  are met in  $I$  is enough to ensure the convergence of the itineraries  $\{\tau^j(p)\}$  to the corresponding fixed point, for all  $\mu \in \mathcal{R}_B$ , the bistochasticity range defined in section II.5. That is to say, all the results that have been proven for values of  $\mu$  smaller than  $\mu_0$  are indeed true, in the present cases, throughout the bistochasticity range (the exception to this is the monotonicity of the convergence, which may not occur in certain cases). For these reasons we regard the examples in this section as completely solved. To see how the result on the convergence is obtained let us consider the case  $p \in (0, \hat{p})$  first. We have  $p < \tau_\mu(p) \leq \hat{p}$ , because  $\tau_\mu$  is non-decreasing in  $I$  and because the disequilibrium parameter is positive in  $(0, \hat{p})$ . It follows that  $\tau_\mu^j(p) \rightarrow \hat{p}$  as  $j$  becomes large. If, instead,  $p \in (\hat{p}, 1]$  we have  $\tau_\mu(p) < p$ , because the disequilibrium parameter is negative, and one of the following two cases holds:

- i)  $\tau_\mu^j(p) \geq \hat{p}$  for all  $j$ 's, in which case monotonic convergence is proven.
- ii)  $\tau_\mu^j(p) \leq \hat{p}$  for some  $j$ , in which case we fall into the case  $p \in (0, \hat{p})$  and convergence is proven, but monotonicity is spoiled.

**Example 1)** Consider all the reactions of the form  $\boxed{(n+1)A \rightleftharpoons nA + B}$  for  $n \geq 1$ . Here the bistochasticity range is  $\mu \leq 1/(n+1)$ . Let  $p$  be the concentration of the autocatalytic element  $A$ . Then

$$\tau_\mu(p) = p - \mu p^{n+1} + \mu p^n(1-p) = p + \mu p^n(1-2p). \quad (\text{III.76})$$

Clearly there are two fixed points only:  $\bar{p} = 0$  and  $\hat{p} = 1/2$ . Also,  $\tau_\mu(p) = 0$  if and only if  $p = 0$  for  $p \in [0, 1]$ , in fact, if  $p \neq 0$ ,  $p + \mu p^n(1-2p) = 0$  implies

$$0 = 1 + \mu p^{n-1}(1-2p) \geq 1 - \frac{2}{n+1}p^n + \mu p^{n-1} \geq 1 - \frac{2}{n+1} + \mu p^{n-1} > 0 \quad (\text{III.77})$$

which is a contradiction. We also have

$$\frac{d\tau_\mu}{dp} = 1 + n\mu p^{n-1}(1-2p) - 2\mu p^n \quad (\text{III.78})$$

from which it is seen that  $\hat{p}$  is exponentially stable and, for  $p \in [0, 1/2]$ ,

$$\frac{d\tau_\mu}{dp} \geq 1 - 2\mu p^n \geq 1 - \mu \left(\frac{1}{2}\right)^{n-1} > 0. \quad (\text{III.79})$$

This completely solves this class of reactions.

**Example 2)** Consider all the reactions of the form  $\boxed{(n+1)A \rightleftharpoons A + nB}$  for  $n \geq 2$ , as the case  $n = 1$  is included in the previous point. Here we have  $\mathcal{R}_B = [0, 1/(n+1)]$  and

$$\tau_\mu(p) = p - n\mu p^{n+1} - n\mu p(1-p)^n = p - n\mu p[p^n - (1-p)^n] \quad (\text{III.80})$$

so the fixed points are  $\bar{p} = 0$  and  $\hat{p} = 1/2$ . Also  $\tau_\mu(p) = 0$  if and only if  $p = 0$ ; in fact, if  $p \neq 0$ , then

$$1 - n\mu[p^n - (1-p)^n] \geq 1 - n\mu p^n \geq 1 - \frac{n}{n+1} > 0 \quad (\text{III.81})$$

which ensures that  $\bar{p}$  is the only zero of  $\tau_\mu$  in  $[0, 1]$ . The expression of  $\tau'_\mu$  is

$$\frac{d\tau_\mu}{dp} = 1 - n\mu \{(n+1)p^n + (1-p)^{n-1}[(n+1)p - 1]\} \quad (\text{III.82})$$

and one can easily see that  $\hat{p}$  is exponentially stable while  $\bar{p}$  is unstable. Now restrict to  $p \in [0, 1/2]$ . Then we can show that  $(n+1)p^n + (1-p)^{n-1}[(n+1)p - 1] \leq (n+1)/n$ , from which we get  $\tau'_\mu \geq 0$  in  $[0, 1/2]$ , as  $n\mu \leq n/(n+1)$ . In fact, we have

$$\begin{aligned} (n+1)p^n + (1-p)^{n-1}[(n+1)p - 1] &\leq (n+1)p(1-p)^{n-1} + [(n+1)p - 1](1-p)^{n-1} \\ &= (1-p)^{n-1}[2(n+1)p - 1] = H(p) \end{aligned} \quad (\text{III.83})$$

and

$$\frac{dH}{dp} = (1-p)^{n-2}[3n+1 - 2n(n+1)p]. \quad (\text{III.84})$$



Now, for  $p \in [0, 1/2]$ , eq. (III.81) has one zero only, i.e.  $p_0 = (3n + 1)/2n(n + 1)$ , which corresponds to the unique maximum of  $H$  in  $[0, 1)$ , and  $p_0 > 1/2$  if  $n = 2$ , while  $p_0 < 1/2$  if  $n \geq 3$ . Thus,

$$\begin{cases} H_{\max} = H(1/2) = 1 < \frac{n+1}{n} = \frac{3}{2}, & \text{if } n = 2 \\ H_{\max} = \left( \frac{2n^2 - n - 1}{2n^2 + 2n} \right)^{n-1} \frac{2n+1}{n} \leq \frac{n+1}{n}, & \text{if } n \geq 3. \end{cases} \quad (\text{III.85})$$

Therefore  $\tau'_\mu \geq 0$  in  $[0, 1/2]$ , and this solves this case.

Example 3) Now we can use Example 2 to cover all the remaining cases of autocatalytic reactions with two chemicals only:  $\boxed{(n+1)A \rightleftharpoons mA + (n-m+1)B}$ , for  $n \geq 2$  and  $m = 1, \dots, n$ . In the following we denote the corresponding map by  $\tau_m$ , omitting for simplicity the subscript  $\mu_m$ . Then we can write

$$\tau_m(p) = p - (n - m + 1)\mu_m [p^{n+1} - p^m(1 - p)^{n-m+1}], \quad (\text{III.86})$$

$\tau_m(p) = 0$  if and only if  $p = 0$ . The other fixed point is  $\hat{p} = 1/2$ . Now assume that  $\tau_m(p) \leq 1/2$ , for  $p \in (0, 1/2]$ . We want to show that  $\tau_{m+1}(p) \leq 1/2$  for every  $\mu_{m+1}$  in the bistochasticity range. In fact, if this is the case, the convergence of the iterations under  $\tau_{m+1}$ , for the reaction  $(n+1)A \rightleftharpoons (m+1)A + (n-m)B$ , is obtained from the convergence of the iterations under  $\tau_m$ . Then, a simple induction allows us to cover all the cases, as the case with  $m = 1$  has been proved in Example 2. Note that  $\mu_m$  and  $\mu_{m+1}$  vary on the same range, which is  $[0, 1/(n+1)]$ , as the highest stoichiometric coefficient is the same for both reactions. Our assumption means that

$$\frac{1}{2} - p \geq \tau_m(p) - p = (n - m + 1)\mu [(1 - p)^{n-m+1} - p^{n-m+1}] p^m \quad (\text{III.87})$$

We want to check whether  $\tau_{m+1}(p) - p \leq 1/2$  or not. For  $p \leq 1/2$  we can write

$$\begin{aligned} \tau_{m+1}(p) - p &= (n - m)\mu [(1 - p)^{n-m} - p^{n-m}] p^{m+1} \\ &\leq (n - m + 1)\mu [(1 - p)^{n-m+1} - p^{n-m+1}] p^m = \tau_m(p) - p \leq \frac{1}{2} - p. \end{aligned} \quad (\text{III.88})$$

Then it is true that  $\tau_{m+1}(p) \leq 1/2$  for  $p \in (0, 1/2]$  and for every  $\mu_{m+1}$  in the bistochasticity range. This completely solves this case.

Note that the autocatalytic reaction that appears on both the Schlögl and the Brusselator models,  $A + 2X \rightleftharpoons 3X$ , belongs to the class of Example 1.

We conclude this chapter by pointing out that the study of autocatalytic reactions presents some extra difficulty, as compared to the non-autocatalytic case. This makes it more difficult to perform the same accurate analysis on all the possible cases. Nonetheless, the discussion of section II.5, about the spectral gap of the bistochastic matrix  $T$ , allows us to “almost” completely solve the problem of the convergence of the iterations of  $\tau$ . We say almost because some limiting case, like  $\mu = L_B$  and some particular autocatalytic reactions with special initial conditions have not been examined in full detail.

## CHAPTER IV: CONVEX COMBINATIONS OF BOLTZMANN MAPS

### IV.1 Introduction

In Chapter III the analysis has been developed of the discrete time dynamical systems that describe the evolution of single balanced reactions in “stirred tanks”. That study will be generalized in this chapter, so that combinations of reactions, and spatially inhomogeneous systems can be treated. This proves necessary when classical models of complex reactions, like those presented in Section I.4, are considered. As a matter of fact, a distinction between “simple” and “complex” chemical reactions could be drawn by calling simple those studied in Chapter III, and complex those that involve more than a single reaction. Such a definition, that seems to us in agreement with the current literature, is mainly justified in this thesis by the fact that single reactions are all described by one-dimensional dynamical systems, even if not all of them belong to the set of balanced and microscopically reversible reactions. On the contrary, complex reactions are usually described by higher dimensional maps, whose dynamics is more difficult to assess.

The analysis developed in this chapter deals with discrete time and discrete space dynamical systems. The limit to the continuum will be discussed in Chapter V. Section IV.2 shows the need for a theory that says how the rate constants for a complex reaction should be derived from the knowledge of the rate constants of each single component. Section IV.3 proposes one possible solution to this problem, in the framework of a probability theory. Section IV.4 proves some results about the convergence of the iterations of convex combinations of Boltzmann maps. Section IV.5 shows that every discrete diffusion operator can be expressed by a bistochastic map (a Boltzmann map of order one). Finally, Section IV.6 presents some examples and a conjecture that seems to be realistic.

## IV.2 Dynamical Systems for Complex Reactions

Consider the Schlögl model, which is one of the simplest examples of complex chemical reactions:



Let  $p, q$  and  $r$  respectively be the concentrations of  $A, B$  and  $X$ . Then, the law of mass action yields

$$\begin{aligned} \frac{dp}{dt} &= -k_1 pr^2 + k_2 r^3 \\ \frac{dr}{dt} &= k_1 pr^2 - k_2 r^3, \end{aligned} \quad (\text{IV.2})$$

if the first reaction only is studied, and

$$\begin{aligned} \frac{dr}{dt} &= -k_3 r + k_4 q \\ \frac{dq}{dt} &= k_3 r - k_4 q, \end{aligned} \quad (\text{IV.3})$$

if the second reaction is the only one to be considered.

How does one get the rate of change of  $r$ , for instance, from the knowledge of (IV.2) and (IV.3), when the full system is examined? An intuitive argument suggests that the rate of change of the concentration of  $X$  must be the sum of the the two separate rates given in (IV.2) and (IV.3). As a matter of fact, what is found in the current literature is

$$\frac{dr}{dt} = k_1 pr^2 - k_2 r^3 - k_3 r + k_4 q. \quad (\text{IV.4})$$

On the other hand, there are at least two points that need a deeper discussion. First of all, it is not clear why the two reactions should not affect each other, so that the rates of one reaction remain unchanged in the presence of the other. The second point regards the discretized version of (IV.4), which is relevant to the results of numerical simulations. Consider, for instance, the 1-step method given by

$$r^* = r + \mu_1 pr^2 - \mu_2 r^3 - \mu_3 r + \mu_4 q, \quad (\text{IV.5})$$

and let the initial conditions, at time  $t = 0$ , be  $r = 1$ ,  $p = 0 = q$ . Then at time  $t = 1$  we get

$$r^* = 1 - \mu_2 - \mu_3 < 0, \quad \text{if } \mu_2 + \mu_3 > 1. \quad (\text{IV.6})$$

Now, if we assume that  $\mu_1 = \mu_2$  and  $\mu_3 = \mu_4$ , the theory developed in Chapter II and Chapter III can be applied, and brings us to the conclusion that all the values of  $\mu_2$  in  $(0, 1/3]$  and those of  $\mu_3$  in  $(0, 1]$  can be used. Thus, the occurrence of the case  $\mu_2 + \mu_3 > 1$  becomes possible.

These two problems can be solved by the “appropriate” choice of the parameters. In fact, the first difficulty is eliminated by adopting effective rates that take into account the interplay of the two reactions. The second problem, in turn, does not arise if the parameters  $\mu_i$  are small, which is the case when the discrete scheme is used to approximate the solution of the ordinary differential equation. In fact, if the  $\mu_i$ 's are defined by  $\mu_i = k_i \cdot \Delta t$ , for  $i = 1, 3$ , where  $\Delta t$  is the time step of the discrete scheme, it is necessary that they be small, in order to have a good approximation of (IV.4) by (IV.5). Then the problem of negative concentrations is automatically solved.

Hence, it is clear that some rules must be given, in order to attribute a precise meaning to the word “appropriate”, for the range of the parameters. Moreover, it is desirable that such rules be derived from within the theory itself, and not be just an appendix added to the theory from external arguments. In the next section it will be shown that this can be done at least in one way, in the framework of a probability theory.

### IV.3 Convex Combinations

The point of view of this thesis is that of casting the dynamical systems given by the law of mass action into a probability theory. Therefore, we resort to the theory of Boltzmann maps, which requires all the reactions to be balanced and microscopically reversible. For

instance, consider the reaction described by (IV.1), and assume that  $k_1 = k_2$  and  $k_3 = k_4$ . Then, it is possible to associate a Boltzmann map with each of the two components of the reaction, since they are both balanced. Call these maps  $\tau_1$  and  $\tau_2$  respectively. Let  $\Omega = (A, B, X)$  be the sample space, and  $\mathcal{Q} \subset \mathbb{R}^3$  the simplex of probability measures on it. Let  $P = (p, q, r) \in \mathcal{Q}$  and call  $P_1^*$  the result of the action of  $\tau_1$  on  $P$ , and similarly define  $P_2^*$  the result of the action of  $\tau_2$  on  $P$ . Then, we can write

$$\tau_1(P) = P_1^* = \begin{pmatrix} p \\ q \\ r \end{pmatrix} + \begin{pmatrix} -\mu_1(pr^2 - r^3) \\ \mu_1(pr^2 - r^3) \\ 0 \end{pmatrix}, \quad (\text{IV.7})$$

which describes the first reaction, and

$$\tau_2(P) = P_2^* = \begin{pmatrix} p \\ q \\ r \end{pmatrix} + \begin{pmatrix} 0 \\ -\mu_3(r - q) \\ \mu_3(r - q) \end{pmatrix}, \quad (\text{IV.8})$$

which relates to the second. The bistochastic matrices associated with  $\tau_1$  and  $\tau_2$  are respectively  $T_1$  and  $T_2$ , where  $T_1 = T_{10} \oplus M_1 \oplus \dots \oplus M_8$ , and

$$T_2 = \begin{matrix} & A & B & X \\ \begin{matrix} A \\ B \\ X \end{matrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 - \mu_3 & \mu_3 \\ 0 & \mu_3 & 1 - \mu_3 \end{pmatrix} \end{matrix} = M_9 \oplus T_{20}, \quad (\text{IV.9})$$

where  $M_9$  is just a  $1 \times 1$  identity matrix, and  $T_{20}$  is a bistochastic block that is mixing for  $\mu_3 \in (0, 1)$ . Concerning  $T_{10}$ , we have

$$T_{10} = \begin{matrix} & XXX & XXA & XAX & AXX \\ \begin{matrix} XXX \\ XXA \\ XAX \\ AXX \end{matrix} & \begin{pmatrix} 1 - 3\mu_1 & \mu_1 & \mu_1 & \mu_1 \\ \mu_1 & \frac{1 - \mu_1}{3} & \frac{1 - \mu_1}{3} & \frac{1 - \mu_1}{3} \\ \mu_1 & \frac{1 - \mu_1}{3} & \frac{1 - \mu_1}{3} & \frac{1 - \mu_1}{3} \\ \mu_1 & \frac{1 - \mu_1}{3} & \frac{1 - \mu_1}{3} & \frac{1 - \mu_1}{3} \end{pmatrix} \end{matrix}, \quad (\text{IV.10})$$

while  $M_1$  is a  $6 \times 6$  matrix whose entries are all equal to  $1/6$ , and it is relevant to the permutations of  $ABX$ . In turn,  $M_2, \dots, M_6$  are the  $3 \times 3$  matrices, with entries equal to  $1/3$ ,

relative to the permutations of  $AAB$ ,  $AAX$ ,  $BBA$ ,  $BBX$  and of  $BXX$ , and finally  $M_7$  and  $M_8$  are  $1 \times 1$  and relative to  $AAA$  and to  $BBB$ .

Observe that equation (IV.5) amounts to having taken  $P^* = P_1^* + P_2^* - P$ . Thus, the result in eq. (IV.6) is no surprise at all, as  $P$ ,  $P_1^*$  and  $P_2^*$  are probability measures in  $\mathcal{Q}$  and, as such, their linear combinations need not to be probabilities, in general. The natural way of taking linear combinations of elements of  $\mathcal{Q}$  is that of forming convex combinations. For instance,

$$P^* = \lambda P_1^* + (1 - \lambda)P_2^*, \quad \lambda \in (0, 1) \quad (\text{IV.11})$$

surely is a probability. Consider also that the maps  $\tau_i$  may be much more complicated, if the reactions involve many more chemicals. In such a situation, it would not be feasible to determine the ranges of such maps, and the only safe choice for getting probabilities, from the probabilities that these maps produce, would be to take convex combinations.

Therefore, we conclude that to have a general theory of complex chemical reactions requires that convex combinations only be taken, and this provides us with a way of choosing the parameters of a complex reaction, once that those of each single component are known. The rule will be that the dynamical system, resulting from the combination of an arbitrary number  $\Phi$  of reactions, must have the form of a convex combination:

$$\tau = \sum_{i=1}^{\Phi} \lambda_i \tau_i, \quad \lambda_i > 0, \quad \sum_{i=1}^{\Phi} \lambda_i = 1, \quad (\text{IV.12})$$

where the  $\tau_i$ 's are properly defined. Considering one of the single components of the full reaction described by  $\tau$ ,  $\tau_i^*$  say, we have that its application to  $P_i \in \mathcal{Q}_i$ , the simplex of probabilities on the sample space of the chemicals of  $\tau_i^*$ , can be written as

$$\tau_i^*(P_i) = P_i + \mu_i \vec{n}_i^* D_i(P_i). \quad (\text{IV.13})$$

Here  $\mu_i$  is the coupling constant,  $\vec{n}_i^*$  is the vector containing the stoichiometric coefficients of the associated non-autocatalytic reaction, with “+” or “-” sign, and  $D_i(P_i)$  is the disequilibrium parameter. Then, the application of  $\tau$  to  $P \in \mathcal{Q}$  can be defined by something

like

$$\tau(P) = P + \sum_{i=1}^{\Phi} \lambda_i \mu_i \vec{n}_i D_i(P_i), \quad (\text{IV.14})$$

which gives the form of the parameters of  $\tau$  in terms of the  $\mu_i$ 's. Note that  $\vec{n}_i^*$  and  $P_i$  are related to  $\vec{n}_i$  and  $P$ , but are not exactly the same, because each of the  $\tau_i^*$ 's need not to be defined on  $\mathcal{Q}$ . We will address this question in the next section. Here we want to remark the fact that the arbitrariness that still remains in the choice of the  $\lambda_i$ 's may be used to attribute different weights to the different reactions in  $\tau$ , in the case that some of them are dominant with respect to the others.

#### IV.4 Convergence for Convex Combinations

Consider a set of  $\Phi \in \mathbb{N}$  reactions, each represented by a Boltzmann map  $\tau_i^*$ , with coupling constant  $\mu_i \in (0, L_i) = \mathcal{R}_i \setminus \{0, L_i\}$ , where  $\mathcal{R}_i$  is the bistochasticity range for  $\tau_i$ , and  $L_i$  is its bistochasticity limit. Let  $\Omega_i = \{(i, 1), \dots, (i, N_i)\}$  be the sample space relative to the  $i$ -th reaction, and  $\mathcal{Q}_i$  the set of the probability measures on it. In this notation, by the couple  $(i, j)$  we mean the  $j$ -th chemical in the reaction  $\tau_i$ , according to some ordering. Introduce a new sample space,  $\Omega = \bigcup_{i=1}^{\Phi} \Omega_i$ , which contains  $K$  elements ( $K \geq N_i, i = 1, \dots, \Phi$ ), and call  $\mathcal{Q}$  the simplex of probabilities on it. To define  $\tau$  as a convex combination of the  $\tau_i^*$ , we must recall that  $\tau_i^*$  need not to be defined on  $\mathcal{Q}$ , in general. Therefore, each  $\tau_i^*$  must be associated with a new map  $\tau_i$  that is defined on  $\mathcal{Q}$ , and such that

$$\tau_i \Big|_{\mathcal{Q}_i} = \tau_i^* \quad \text{and} \quad \tau_i \Big|_{\mathcal{Q} \setminus \mathcal{Q}_i} = \text{Id}_i, \quad (\text{IV.15})$$

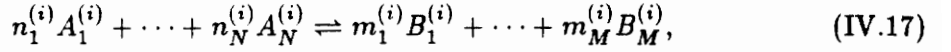
where “ $\text{Id}_i$ ” is the identity map on  $\mathcal{Q} \setminus \mathcal{Q}_i$ . Similarly to the example in the previous section, summarized by equations (IV.7) and (IV.8),  $\tau_i$  must be a Boltzmann map of the same order as  $\tau_i^*$ . Its bistochastic matrix  $T_i$  is then the direct sum of a number of bistochastic blocks whose entries are all equal to  $1/(\# \text{of their rows})$  –and act like the identity on product



vectors— plus the same mixing block of the bistochastic matrix associated to  $\tau_i^*$ . So, for every  $P \in \mathcal{Q}$ , we can write

$$\tau_i(P) = P + \mu_i \vec{n}_i D_i(P_i) = P^{(i)*}, \quad (\text{IV.16})$$

where  $\mu_i$  is the coupling constant of  $\tau_i^*$ ,  $\vec{n}_i$  is a vector that contains  $\vec{n}_i^*$  and that has zeroes on the remaining  $K - N_i$  components,  $P_i$  is the semiprobabilty obtained from  $P$  by taking the components that lie in  $\mathcal{Q}_i$  only, and  $D_i(P_i)$  is the disequilibrium parameter of  $\tau_i^*$  evaluated at  $P_i$ . For instance, let the  $i$ -th reaction be the following non-autocatalytic one



and let  $K > N + M$ . Then, denoting the probability of the chemical  $A_j^{(i)}$  by  $p_{(i,j)}$ , we have

$$\begin{aligned} P_i &= (p_{(i,j)})_{j=1}^{N+M} \in \mathcal{Q}_i \\ D_i(P_i) &= p_{(i,1)}^{n_1^{(i)}} \dots p_{(i,N)}^{n_N^{(i)}} - p_{(i,N+1)}^{m_1^{(i)}} \dots p_{(i,N+M)}^{m_M^{(i)}} \\ \vec{n}_i &= (0, \dots, 0, n_1^{(i)}, \dots, m_M^{(i)}, 0, \dots, 0), \end{aligned} \quad (\text{IV.18})$$

where  $\vec{n}_i$  contains  $K - N - M$  zeroes. It makes sense now to define the convex combination of maps,  $\tau$ , given in eq. (IV.12) by the expression (IV.14), where the symbols take the meaning given to them in this section. We call such a  $\tau$  a **Generalized Boltzmann map**.

We can now start the study of complex systems that are described by generalized Boltzmann maps. First of all let us define the entropy of  $P = (p_1, \dots, p_K) \in \mathcal{Q}$  as

$$S(P) = - \sum_{i=1}^K p_i \log p_i, \quad (\text{IV.19})$$

and observe that the entropy of a convex combination of elements of  $\mathcal{Q}$  is greater or equal to the convex combination of the respective entropies, i.e.

$$S \left( \sum_{i=1}^{\Phi} \lambda_i P_i \right) \geq \sum_{i=1}^{\Phi} \lambda_i S(P_i). \quad (\text{IV.20})$$

This implies that  $P \in \mathcal{Q}$  is a fixed point for  $\tau$  if and only if it is a fixed point of each of the  $\tau_i$ 's. In fact, assume that  $\tau(P) = P$ , and that  $\tau_i(P) \neq P$ , for some  $i$ . The fact that  $T_i$  contains a block with a spectral gap  $\Delta_i$ , implies that  $S(\tau_i(P)) > S(P)$ . Moreover,  $S(\tau_j(P)) \geq S(P)$  for every other  $j \neq i$ . Then, we obtain

$$\begin{aligned} S(\tau(P)) &= S\left(\sum_{j=1}^{\Phi} \lambda_j \tau_j(P)\right) \geq \sum_{j=1}^{\Phi} \lambda_j S(\tau_j(P)) \\ &> \sum_{j=1}^{\Phi} \lambda_j S(P) = S(P), \end{aligned} \tag{IV.21}$$

which is a contradiction because  $S$  is single valued. Therefore,  $\tau(P) = P$  if and only if  $\tau_i(P) = P$  for every  $i$ .

Now, let  $P$  be in  $\mathcal{Q}$  and form the tensor product of  $n$  copies thereof:  $\sigma(P) = \otimes_1^n P$ , and apply to  $\sigma(P)$  a bistochastic matrix  $T$  with a bistochastic block  $T'$  that has a spectral gap  $\Delta > 0$ . Call  $P_n^*$  the result of this operation, take the conditional expectation onto the first factor

$$[E(P_n^*)]_l = \sum_{i_2, \dots, i_n} P_{l, i_2, \dots, i_n}^* = p_l^*, \tag{IV.22}$$

and call  $P^*$  the vector whose components are the  $p_l^*$ 's. Then the following holds

LEMMA IV.1. (a)  $S(\sigma(P)) = nS(P)$ .

(b)  $S(P_n^*) = S(T(\sigma(P))) \geq S(\sigma(P)) + \frac{\Delta}{2} \|\sigma^*(P) - \hat{P}\|_2^2$ .

(c)  $S(P^*) \geq \frac{1}{n} S(P_n^*) + \frac{1}{2n} \|\otimes_1^n P^* - P_n^*\|_2^2$ .

Then, if  $\tau$  is a Boltzmann map whose bistochastic matrix is  $T$ , we have

(d)  $S(\tau(P)) \geq S(P) + \frac{1}{2n} \left( \Delta \|\sigma^*(P) - \hat{P}\|_2^2 + \|\otimes_1^n P^* - P_n^*\|_2^2 \right)$ , where  $n$  is the order of the map.

Here, a small abuse of notation has been made by using the same symbol  $S$  for the entropy of  $P$  and  $P^* \in \mathcal{Q}$  as well as for the entropy of  $P_n^*$  and  $\sigma(P)$  in  $\mathcal{Q}_n$ . Also, by  $\sigma^*(P)$  we mean the orthogonal projection of  $\sigma(P)$  onto the  $N$ -dimensional invariant subspace,  $\mathcal{H}$  say, of  $T'$ , and  $\hat{P} = \|\sigma^*(P)\|_1(1, \dots, 1)/N$  is the uniform distribution in  $\mathcal{H}$  of

the portion of probability that pertains to  $\sigma^*(P)$ . The inner product we have adopted is  $\langle (\mathbf{x}_1, \dots, \mathbf{x}_K), (\mathbf{y}_1, \dots, \mathbf{y}_K) \rangle = \sum_i x_i y_i$ .

**PROOF:** Let us do part (a) first. We have

$$\begin{aligned} S(\sigma(P)) &= - \sum_{i_1, \dots, i_n} p_{i_1} \cdots p_{i_n} \log(p_{i_1} \cdots p_{i_n}) \\ &= - \sum_{i_1, \dots, i_n} p_{i_1} \cdots p_{i_n} (\log p_{i_1} + \dots + \log p_{i_n}) \\ &= - \sum_{i_1} p_{i_1} \log p_{i_1} - \dots - \sum_{i_n} p_{i_n} \log p_{i_n} = nS(P). \end{aligned} \quad (\text{IV.23})$$

For (b) simply apply Theorem II.7, and observe that all the components of  $\sigma(P)$  that are not in  $\sigma^*(P)$  are left unchanged by  $T$ . For part (c) observe that we can write

$$\begin{aligned} -S(P_n^*) &= \sum_{i_1, \dots, i_n} p_{i_1, \dots, i_n}^* \log p_{i_1, \dots, i_n}^* \geq \quad (\text{Lemma II.1}) \\ &\geq \sum_{i_1, \dots, i_n} p_{i_1, \dots, i_n}^* \log(p_{i_1}^* \cdots p_{i_n}^*) + \frac{1}{2} \|\otimes_1^n P^* - P_n^*\|_2^2 \\ &= \sum_{i_1, \dots, i_n} p_{i_1, \dots, i_n}^* (\log p_{i_1}^* + \dots + \log p_{i_n}^*) + \frac{1}{2} \|\otimes_1^n P^* - P_n^*\|_2^2 \\ &= -nS(P^*) + \frac{1}{2} \|\otimes_1^n P^* - P_n^*\|_2^2, \end{aligned} \quad (\text{IV.24})$$

where  $p_{i_1, \dots, i_n}$  is the generic component of  $P_n^*$ . Finally, part (d) is a direct consequence of (a), (b), (c), and of the definition of a Boltzmann map (Definition II.3).  $\blacksquare$

We can now prove the following

**THEOREM IV.1.** *Consider a set of reactions, each described by a Boltzmann map  $\tau_i^*$  of order  $n_i$ ,  $i = 1, \dots, \Phi$ , with  $\mu_i \in (0, L_i)$ . Let  $\tau$  be the convex combination (IV.12), where the  $\tau_i$ 's are obtained from the  $\tau_i^*$ 's as above. Then*

(a)  $S$  is a strict Liapunov function for  $\tau$ .

(b) Let  $\mathcal{M}$  be the manifold of the fixed points of  $\tau$ , and let  $d(x, \mathcal{M}) = \min_{y \in \mathcal{M}} \|x - y\|$ .

Then, for every  $P \in \mathcal{Q}$  and every  $\epsilon > 0$ , there exists a  $k \in \mathbb{N}$  such that  $d(\tau^j(P), \mathcal{M}) < \epsilon$  whenever  $j \geq k$ .

**PROOF:** (a) Because of the fact that  $\mu_i \in (0, L_i)$  for every  $i$ , all the  $T_i$ 's have a mixing block, and so  $S$  is a strict Liapunov function for every  $\tau_i$ . It follows that  $S(\tau(P)) > S(P)$  if  $P$  is not a fixed point of every  $\tau_i$ , i.e. if  $P$  is not a fixed point of  $\tau$ .

(b) Let  $P^{(k)}$  and  $\hat{P}_i^{(k)}$  be respectively the  $k$ -th iterate of  $P$  under  $\tau$  and the uniform redistribution on  $\mathcal{H}_i$ , the invariant subspace of  $T_i'$ , of the part of  $\otimes P^{(k)}$  that falls into  $\mathcal{H}_i$ . Also, let  $P^{(k,i)} = \tau_i(P^{(k)})$  and  $P_{n_i}^{(k)} = T_i(\otimes_1^{n_i} P^{(k)})$ , where  $n_i$  is the order of the map  $\tau_i$ . Then we have

$$\begin{aligned}
 S(P^{(k+1)}) &= S\left(\sum_{j=1}^{\Phi} \lambda_j \tau_j(P^{(k)})\right) \geq \sum_{j=1}^{\Phi} \lambda_j S(\tau_j(P^{(k)})) \\
 &\geq \sum_{i=1}^{\Phi} \lambda_i \left\{ S(P^{(k)}) + \frac{1}{2n_i} \left[ \Delta_i \|\sigma_i^*(P^{(k)}) - \hat{P}_i^{(k)}\|_2^2 + \|\otimes_1^{n_i} P^{(k,i)} - P_{n_i}^{(k)}\|_2^2 \right] \right\} \\
 &= S(P^{(k)}) + \frac{\lambda_{\min}}{2n_{\max}} \sum_{i=1}^{\Phi} \left[ \Delta_i \|\sigma_i^*(P^{(k)}) - \hat{P}_i^{(k)}\|_2^2 + \|\otimes_1^{n_i} P^{(k,i)} - P_{n_i}^{(k)}\|_2^2 \right],
 \end{aligned} \tag{IV.25}$$

where  $\sigma_i^*$  is the operator defined in Lemma IV.1 relative to  $\tau_i$ ,  $\lambda_{\min} = \min_i(\lambda_i)$  and  $n_{\max} = \max_i(n_i)$ . Therefore, since  $S$  is bounded we must have

$$\begin{aligned}
 \Delta_i \|\sigma_i^*(P^{(k)}) - \hat{P}_i^{(k)}\|_2^2 &\rightarrow 0, \quad \text{as } k \rightarrow \infty, \quad \text{for every } i, \quad \text{and} \\
 \|\otimes_1^{n_i} P^{(k,i)} - P_{n_i}^{(k)}\|_2^2 &\rightarrow 0, \quad \text{as } k \rightarrow \infty, \quad \text{for every } i.
 \end{aligned} \tag{IV.26}$$

Here, the first equation states that  $P^{(k)}$  converges to the manifold of the fixed points of  $\tau_i$ , for every  $i$ , i.e.  $P^{(k)}$  converges to  $\mathcal{M}$ . The second equation says that  $T_i(\otimes_1^{n_i} P^{(k)}) \rightarrow \otimes_1^{n_i} \tau_i(P^{(k)})$  for every  $i$ , which is also satisfied if  $P^{(k)}$  tends to the manifold of the fixed points of  $\tau$ . ■

Note that  $\tau$  has one fixed point at least: the uniform distribution. In many instances, that is the only fixed point of  $\tau$ , in which case the theorem states that every initial condition  $P(0) \in \mathcal{Q}$  converges to such a point. In other cases, the manifold  $\mathcal{M}$  contains more than one point, but other selection rules become effective and imply that for every initial condition  $P(0)$  a  $\hat{P}$  can be found such that  $\tau^k(P(0)) \rightarrow \hat{P}$ . Here are summarized three of these rules, which may be useful in many practical cases.

**THEOREM IV.2.** Consider the generalized Boltzmann map  $\tau$  and let  $P(0) \in \mathcal{Q}$ .

- (a) Assume that one of the convergent subsequences of  $\{\tau^k(P(0))\}_k$  converges to the unique point  $\hat{P}$  that maximizes the entropy, under the constraints imposed by the constants of motion. Then, it follows that  $\tau^k(P(0)) \rightarrow \hat{P}$  as  $k \rightarrow \infty$ .
- (b) If there is one fixed point only,  $\hat{P}$  say, with the property  $S(\hat{P}) \geq S(P(0))$ , then  $\tau^k(P(0)) \rightarrow \hat{P}$ , as  $k \rightarrow \infty$ .
- (c) If the fixed points of  $\tau$  are isolated, then  $\tau^k(P(0))$  converges to one of them.

**PROOF:** (a)  $\{\tau^k(P(0))\}_k$  is contained in a compact set, and so it has convergent subsequences. Assume that the subsequence  $\{\tau^{k_i}(P(0))\}_i$  converges to  $P_0$ . Then  $P_0$  is a fixed point for  $\tau$ . In fact,  $\tau \circ \tau^{k_i}(P(0)) \rightarrow \tau(P_0)$  as  $i \rightarrow \infty$  because of the continuity of  $\tau$ . Moreover,  $S$  is continuous, and so

$$S(\tau^{k_i}(P(0))) \rightarrow S(P_0), \quad \text{and} \tag{IV.27}$$

$$S(\tau^{k_i+1}(P(0))) \rightarrow S(\tau(P_0)) = S(P_0),$$

because  $S$  is also monotonic and bounded, and so it converges. Now, recall that  $S$  is a strict Liapunov function for  $\tau$ , and conclude that  $S(\tau(P_0)) = S(P_0)$  if and only if  $\tau(P_0) = P_0$ . Note that all the other convergent subsequences of  $\{\tau^k(P(0))\}_k$  have limits whose entropy equals that of  $P_0$ , due to the fact that  $\{S(\tau^k(P(0)))\}_k$  is a convergent sequence. Therefore, if  $\hat{P} = P_0$ , all the convergent subsequences of  $\{\tau^k(P(0))\}_k$  have limits whose entropy is the maximum, given the particular choice of the constants of motion performed by  $P(0)$ . But the only point whose entropy is maximum is  $\hat{P}$  itself. In fact, the constants of motion of  $\tau$ , if any, are hyperplanes whose intersection with  $\mathcal{Q}$  is a convex set, and  $S$  can only have one maximum on a convex set. To see this let us use Kulback's Lemma (Lemma II.1). Then, for  $P' \in \mathcal{Q}$ , we can write

$$\begin{aligned} S(P_1) &= S(\lambda \hat{P} + (1 - \lambda)P') \\ &\geq \lambda S(\hat{P}) + (1 - \lambda)S(P') + \frac{\lambda}{2} \|P_1 - \hat{P}\|_2^2 + \frac{1 - \lambda}{2} \|P_1 - P'\|_2^2, \end{aligned} \tag{IV.28}$$

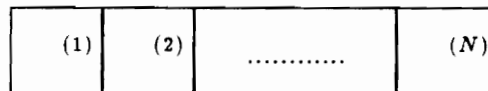
and so  $S(P_1) > S(\hat{P})$  if  $S(P') = S(\hat{P})$  and  $P' \neq \hat{P}$ .

(b) The proof of the second part follows from the obvious observation that  $S$  is non-decreasing and that all the convergent subsequences of  $\{\tau^k(P(0))\}_k$  converge to a fixed point. Therefore, if there is one fixed point only, whose entropy is greater than or equal to that of  $P(0)$ , all the convergent subsequences tend to that point, and this is enough to ensure the convergence of the full sequence, as  $\mathcal{Q}$  is compact.

(c) If the fixed points of  $\tau$  are isolated, and  $\mathcal{M}$  is the set of such points, we have that  $d_0 = \min_{P_i, P_l \in \mathcal{M}} d(P_i, P_l)$  is a positive quantity. Then, consider that  $d(\tau^j(P(0)), \tau^{j-1}(P(0)))$  converges to 0, as  $\tau^j(P(0))$  approaches  $\mathcal{M}$ , since the disequilibrium parameters in  $\tau$  are continuous functions and they all vanish in  $\mathcal{M}$ . This means that there exists a minimum distance,  $d_1$  say, such that  $d(\tau^j(P(0)), \tau^{j-1}(P(0))) < d_0/3$  whenever  $d(\tau^{j-1}(P(0)), \mathcal{M}) \leq d_1$ . At the same time, we know, from theorem IV.1, that there is a  $k \in \mathbb{N}$  such that  $d(\tau^j(P(0)), \mathcal{M}) < \min(d_1, d_0/3) = d'$  for all  $j \geq k$ . It follows that for  $j \geq k$  it is impossible for the iterations to jump from the ball of radius  $d'$  around  $P_i \in \mathcal{M}$  to the ball of the same size around  $P_l \in \mathcal{M}$ , because it would be necessary to pass through points that are at a distance bigger than  $d'$  from  $\mathcal{M}$ . As we know that the separation between  $\tau^j(P(0))$  and  $\mathcal{M}$  shrinks to zero, we must conclude that the iterations converge to a given point of  $\mathcal{M}$ . ■

#### IV.5 Discrete Diffusion

In Chapter III it has been shown that the process of diffusion of a chemical, in a medium subdivided into two cells, can be described by a bistochastic matrix, also regarded as a Boltzmann map of order one. Here that argument will be generalized to the case of an arbitrary number of cells, that cover a subset of  $\mathbb{R}^\nu$ , for any  $\nu \in \mathbb{N}$ . Consider a 1-dimensional medium first, that is made of  $N$  cells,



and let  $A$  be one chemical that diffuses in it. Let the discrete law of diffusion be expressed

by

$$\begin{aligned}
 p_1^* &= p_1 - d_1(p_1 - p_2) \\
 p_i^* &= p_i - d_{i-1}(p_i - p_{i-1}) - d_i(p_i - p_{i+1}), \quad i = 2, \dots, N-1 \\
 p_N^* &= p_N - d_{N-1}(p_N - p_{N-1}),
 \end{aligned} \tag{IV.29}$$

where  $p_i$  is the concentration of  $A$  in the  $i$ -th cell at the instant  $t$ ,  $p_i^*$  is the same concentration at the instant  $t + 1$ , and  $\sum_1^N p_i = 1$ . Each  $d_i$  is called the **Diffusion Coefficient** between the  $i$ -th and the  $(i + 1)$ -th cells. It is assumed that diffusion is microscopically reversible, i.e. the diffusion probability of one particle in the  $i$ -th cell towards the  $(i + 1)$ -th cell is equal to the diffusion probability of one particle in the  $(i + 1)$ -th cell towards the  $i$ -th cell. In the special case that all the  $d_i$ 's are equal, to  $d$  say, we get

$$p_i^* = p_i + d(p_{i-1} - 2p_i + p_{i+1}), \tag{IV.30}$$

which is the well known central difference scheme for the partial differential equation

$$\frac{\partial p(\mathbf{x}, t)}{\partial t} = D \frac{\partial^2 p(\mathbf{x}, t)}{\partial \mathbf{x}^2}, \tag{IV.31}$$

where it has been supposed that the following holds

$$\begin{aligned}
 \left. \frac{\partial p(\mathbf{x}, t)}{\partial t} \right|_{\mathbf{x}_i, t_j} &\approx \frac{p_i^* - p_i}{\Delta t}, \quad \text{and} \\
 D \left. \frac{\partial^2 p(\mathbf{x}, t)}{\partial \mathbf{x}^2} \right|_{\mathbf{x}_i, t_j} &\approx \frac{D}{h^2} (p_{i-1} - 2p_i + p_{i+1}),
 \end{aligned} \tag{IV.32}$$

where  $\Delta t$  is the time step size,  $h$  is the width of one cell,  $d = D\Delta t/h^2$ , and  $p_i$  and  $p_i^*$  are the concentrations in the  $i$ -th cell at times  $t_j$  and  $t_j + \Delta t$ . It is interesting to note, at this point, that the bistochasticity limit for  $\delta$  – which is defined below – requires  $d \leq 1/2$ , and so a natural relation is found between  $\Delta t$  and  $h$ , namely:  $\Delta t \leq h^2/2D$ . This is of interest in the numerical analysis of (IV.31). In fact, this relation is nothing but the usual condition required in numerical analysis for the convergence of the scheme (IV.30) to the solution of (IV.31) [39].

We can make this into a probability theory by taking  $\Omega = \{A_1, \dots, A_N\}$  as the sample space, and  $\delta : \mathcal{Q} \rightarrow \mathcal{Q}$  as the diffusion operator, which is a Boltzmann map of order one, and defines a dynamics on  $\mathcal{Q}$ , the simplex of probability measures on  $\Omega$ . In this case,  $\delta$  is symmetric, because of the principle of microscopic reversibility, and it has the form

$$\begin{array}{c}
 \begin{array}{cccccccc}
 & 1 & 2 & 3 & 4 & \dots & N-1 & N \\
 1 & \left( \begin{array}{cccccccc}
 1-d_1 & d_1 & 0 & 0 & \dots & 0 & 0 & 0 \\
 d_1 & 1-d_1-d_2 & d_2 & 0 & \dots & 0 & 0 & 0 \\
 0 & d_2 & 1-d_2-d_3 & d_3 & \dots & 0 & 0 & 0 \\
 0 & 0 & d_3 & 1-d_3-d_4 & \dots & 0 & 0 & 0 \\
 \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\
 \vdots & 0 & 0 & 0 & 0 & \dots & 1-d_{N-2}-d_{N-1} & d_{n-1} \\
 N & 0 & 0 & 0 & 0 & \dots & \dots d_{N-1} & 1-d_{n-1}
 \end{array} \right) \\
 & & & & & & & \text{(IV.33)}
 \end{array}
 \end{array}$$

This matrix is bistochastic provided that  $d_i \geq 0$  and  $d_{i-1} + d_i \leq 1$  for every  $i$ . However, if some  $d_i$  vanishes, there is no diffusion between the cells to the left of the  $(1+i)$ -th cell and all the others. Therefore, this case corresponds to that of two separate media that can be studied separately. Consequently, we will always assume that  $d_i > 0$  for every  $i$ . Under this hypothesis, it is easy to see that the product of the diffusion operator and its adjoint,  $\delta\delta^* = \delta^2$ , is a 5-diagonal matrix, and there exists one  $k \in \mathbb{N}$  such that  $\delta^{2k}$  is a positive bistochastic matrix. Then, Theorem II.9 says that  $\delta\delta^*$  has a spectral gap  $\Delta > 0$ , and Theorem II.7 ensures that for every  $P \in \mathcal{Q}$  we have  $\delta^j(P) \rightarrow \hat{P} = (1, \dots, 1)/N$  as  $j \rightarrow \infty$ .

Consider now diffusion in a 2-dimensional medium made of  $N$  columns and  $M$  rows of cells. Let  $P = (p_{i,j})$  be the vector of the normalized concentrations, and  $d_{i,j}^H$  the horizontal diffusion coefficient between the  $(i, j)$  and the  $(i+1, j)$  cells. Similarly, let  $d_{i,j}^V$  be the vertical diffusion coefficient between the  $(i, j)$  and  $(i, j+1)$  cells. In this case the discrete law of diffusion can be expressed as



$$\begin{aligned}
p_{i,j}^* &= p_{i,j} - d_{i-1,j}^H(p_{i,j} - p_{i-1,j}) - d_{i,j}^H(p_{i,j} - p_{i+1,j}) \\
&\quad - d_{i,j-1}^V(p_{i,j} - p_{i,j-1}) - d_{i,j}^V(p_{i,j} - p_{i,j+1}), \quad \text{for all } i, j
\end{aligned} \tag{IV.34}$$

where  $d_{0,j}^H = 0 = d_{N,j}^H$ , and  $d_{i,0}^V = 0 = d_{i,M}^V$ . Then a bistochastic map  $\delta$  can be associated with this process, provided that  $d_{i,j}^H, d_{i,j}^V \geq 0$  for every  $i, j$ , and that  $d_{i-1,j}^H + d_{i,j}^H + d_{i,j-1}^V + d_{i,j}^V \leq 1$ . Note that this time the fact that some of the diffusion coefficients are zero does not necessarily imply that the full system is not mixing. However, we will assume for simplicity that such coefficients are all positive, as the analysis of the most general case introduces merely technical difficulties, and it can be dealt with by the theory here developed. Furthermore,  $\delta$  turns out to be a 5-diagonal  $MN \times MN$  matrix whose square,  $\delta^2 = \delta\delta^*$  is shown to have a spectral gap as for the 1-dimensional case.

In general, diffusion in  $\nu$  dimensions can be described by an  $N_1 \cdots N_\nu \times N_1 \cdots N_\nu$  matrix, which is  $(2\nu + 1)$ -diagonal and bistochastic if all the diffusion coefficients in the  $k$ -th direction  $d_{i_1 \dots i_\nu}^{(k)}$  are nonnegative, for every  $k$ , and if

$$\sum_{k=1}^{\nu} (d_{i_1 \dots i_k \dots i_\nu}^{(k)} + d_{i_1 \dots i_{k-1} \dots i_\nu}^{(k)}) \leq 1, \quad \text{for every } i_1, \dots, i_\nu. \tag{IV.35}$$

Moreover,  $\delta$  is mixing if all the diffusion coefficients are positive. Here  $N_k$  is the number of cells of the medium in the  $k$ -th direction. Then the following holds.

**LEMMA IV.2.** *Let  $\delta$  be a diffusion operator for one chemical in  $k$  dimensions, whose diffusion coefficients are all positive. Then, for every  $P \in \mathcal{Q}$  we have  $\tau^j(P) \rightarrow \hat{P}$ , where  $\hat{P}$  is the uniform distribution in the  $N_1 \cdots N_\nu$  cells which the medium is made of.*

Let us go back, now, to the diffusion in one dimension, but with two diffusing chemicals,  $A$  and  $B$ . If there are  $N$  cells, the sample space will be  $\Omega = (A_1, \dots, A_N, B_1, \dots, B_N)$ . Then the diffusion operator for this process has the form  $\delta = \delta_A \oplus \delta_B$ , where the two terms on the right are the respective diffusion operators for  $A$  and  $B$  separately. The generalization of this

to  $\nu$  dimensions and  $\Phi$  chemicals,  $A_1, \dots, A_\Phi$ , is immediate, and we get  $\delta = \delta_{A_1} \oplus \dots \oplus \delta_{A_\Phi}$ . Hence the following holds.

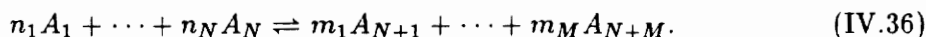
**THEOREM IV.4.** *Let  $\delta = \bigoplus_1^\Phi \delta_{A_i}$  be a diffusion operator in  $\nu$  dimensions, with all positive diffusion coefficients. Then, for every  $P \in \mathcal{Q}$ , the simplex of probability measures on  $\Omega = \{A_1^{11\dots 1}, A_1^{11\dots 2}, \dots, A_1^{N_1\dots N_\nu}, \dots, A_\Phi^{N_1\dots N_\nu}\}$ ,  $\delta^j(P)$  converges to the uniform distribution of each of the separate chemicals, under the iterations of  $\delta$ .*

The reason is that the  $A_i$ 's don't mix with each other, and each of the  $\delta_{A_i}$  makes its system converge to the uniform distribution. Therefore, it is like having  $\Phi$  distinct systems, whose separate sum of concentrations is less than one, that converge to a uniform redistribution of that sum. In more explicit terms, assume that the sum of the concentrations of  $A_j$  in the whole medium is  $p_j \leq 1$ ; then, at the fixed point, the concentration of  $A_j$  in each cell will be  $p_j/(N_1 \cdots N_\nu)$ , where  $N_k$  is the number of cells of the medium in the  $k$ -th direction.

#### IV.6 Discrete Reaction and Diffusion

The results described in section IV.4 do not mention the order of the maps of which convex combination is taken. It follows that one of the maps in the combination can be a diffusion operator. If this is the case, we are in a situation usually called "Reaction-Diffusion" process. Although no new results can be drawn by looking at this special case, it is worth considering some examples, to see what is the interplay of reaction and diffusion in our framework.

**Example 1.** Consider a 1-dimensional medium made of  $L$  cells, in which a single non-autocatalytic reaction takes place:



For simplicity, assume that the diffusion coefficients of each chemical do not vary from cell to cell, and call  $d_i > 0$  the cell relative to the chemical  $A_i$ . Let  $p_{ij}$  be the concentration of  $A_i$  in the  $j$ -th cell, and assume that

$$\sum_{i=1}^{N+M} \sum_{j=1}^L p_{ij} = 1. \quad (\text{IV.37})$$

Then, the diffusion operator has the form  $\delta = \delta_1 \oplus \dots \oplus \delta_{N+M}$ , where  $\delta_i$  describes the diffusion of the chemical  $A_i$ .

As for the reaction, the fact that it involves nearby molecules only, allows us to assume that this process is a set of  $L$  independent replicas of (IV.36), in the  $L$  different cells. Consequently, the full reaction operator takes the form

$$\tau_r = \sum_{i=1}^L \lambda_i \tau_i, \quad (\text{IV.38})$$

where  $\tau_i$  describes (IV.36) in the  $i$ -th cell. Now, the combination of the reaction term with  $\delta$  is also convex, and it can be written as  $\tau = \tau_r + (1 - \lambda)\delta$ , for  $\lambda \in (0, 1)$ , if we have  $\lambda_i > 0$  and  $\sum_i \lambda_i = \lambda$ . Then, given a  $P \in \mathcal{Q}$ , the simplex of probabilities on  $\Omega = \{A_{1i}, \dots, A_{N+M,i}\}_{i=1}^L$ , the action of  $\tau$  on  $P$  produces a new probability  $P^*$ , whose components  $p_{ji}^*$  can be computed as follows:

$$\begin{aligned} p_{j1}^* &= p_{j1} - \lambda_1 \mu n_j (p_{11}^{n_1} \cdots p_{N1}^{n_N} - q_{11}^{m_1} \cdots q_{M1}^{m_M}) - (1 - \lambda) d_j (p_{j1} - p_{j2}) \\ p_{ji}^* &= p_{ji} - \lambda_i \mu n_j (p_{1i}^{n_1} \cdots p_{Ni}^{n_N} - q_{1i}^{m_1} \cdots q_{Mi}^{m_M}) + (1 - \lambda) d_j (p_{j,i-1} - 2p_{ji} - p_{j,i+1}), \\ &\quad (i = 2, \dots, L - 1) \end{aligned} \quad (\text{IV.39})$$

$$p_{jL}^* = p_{jL} - \lambda_L \mu n_j (p_{1L}^{n_1} \cdots p_{NL}^{n_N} - q_{1L}^{m_1} \cdots q_{ML}^{m_M}) + (1 - \lambda) d_j (p_{j,L-1} - p_{jL}),$$

for the chemicals on the left hand side of (IV.36), and

$$\begin{aligned} q_{j1}^* &= q_{j1} + \lambda_1 \mu m_j (p_{11}^{n_1} \cdots p_{N1}^{n_N} - q_{11}^{m_1} \cdots q_{M1}^{m_M}) - (1 - \lambda) d_{N+j} (q_{j1} - q_{j2}) \\ q_{ji}^* &= q_{ji} + \lambda_i \mu m_j (p_{1i}^{n_1} \cdots p_{Ni}^{n_N} - q_{1i}^{m_1} \cdots q_{Mi}^{m_M}) + (1 - \lambda) d_{N+j} (q_{j,i-1} - 2q_{ji} - q_{j,i+1}), \\ &\quad (i = 2, \dots, L - 1) \end{aligned}$$

$$q_{jL}^* = q_{jL} + \lambda_L \mu m_j (p_{1L}^{n_1} \cdots p_{NL}^{n_N} - q_{1L}^{m_1} \cdots q_{ML}^{m_M}) + (1 - \lambda) d_{N+j} (q_{j,L-1} - q_{jL}), \quad (\text{IV.40})$$

for the chemicals on the right, where we have used  $q_{ji} = p_{N+j,i}$ . Let us define now the total probability of the substance  $A_j$  by  $p_j = \sum_{i=1}^L p_{ji}$ . Then, clearly, the  $p_j$ 's obey the same constants of motion that the corresponding concentrations would respect in a stirred reactor. In fact, in  $p_j^*$  the diffusion terms cancel (due to the fact that the system is closed), and we get

$$\begin{aligned} p_j^* &= p_j - \mu n_j \sum_{i=1}^L \lambda_i D_i(P), \quad \text{and} \\ q_j^* &= q_j + \mu m_j \sum_{i=1}^L \lambda_i D_i(P), \end{aligned} \quad (\text{IV.41})$$

where  $D_i(P) = p_{1i}^{n_1} \cdots p_{Ni}^{n_N} - q_{1i}^{m_1} \cdots q_{Mi}^{m_M}$ . It follows that

$$\begin{aligned} n_j p_1 - n_1 p_j &= K_j, \quad j = 2, \dots, N \\ m_j p_1 + n_1 q_j &= L_j, \quad j = 1, \dots, M. \end{aligned} \quad (\text{IV.42})$$

We can now find the fixed points of  $\tau$ , given some initial condition  $P(0) \in \mathcal{Q}$ . Recall that  $\tau(\hat{P}) = \hat{P}$  if and only if  $\tau_r(\hat{P}) = \hat{P}$  and  $\delta(\hat{P}) = \hat{P}$ . Then, if we call  $\hat{p}_{ji}$  the components of a fixed point  $\hat{P}$  of  $\tau$ , we must have  $\hat{p}_{j1} = \dots = \hat{p}_{jL} = \hat{p}_j/L$  for every  $j = 1, \dots, N + M$ . Moreover,  $\tau_r(\hat{P}) = \hat{P}$  if and only if  $\tau_i(\hat{P}) = \hat{P}$  for every  $i$ , that is to say if and only if  $D_i(\hat{P}) = 0$  for every  $i$ . Then we must have

$$D_i(\hat{P}) = \frac{1}{L^n} (\hat{p}_1^{n_1} \cdots \hat{p}_N^{n_N} - \hat{q}_1^{m_1} \cdots \hat{q}_M^{m_M}) = \frac{1}{L^n} D(\hat{P}) = 0, \quad (\text{IV.43})$$

if  $n = \sum n_i = \sum m_i$ , and  $D(\hat{P})$  is the disequilibrium parameter of the stirred reaction, evaluated at the point whose components are the  $\hat{p}_j$ 's. Hence, we know that there exists a unique solution to (IV.43), given the particular choice of the constants of motion due to  $P(0)$ , and we conclude that for every  $P(0) \in \mathcal{Q}$  there exists a unique  $\hat{P} \in \mathcal{Q}$  such that  $\tau^k(P(0)) \rightarrow \hat{P}$  as  $k \rightarrow \infty$ . Moreover,  $\hat{P}$  is stable, as the fixed points of the stirred reaction are. The generalization to single autocatalytic reactions is immediate.

**Example 2.** This case is relevant to the theory of blood. There are two reactions



and we assume that the chemicals  $A, \dots, E$  and the photons  $\gamma$  can diffuse in a 1-dimensional medium made of  $N$  cells. The same analysis performed in the previous example leads us to conclude that every fixed point of the overall map (reaction and diffusion) will be a uniform distribution  $\hat{p}_{ji} = \hat{p}_j/N$ ,  $j = 1, \dots, 6$ , and it will satisfy  $p_1 p_2 = p_3 p_6$  and  $p_1 p_4 = p_5 p_6$ , where  $1 = A, 2 = B, \dots, 6 = \gamma$ . Moreover, given  $P(0) \in \mathcal{Q}$ , it is easy to see that there are 4 conserved quantities:

$$\begin{aligned} p_1 - p_2 - p_4 &= C_1 \\ p_1 + p_3 + p_5 &= C_2 \\ p_1 + p_6 &= C_3 \\ p_5 + p_6 &= C_4, \end{aligned} \tag{IV.45}$$

thus the map is 2-dimensional. We conclude that there is a unique fixed point to which the map converges, provided that all the diffusion coefficients and the reaction rates are strictly contained in their respective bistochasticity ranges. Furthermore, the fixed points are stable, due to the convergence and to their continuous dependence on the initial conditions.

**Example 3.** Consider the reaction  $2A \rightleftharpoons A + B$ , in the 0-th cell of a 1-dimensional medium made of  $N + 1$  cells. Assume that  $B$  cannot diffuse out of the 0-th cell, and that its concentration in the other cells is zero. Then, the overall map is  $\tau = \lambda\tau_r + (1 - \lambda)\delta$ , where  $\tau_r$  describes the reaction in the 0-th cell, and  $\delta$  describes the diffusion of  $A$ . Assuming that both  $\tau_r$  and  $\delta$  are mixing, the iterations of  $P(0)$  under  $\tau$  converge to a limit that obeys

$$\begin{aligned} p_0^2 - p_0 q_0 &= 0 \\ p_0 &= p_1 = \dots = p_N \\ p + q_0 &= \sum p_i + q_0 = 1. \end{aligned} \tag{IV.46}$$

We find that  $p_i = 0, q_0 = 1$  is an unstable fixed point, while  $p_i = 1/(N + 2)$  for all  $i$ 's and  $q_0 = 1/(N + 2)$  is stable and it is the limit of every initial condition that is not the unstable fixed point.

Observe that, in all these examples, the value of  $\lambda$  could have been anything in  $(0, 1)$ . Therefore, in the case that  $\lambda \approx 1$ , we have that diffusion almost doesn't take place until the reactions have practically reached their equilibrium points. After that, the system "diffuses" close to the manifold of the fixed points of the reaction map, possibly converging to a precise point. On the contrary, if  $\lambda \approx 0$ , we have that the uniform distribution is the first to be reached, and after that the reactions will take place in a fashion that makes the system evolve closely to what would happen in a stirred reactor. This can be inferred by looking at the form of (IV.39) and (IV.40), for example.

We conclude this chapter with a conjecture prompted by the examples in this section and by many others that have been worked out.

**CONJECTURE IV.1.** *Consider a generalized Boltzmann map  $\tau$ , and let  $P(0) \in \mathcal{Q}$  be some initial condition in the domain of  $\tau$ . Then there is a unique fixed point  $\hat{P} \in \mathcal{Q}$  such that  $S(\hat{P}) \geq S(P(0))$ , given the constraints imposed by the the constants of motion.*

If this is true, then Theorem IV.2(b) always holds, and so we have that for every initial condition there exists a unique fixed point to which the iterations converge, provided that the parameters are strictly within the bistochasticity range. This conjecture could be proved, for instance, by showing that the equations for the fixed point and for the point of maximum entropy coincide, which is the case in all the examples we examined, with the exception of the trivial fixed points.

## **CHAPTER V: THE LIMIT TO THE CONTINUUM**

### **V.1 Introduction**

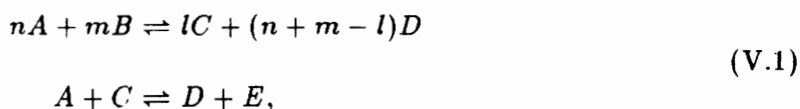
This chapter contains the final results of Part One of this thesis. Such results concern the continuous time and continuous space versions of the dynamical systems associated with chemical reactions, together with their relations to the discrete models. Simple and complex reactions will be studied, both for the stirred and for the nonhomogeneous problems. The running hypothesis will be the usual assumptions of balanced and microscopically reversible reactions, which allow us to use the formalism of Boltzmann maps.

Sections V.2 and V.3 present some examples that shed some light into the “real form” of the dynamical systems investigated in this thesis, and that give some further insight into the caution we must use in trusting certain numerical simulations. Sections V.4 and V.5 deal with taking the limit from discrete to continuous dynamical systems.

### **V.2 Iterations of Maps**

In this section we want to show some simple-minded examples of chemical reactions, in which oscillations can be “artificially” found as a consequence of the numerical scheme adopted for the solution of the associated O.D.E..

Consider the complex reaction



whose second component (  $A + C \rightleftharpoons D + E$  ) is infinitely fast, for different values of the stoichiometric coefficients  $n$ ,  $m$ , and  $l$ . A numerical scheme, for the solution of the O.D.E. system that the law of mass action associates with (V.1), must account for the fact that

the second reaction reaches its equilibrium point in one step, no matter how short this step is. Thus, such reaction does not take place in the following time step, and there is a time interval in which the contribution of the second reaction is negligible. A possible way of modeling (V.1), which accounts for these features, is the following. Take some initial condition  $P \in \mathcal{Q} \subset \mathbb{R}^5$ , and define the iterations as

$$\begin{aligned} P^{(2k)} &= (\tau_1 \circ \tau_2)^k (P), \quad k \in \mathbb{N} \cup \{0\}, \quad \text{and} \\ P^{(2k+1)} &= \left[ \tau_2 \circ (\tau_1 \circ \tau_2)^k \right] (P), \end{aligned} \tag{V.2}$$

where  $\tau_1$  is the map relative to the first reaction in (V.1), and  $\tau_2$  is related to the second. In this scheme we must reproduce the fact that  $\tau_2$  is independent of the time step, as it is infinitely fast, while  $\tau_1$  depends linearly on it. It will be seen, in section V.3, that the way of modelling an infinitely fast rate for a reaction of the kind of  $\tau_2$  is to take its coupling constant  $\mu_2$  equal to one. We call an **iteration of maps** every scheme that, similarly to (V.2), has one reaction only taking place at each instant of time, to distinguish it from the case of convex combinations of maps, where all the reactions give a contribution at the same time. It is easy to see that also the iterations of maps lead to a probability theory, provided that each single map lies in its own bistochasticity range.

Figure V.1 shows the result of a calculation of  $p_A$  based on (V.2), for the first 150 iterations of a given initial condition. The different curves refer to different reactions with different choices of the stoichiometric coefficients  $n \ m \ l \ (n + m - l)$ . The labels of the curves are the 4-tuples of these coefficients in the given order, for the reaction that they represent.

Clearly, one can imagine many alternative ways in which to arrange  $\tau_1$  and  $\tau_2$ , and, in general, each one of them will produce different results. Figures V.2 – V.6 show three examples with two infinitely fast reactions, the first and the last, while the remaining reaction is taken with different stoichiometric coefficients in the different cases. The scheme



of the reactions is



Finally, consider a complex reaction of the form



where there are two infinitely fast reactions and two autocatalytic ones. Here, it is interesting to note that both the iterations of maps and the convex combinations appear to converge rather quickly to certain “solutions”, but they are strikingly different from each other. In section V.4, we will see that the results to be trusted are those produced by the convex combinations. This raises some concern about the validity of certain numerical simulations, based on singular perturbation theory, that are found in the current literature. In fact, the iteration of maps for (V.4) has two very fast reactions, which are switched off for most of the process and switched on at given critical points, which makes (V.4) similar to certain numerical schemes used in the analysis of the Belousov-Zhabotinskii reaction –in stirred and closed reactors– that claim the occurrence of oscillations. Figure V.7 through Figure V.13 present the results of the iterations of maps, for decreasing values of the time step, together with their convergence to a given shape. The following set of figures (Fig. V.14 through Fig. V.21) shows the results related to convex combinations, for decreasing time steps. Also here convergence is reached, but the results are remarkably different from those obtained from the iterations of maps. Note that all the figures from Figure V.9 through Figure V.21 span the same interval of time. The increasing number of points in the horizontal axis is due to the refinement of the time step.

### V.3 Chaos from Chemical Reactions

In the previous section we have seen how highly model-dependent are certain calculations. We now want to see what can be rigorously said about the onset of chaos in some simple model of chemical reactions. To do this let us look at some particular autocatalytic and non-autocatalytic maps, and see for what values of the parameters their fixed points become unstable.

Example 1)  $2A \rightleftharpoons A + B$ . In this case the map has the form

$$\tau(p) \equiv p^* = (1 + \mu)p - 2\mu p^2, \quad (\text{V.5})$$

and its fixed points are  $p = 0$  and  $\hat{p} = 1/2$ , hence the manifold of fixed points of  $\tau$  has boundaries. Defining  $p = \alpha y + \beta$  with  $\alpha = (\mu^2 - 1)/8\mu$ ,  $\beta = (1 + \mu)/4\mu$ , and substituting in the expression for  $p^*$ , we get  $y^* = 1 - \nu y^2$ , the logistic map [40], 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  $\tau^n(p)$ ,  $n = 1, 2, \dots$ , by letting  $\mu$  vary in  $[2, \sqrt{7}]$ , and choosing an initial condition  $p \in [\beta - \alpha, \beta + \alpha] \subset [0, 1]$ .

Figure V.22 through Figure V.27 show some of the possible different patterns that  $\tau$  can generate, for different values of  $\mu$ .

Example 2)  $2A \rightleftharpoons B + C$  Here the map can be written as

$$\tau(p) \equiv p^* = p - 2\mu(p^2 - q_1 q_2), \quad (\text{V.6})$$

and the manifold of its fixed points is shown in Figure V.28, where also three planes of the motion have been drawn. The line at  $-45^\circ$  that connects the point  $(0,1)$  to the point  $(1,0)$  represents the set of points in which  $q_2$  is zero. It is clear that the points  $(0,0)$  and  $(0,1)$  are boundaries for the manifold of fixed points of  $\tau$ .

Similarly to Example 1), we can transform (V.6) 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 chosen such that  $c$  and  $\mu$  can be adjusted to make  $\nu$  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 behaviour. In Figure V.29 through Figure V.32 we can see some of the bifurcations occurring, for the appropriate choice of the parameter and of the initial conditions. Note that positivity is preserved for certain initial conditions only (e.g. for a fixed point as initial condition), but in general such a property is not conserved for  $\mu$  out of the bistochasticity range, as shown in the figures.

Example 3)  $A + B \rightleftharpoons C + D$  This case is particularly easy to study. In fact we can see that

$$\begin{aligned}\tau(p_1) &\equiv p^* = p_1 - \mu(p_1 p_2 - q_1 q_2) \quad \text{and} \\ \tau^2(p_1) &\equiv p^{**} = p_1 - \mu^*(p_1 p_2 - q_1 q_2),\end{aligned}\tag{V.7}$$

where  $\mu^* = 2\mu - \mu^2$ . So, for a given  $\mu$  we can write  $\tau_\mu^{(n)}(p_1) = p_1 - \mu^{(n-1)}(p_1 p_2 - q_1 q_2)$ , and the dynamics can be thrown from the space of probability measures into the dual space –the space of the maps  $\tau_\mu$ – 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  $\mu$  into  $y^* = -y^2$ , from which we deduce that:

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

Therefore, for every initial condition, the reaction reaches the corresponding fixed point in just one step, if  $\mu$  is equal to one. As this doesn't mention how long the time step is, we identify this case with that of an infinitely fast reaction. The manifold of the fixed points of  $\tau$ , which has boundaries, is given in Figure V.33.

Example 4) Consider the following combination of reactions:



Let  $p_A = p$ ,  $p_B = q$  and  $p_C = r$ , and consider a map which is a convex combination of those relative to the first and to the second reaction. Then we have

$$\begin{aligned} p^* &= p - 3\lambda\mu_1 (p^3 - q^2r) + (1 - \lambda)\mu_2 (r^2 - pq) \\ q^* &= q + 2\lambda\mu_1 (p^3 - q^2r) + (1 - \lambda)\mu_2 (r^2 - pq) \\ r^* &= r + \lambda\mu_1 (p^3 - q^2r) - 2(1 - \lambda)\mu_2 (r^2 - pq), \end{aligned} \quad (\text{V.9})$$

and there are two fixed points only:  $(0,1,0)$  and  $(1/3, 1/3, 1/3)$ . In fact it is easy to see that no fixed point can have  $q = 0$ . Then, for  $q \neq 0$ , we obtain that a fixed point must obey  $r = p^3/q^2$  and  $r^2 = pq$ . Thus, we end up with  $pq^5 = p^6$ , and we must consider two cases:

- 1)  $p = 0$ , which implies  $r = 0$ , and then  $q$  must be equal to one.
- 2)  $p \neq 0$ , which implies  $q = p$  and then  $r = p$ .

Since there are no other possibilities, the fixed points of (V.8) are only two. Moreover, this system does not have any other constant of motion than  $p + q + r = 1$ , and so it is a two-dimensional map  $\tau : \mathbb{R}^2 \rightarrow \mathbb{R}^2$ . It happens that for certain values of  $\mu_1$  and  $\mu_2$ , respectively the coupling constant of the first and of the second component of the reaction,  $\tau$  maps probabilities to probabilities, while for other values this occurs only accidentally, and the nontrivial fixed point becomes unstable. Figure V.34 through Figure V.37 illustrate these concepts.

Other examples can be easily analyzed, like  $\boxed{(n+1)A \rightleftharpoons nA + B}$ , for which  $p^* = \mu p^n(2p - 1)$  and the only non zero fixed point is  $\hat{p} = 1/2$ . It is easy to see that  $\hat{p}$  becomes unstable for  $\mu > 2^n$ .

On the other hand, if we want to study our reactions within the limits that make physical sense, we must observe that the bistochasticity range for all the examples in this section is given by  $\mu \leq 1/\max\{n_i; m_j\}$ . Thus, the physically meaningful range turns out to be out of the region where instabilities and chaos occur, for the examples here described. Furthermore, if we aim to approximate the solution of the O.D.E.'s associated with these problems by means of a discrete scheme, we are interested in small values of  $\mu$ , and we

fall into the bistochasticity range. Therefore, spurious chaos and negative probabilities can be “discovered” in certain dynamical systems simply by approximating them by discrete schemes with too large a time step, i.e. too large  $\mu$ .

We conclude this section with the observation that the manifolds of the fixed points of all the examples we have analyzed here have boundaries, and so the theory developed in [25] (one of the papers examined in section I.5) cannot be applied to those reactions. Such a theory, indeed, is not applicable for several other reasons. In particular, no autocatalytic reaction could be treated because part of its fixed points are repellers, in contrast with the assumptions of those authors. We conclude that reference [25] is not relevant to the study of chemical reaction-diffusion problems, though it may be of interest in the study of different kinds of reaction-diffusion systems.

#### V.4 Continuous Time Problem for Single Reactions

In Chapter III the continuous and the discrete time dynamical systems associated with a chemical reaction were introduced. In particular, the O.D.E. system (III.2) and the discrete map (III.3) are relevant to the non-autocatalytic reaction (III.1); while (III.55) and (III.56) are associated with the autocatalytic reaction (III.54). Clearly, the non-autocatalytic reaction is just a special case of the autocatalytic one, from many points of view. Therefore, in this section we will use the notation introduced in section III.7, relative to the autocatalytic reactions, as the range of parameters we will consider allows us to perform a joint analysis of the two cases. Recall that each single reaction defines a one-dimensional dynamical system, either with continuous or with discrete time, and so it can be described by just one reference variable.

Now, let  $\mu$  in equation (III.56) equal  $\eta\Delta t$ , where  $\eta$  is the rate constant of equation

(III.55), and  $\Delta t$  is a time interval. Then (III.56) can be written, in compact notation, as

$$P(t + \Delta t) = P(t) + \eta \vec{n} D(P(t)) \Delta t, \quad (\text{V.10})$$

where  $\vec{n}$  is the vector of the stoichiometric coefficients of the associated non-autocatalytic reaction, with their sign. Equation (V.10) is nothing but the Euler scheme for the numerical solution of (III.55). Thus, we can investigate the problem of the convergence of (V.10) to the solution of (III.55), with initial condition  $P(0) \in \mathcal{Q}$ , provided that such a solution exists and is unique in an open interval  $(\alpha, \beta)$ . The question about existence and uniqueness of the solution to the O.D.E. (III.55) is easily answered. First of all observe that the choice of the initial conditions restricts the problem to one on a compact set:

$$\frac{dp_1}{dt} = -n_1 \eta D(p_1) \quad , \quad p_1 \in [B, C] \quad (\text{V.11})$$

and of course  $D$  is a  $C^\infty$  function in  $[B, C]$ . Also, observe that the vector field,  $-n_1 \eta D$ , either points inside the interval or it is zero at its endpoints, which are always repellers for the flow. Then Theorem II.14, Theorem II.15 and Theorem II.16 all apply, and guarantee that (III.55) has a unique solution in  $\mathcal{Q}$ ,  $P(\cdot)$  say, defined for all positive times. At this point, given any interval  $J = [a, b] \subset [0, \infty)$ , we have that (V.11) converges in norm to the solution of (III.55) in  $J$  as  $\Delta t \rightarrow 0$ . In fact, the condition of Lipschitz continuity in  $\mathcal{Q}$  is obviously satisfied by  $D$ , and so Theorem II.17 holds.

We will use this fact to analyze the properties of  $P(\cdot)$ , instead of the simple standard arguments, because this will provide us with a new tool for the analysis of the more complicated higher dimensional systems associated with complex chemical reactions. Before doing that, we need to prove the following corollary to Theorem III.3, and, to allow for the fact that a different choice of  $\mu$  determines a different map for the evolution of a given chemical reaction; we denote by  $\tau_\mu$  the map whose coupling constant is  $\mu$ .

**COROLLARY V.1.** *For every  $\epsilon \in (0, 1/2]$  there exists  $t_\epsilon \in [0, \infty)$  such that  $|\hat{p}_1 - \tau_\mu^j(p_1)| < \epsilon$  provided that  $j\Delta t > t_\epsilon$ , and  $\mu = \eta\Delta t < \mu_0$ . Moreover,  $t_\epsilon$  does not depend on  $\mu$ .*

PROOF: If  $p_1$  is a fixed point, the result is trivial. If  $p_1$  is not a fixed point, then Theorem III.3(d) says that  $\tau_\mu^j(p_1)$  converges monotonically to  $\hat{p}_1$ , the fixed point of the associated non-autocatalytic reaction. Then assume that  $p_1 < \hat{p}_1$  and consider  $p'_1 = \hat{p}_1 - \epsilon/2$ ,  $p'_1 > p_1$ , and  $I_\epsilon = [p_1, p'_1]$ . There is no zero of  $r_i(p_1)$  nor of  $s_j(p_1)$ ,  $i = 1, \dots, \alpha$ ,  $j = 1, \dots, \beta$ , in  $I_\epsilon$  and, because of the fact that all the  $r$ 's increase linearly with  $p_1$  while all the  $s$ 's decrease linearly, we have  $(r_i)_{\min} = r_i(p_1)$ ,  $(s_j)_{\min} = s_j(p'_1)$ , in  $I_\epsilon$ . So

$$r_1^{k_1} \cdots s_\beta^{l_\beta} \geq (r_1)_{\min}^{k_1} \cdots (s_\beta)_{\min}^{l_\beta} = \delta_\epsilon > 0. \quad (\text{V.12})$$

We also have  $D < 0$  throughout the process and, since all the  $p$ 's increase with  $p_1$  while all the  $q$ 's decrease, we have  $-D \geq -D(p'_1) = D_\epsilon > 0$ . Then

$$\tau_\mu^j(p_1) - \tau_\mu^{j-1}(p_1) = -n_1 \mu D(\tau_\mu^{j-1}(p_1)) \cdot r_1^{k_1} \cdots s_\beta^{l_\beta} \geq n_1 \mu D_\epsilon \delta_\epsilon = \Delta_\epsilon > 0. \quad (\text{V.13})$$

Then the distance  $d_\epsilon = p'_1 - p_1$  will be covered in at most

$$j_\epsilon = \frac{d_\epsilon}{\Delta_\epsilon} = \frac{d_\epsilon}{n_1 \mu D_\epsilon \delta_\epsilon} = \frac{d_\epsilon}{n_1 \eta \Delta t D_\epsilon \delta_\epsilon} \quad (\text{V.14})$$

steps. Therefore it suffices to take  $t_\epsilon = j_\epsilon \Delta t$ , which is clearly independent of  $\mu$  as long as  $\mu < \mu_0$ , where  $\mu_0$  is the value given by Theorem III.3. If  $p_1 > \hat{p}_1$ , a similar argument yields the same conclusions. This proves the corollary. ■

**THEOREM V.1.** *The set of the stationary points of (III.55) coincides with that of the fixed points of the corresponding discrete map  $\tau$ , (III.56), and their stability is also the same. Given one set of initial conditions,  $P(0)$ , there exists a unique  $\hat{P}$  such that the solution  $p_1(t)$  of (V.11) converges monotonically to  $\hat{p}_1$  as  $t \rightarrow \infty$ . The subsets that are invariant under  $\tau$  are invariant for the O.D.E. system as well.*

PROOF: The equations that determine the manifold of the fixed points of a discrete map  $\tau$  are the same as those for the stationary points of the corresponding O.D.E. system. Therefore the fixed points of (III.56) coincide with the stationary points of (III.55).

Given one set of initial conditions,  $P(0)$ , the itineraries based at  $P(0)$  under every map  $\tau_\mu$ , such that  $\mu < \mu_0$ , converge to a given  $\hat{P}$ . Furthermore, because of Corollary V.1, for every  $\epsilon > 0$  there exists one  $t_{\epsilon/3} > 0$  such that the itineraries for all the  $\mu$ 's smaller than  $\mu_0$  take the first component of  $P$  within a distance smaller than  $\epsilon/3$  from  $\hat{p}_1$ , at all times later than  $t_{\epsilon/3}$ . We know that the solution of (III.55) is a continuous function of the time variable  $t$ . Therefore, given a time interval  $I = [0, T]$ , there exists  $\delta > 0$  such that  $|p_1(t) - p_1(t')| < \epsilon/3$ , for  $t, t' \in I$ , whenever  $|t - t'| < \delta$ . Finally, we know that, for every time interval like  $I$ , we can choose  $(\Delta t)_0 > 0$  such that  $|\tau_\mu^j(p_1(0)) - p_1(j\Delta t)| < \epsilon/3 \quad \forall j = 0, 1, \dots, \text{Int}(T/\Delta t)$ , if  $\mu = \eta\Delta t$  and  $\Delta t < (\Delta t)_0$ , where by  $\text{Int}(T/\Delta t)$  we mean the integer part of  $T/\Delta t$ .

Now, take  $T > t > t_{\epsilon/3}$ , let  $\delta$  be the corresponding positive quantity introduced above. Let  $\delta' < t - t_{\epsilon/3}$  and define  $\delta_0 = \min(\delta, \delta')/2$ , then choose  $t' = t - \delta_0$  and take  $\Delta t < \min[(\Delta t)_0, \delta_0]$ . Then there exists  $j_0$  such that  $j_0\Delta t \in [t', t]$  and

$$\begin{aligned} |p_1(t) - \hat{p}_1| &= |p_1(t) - p_1(j_0\Delta t) + p_1(j_0\Delta t) - \tau_\mu^{j_0}(p_1(0)) + \tau_\mu^{j_0}(p_1(0)) - \hat{p}_1| \leq \\ &|p_1(t) - p_1(j_0\Delta t)| + |p_1(j_0\Delta t) - \tau_\mu^{j_0}(p_1(0))| + |\tau_\mu^{j_0}(p_1(0)) - \hat{p}_1| < \epsilon. \end{aligned} \quad (\text{V.15})$$

Finally, recall that if  $\hat{p}_1$  is exponentially stable along the line of the motion  $\Gamma$ , then there exists  $\epsilon_0 > 0$  such that  $p_1(t)$  converges to  $\hat{p}_1$  as  $t$  grows, provided that  $p_1(0) \in \Gamma \cap (\hat{p}_1 - \epsilon_0, \hat{p}_1 + \epsilon_0)$ . Therefore, it is enough to choose  $\epsilon < \epsilon_0$  in (V.14). In the case that  $\hat{p}_1$  is not exponentially stable along  $\Gamma$ , we must observe that  $\Gamma = \{\hat{p}_1\}$ , and so the convergence to the fixed point is trivially verified. Indeed, equation (III.74) says that  $\hat{p}_1$  is not hyperbolic along  $\Gamma$  if and only if some autocatalytic element vanishes or if one  $p_i$  vanishes together with one  $q_j$ . Then, the same argument given in the proof of Theorem III.4 proves that  $\Gamma = \{\hat{p}_1\}$ . Therefore  $p_1(t) \rightarrow \hat{p}_1$  as  $t \rightarrow \infty$  in all possible cases, which answers also the question about the stability of  $\hat{P} \in \mathcal{Q}$ , as the manifold of the fixed points of the O.D.E. is the same as that of the discrete maps.

The final statement in the theorem follows from the fact that, given one reaction, the



invariant subsets of  $\tau_\mu$  are invariant also for  $\tau_{\mu'}$  if  $\mu' \leq \mu$ . Then the continuity of the solution of (III.55) together with the convergence of the discrete scheme to such a solution ensures that if  $p_1(0)$  lies in an invariant subset  $E$  for  $\tau_\mu$ , then  $p_1(t) \in E$  for every  $t > 0$ .

It remains to prove that the convergence to  $\hat{p}_1$  is monotonic, i.e.  $p_1(t) \leq p_1(t')$  for  $t \leq t'$  if  $p_1(0) \leq \hat{p}_1$ , and  $p_1(t) \geq p_1(t')$  for  $t \leq t'$  if  $p_1(0) \geq \hat{p}_1$ . But this follows easily from the monotonicity of all the itineraries  $\{\tau_\mu^j(P(0))\}$  with  $\mu < \mu_0$ . ■

Finally if we use (III.62) as our definition of the entropy also for the continuous time case, we can prove the following:

**COROLLARY V.2.** *Given (III.55) and a set of initial conditions,  $P(0)$ , the entropy of the system is a continuous non-decreasing function of  $t \in [0, \infty)$ . Moreover, either  $P(0)$  is a stationary point of (III.55) or  $\lim_{t \rightarrow \infty} S(t) - S(0) > 0$ .*

**PROOF:** As  $S(t) \equiv S(P(t))$  is the composition of continuous functions, it is continuous. In particular, given  $\epsilon > 0$ , the continuity of  $S$  as a function of  $P \in \mathcal{Q}$  ensures that there exists  $\delta > 0$  such that  $|S(P_1) - S(P_2)| < \epsilon$  if  $\|P_1 - P_2\| < \delta$ . Now, take any two instants of time,  $t_2 > t_1 \geq 0$ , define  $\mu_n = \eta(t_2 - t_1)/n \equiv \eta(\Delta t)_n$  and let  $\tau_n$  be the corresponding discrete map with coupling constant  $\mu = \mu_n$ . Then there exists  $n_0 \in \mathbb{N}$  such that  $\mu_{n_0} < \mu_0$ , where  $\mu_0$  is the value introduced in Theorem III.3. By the convergence of the discrete scheme to the solution of (III.55), for a given  $\delta > 0$  it is possible to find  $(\Delta t)_0 > 0$  such that  $\|\tau_n^n(P(t_1)) - P(t_2)\| < \delta$  whenever  $(\Delta t)_n < (\Delta t)_0$ . Call  $n'$  the smallest integer that makes this inequality true. Then let  $n_1$  be the maximum between  $n_0$  and  $n'$  and take any  $n > n_1$ .

We get

$$S(t_2) - S(t_1) = S(t_2) - S(\tau_n^n(P(t_1))) + S(\tau_n^n(P(t_1))) - S(t_1) \geq \quad (\text{V.16})$$

$$S(P(t_2)) - S(\tau_n^n(P(t_1))) + 0 > -\epsilon$$

because the maps  $\tau_n$  do not decrease the entropy [28]. As  $\epsilon$  is arbitrary, we have  $S(t_2) - S(t_1) \geq 0$  i.e.  $S$  is a non-decreasing function of  $t$ . Finally, if  $P(0)$  is a stationary point of (III.55),  $P(t) = P(0)$  for all times, and the corollary is true. If, instead,  $P(0)$  is not a

stationary point of (III.55), then it is enough to observe that  $\lim_{t \rightarrow \infty} P(t) = \hat{P}$ , which is a maximum and the only one point along the line of the motion at which

$$\frac{dS}{dp_1} = 0. \quad (\text{V.17})$$

This completes the proof of the Corollary. ■

We note that the strict relationship between the discrete map  $\tau$  and the O.D.E. system (III.55), that we have outlined here, implies some consequences in the choice of  $\Delta t$  for the numerical solution of (III.55). In fact, if  $\Delta t$  is chosen in such a way that  $L_B < \eta \Delta t$ , then it is easy to find initial conditions for which both the iterations of  $\tau$  and the numerical scheme produce negative probabilities. The reason lies in the fact that the bistochasticity range for  $\tau$ ,  $\mathcal{R}_B = [0, L_B]$ , limits also the range for a probability theory to exist. Similarly, if  $1/n_0 < \eta \Delta t$  we observe that the solutions obtained by numerical integration might show some complex behaviour, but this is not a characteristic of the solution of (III.55).

## V.5 Continuous Time Problem for Complex Reactions

The analysis of higher dimensional systems, like those related to general complex reactions, is rather more complicated than that of the previous section. To approach this problem we will use the notation of section IV.4, and so the continuous time dynamical system associated with a complex reaction will be written as

$$\frac{dP}{dt} = \sum_{i=1}^{\Phi} \lambda_i \eta_i \vec{n}_i D_i(P_i). \quad (\text{V.18})$$

Then, letting  $\mu_i = \eta_i \Delta t$  for every  $i$ , we have that equation (IV.14) represents the Euler scheme for (V.18). In that case (IV.14) can be rewritten as

$$P(t + \Delta t) \approx \tau_{\Delta t}(P(t)) = P(t) + \Delta t \sum_{i=1}^{\Phi} \lambda_i \eta_i \vec{n}_i D_i(P_i), \quad (\text{V.19})$$

where  $P(t)$  is supposed to be the solution of (V.18) with some initial condition  $P(0) \in \mathcal{Q}$ , and  $\tau_{\Delta t}$  is the discrete map whose time step is  $\Delta t$ . Obviously, such a solution exists and is unique in some interval  $(\alpha, \beta)$ , because the right hand side of (V.18) is a linear combination of smooth functions, and so Theorem (II.14) and Theorem (II.15) hold. Moreover, such a solution is defined for all times, since the boundaries of the compact set  $\mathcal{Q}$  are repellers for the flow due to all the components  $\lambda_i \eta_i \vec{n}_i D_i(P_i)$ , and so they are repellers for the flow due to the total vector field. Then, the smoothness of such a vector field satisfies the hypothesis of Theorem II.17, and ensures that the Euler scheme (V.19) converges to the solution of (V.18) on every interval  $[a, b] \subset [0, \infty)$ , as  $\Delta t \rightarrow 0$ .

We must observe that the proof of theorem V.1 was based on the existence of a maximum time  $t_\epsilon \in [0, \infty)$ , beyond which all the iterations of  $P(0)$  under  $\tau_{\Delta t}$ , with  $\Delta t < (\Delta t)_0$ , fall within a distance  $\epsilon$  from the fixed point. In the case of complex reactions that happen to be one-dimensional, the same result can be proven in the same way as in the previous section. However, in general, it is difficult to give a proof of the existence of a finite  $t_\epsilon$  for higher dimensional systems. Therefore, we must limit our study to the cases in which such a limiting time is known to exist. This, indeed, can be found to be the case in many different ways. For instance one may prove that there is maximum path for the iterations of  $\tau_{\Delta t}$ , to go from  $P(0)$  to a distance  $\epsilon$  from the manifold of fixed points, and that such a distance is non-increasing with time, for all the  $\Delta t$ 's smaller than some finite  $(\Delta t)_0$ . Then the following can be proved

**THEOREM V.2.** *Assume that there exists a  $(\Delta t)_0 > 0$  such that for every  $\epsilon > 0$  a  $t_{\epsilon/3} \in [0, \infty)$  can be found, with the property that  $d(\tau_{\Delta t}^j(P(0)), \mathcal{M}) < \epsilon/3$  whenever  $j\Delta t \geq t_{\epsilon/3}$  and  $\Delta t < (\Delta t)_0$ . Then  $d(P(t), \mathcal{M}) \leq \epsilon$  for every  $t > t_{\epsilon/3}$ , where  $P(\cdot)$  is the solution of (V.18).*

**PROOF:** The proof is very similar to that of theorem V.1. The continuity of  $P(t)$  tells us that there exists a  $\delta > 0$  such that  $\|P(t) - P(t')\| < \epsilon/3$  whenever  $t, t' \in I = [0, T]$  and

$|t - t'| < \delta$ . We also know that for every interval like  $I$  there exists a  $(\Delta t)' > 0$  such that  $\|\tau_{\Delta t}^j(P(0)) - P(j\Delta t)\| < \epsilon/3$  for all  $j\Delta t \in [0, T]$ , if  $\Delta t < (\Delta t)'$ . Finally, our hypothesis says that there exists a  $t_{\epsilon/3}$  such that  $d(\tau_{\Delta t}^j(P(0)), \mathcal{M}) < \epsilon/3$  if  $j\Delta t \geq t_{\epsilon/3}$  and  $\Delta t$  is smaller than some  $(\Delta t)_0 > 0$ . Then take  $T > t_0 > t_{\epsilon/3}$  and  $\delta' < t_0 - t_{\epsilon/3}$ , and define  $\delta_0 = \min(\delta, \delta')/2$ . Choose  $t' = t_0 - \delta_0$ , and assume that  $\Delta t < \min[(\Delta t)_0; (\Delta t)'; \delta_0]$ . Then, there exists  $j_0 \in \mathbb{N}$  such that  $j_0\Delta t \in [t', t_0]$  and

$$\begin{aligned} d(P(t_0), \mathcal{M}) &\leq d(P(t), P(j_0\Delta t)) + d(P(j_0\Delta t), \tau_{\Delta t}^{j_0}(P(0))) + d(\tau_{\Delta t}^{j_0}(P(0)), \mathcal{M}) \\ &< \epsilon. \end{aligned} \quad (\text{V.20})$$

Thus, we have found a  $t_0$  for which the distance between  $P(t_0)$  and  $\mathcal{M}$  is smaller than  $\epsilon$ . To see what happens at later times, assume that there exists a  $t'' > t_0$  such that

$$d(P(t''), \mathcal{M}) = \epsilon + \nu > \epsilon. \quad (\text{V.21})$$

Then, consider the interval  $J = [t_0, t'']$ . We know that we can make  $d(\tau_{\Delta t}^j(P(0)), \mathcal{M}) < \epsilon$ , for every  $j\Delta t \in [t_0, t'']$ , by taking  $\Delta t < (\Delta t)_0$ . Also, for every  $\epsilon' > 0$  we can find a  $(\Delta t)' > 0$  so small that  $d(\tau_{\Delta t}^j(P(0)), P(j\Delta t)) < \epsilon'$  for all  $j\Delta t \in [t_0, t'']$ , and there exists a  $\delta > 0$  such that  $d(P(j\Delta t), P(t'')) < \epsilon'$  if  $t'' - j\Delta t < \delta$ . Therefore, taking  $\Delta t < \min[(\Delta t)'; (\Delta t)_0; \delta/2]$ , we find that there exists  $j_0 \in \mathbb{N}$  such that

$$\begin{aligned} d(P(t''), \mathcal{M}) &\leq d(P(t''), P(j_0\Delta t)) + d(P(j_0\Delta t), \tau_{\Delta t}^{j_0}(P(0))) + d(\tau_{\Delta t}^{j_0}(P(0)), \mathcal{M}) \\ &< 2\epsilon' + \epsilon. \end{aligned} \quad (\text{V.22})$$

As we can choose  $\epsilon' < \nu/2$  we get a contradiction. ■

Finally, repeating mutatis mutandis the proof of Corollary V.2, we get the following result.

**COROLLARY V.3.** *The entropy  $S$  is a continuous non-decreasing function of  $t \in [0, \infty)$ . Moreover, either  $P(0)$  is a stationary point of the map  $\tau_{\Delta t}$  or  $\lim_{t \rightarrow \infty} S(t) - S(0) > 0$ .*

## V.6 The Continuous Reaction-Diffusion Problem

The results presented in the previous section include also the case of reaction-diffusion systems, with continuous time and discrete space. In fact, the discrete diffusion can be expressed by a Boltzmann map –as explained in Chapter IV– which then can be included among the other maps that define a complex reaction. That is to say, if we subdivide the volume in which a certain reaction takes place into elementary cells of given size, we can construct a dynamical system like (V.18), where  $P$  is the vector whose components are the concentrations of the different chemicals in the different cells. If the reaction in consideration is not a combination of more elementary processes, then (V.18) is nothing but the continuous time version of (IV.39) and (IV.40). Therefore, the problem of the convergence of the solution of (V.18) to a fixed point, and that of the increase of the entropy, can be analyzed as in the previous section. Now, one may ask whether it is possible to infer something about the limit to the continuum in space, from the knowledge of the qualitative behaviour of the solution of (V.18). For instance, let us assume that the medium is made of  $N$  cells, and that the solution of (V.18),  $P_N(\cdot)$  say, converges to a fixed point  $\hat{P}_N$  as  $t \rightarrow \infty$ . Assume also that this happens for every  $N \in \mathbb{N}$ ; in other words, convergence occurs no matter how fine the spatial mesh is. Can we conclude from this that the solution of

$$\frac{\partial P}{\partial t} = D\Delta P + \text{Reaction Term}, \quad (\text{V.23})$$

with given initial and boundary conditions, converges to some  $\hat{P}(x) = \lim_{N \rightarrow \infty} \hat{P}_N$ , in some sense?

Unfortunately, this question does not appear to have an easy answer. Indeed, one of the main problems is to prove the existence of a unique solution to (V.23) for a sufficiently wide class of reactions and of initial and boundary conditions [41]. Therefore, we will not attempt an answer to this problem in this thesis, although the method of section V.4 and section V.5 could be generalized to the present case, whenever (V.23) has a unique solution, and

the discrete scheme converges to it. However, it is worth making some comments about the connections between the discrete and the continuous reaction-diffusion dynamical systems, as well as about their physical content.

First of all, observe that the discrete dynamical system –as presented in this thesis– can be given initial and boundary conditions that belong to a very wide class. Linear and nonlinear initial-boundary conditions can be treated by the formalism of Boltzmann maps, and these can be taken to approximate Lebesgue integrable functions on  $\mathbb{R}^n$  to any degree of accuracy, as simple functions are dense in that set. This may not be the case for the continuous systems.

The second, and probably most important, observation concerns the physical content of the discrete versus the continuous systems. If we look at the phenomenological models that underlie the construction of either the discrete or the continuous set of equations, we will find at least two important points in favour of the discrete models.

A) The *stosszahlansatz*, which is the basic assumption of the reaction term, requires that particles quickly forget the details of the collisions they undergo. As a consequence, there is a certain time interval  $\Delta t > 0$ , which is necessary for the particles that have collided to lose memory of such events. Any time interval shorter than that will find that the particles have some correlation, and so the law of mass action would not hold. This feature is very well handled by the discrete scheme, for the obvious reason that one can take a time step long enough to allow for the correlations to get lost. On the contrary, the continuous time system is constructed under the hypothesis that  $\Delta t \approx 0$ , so that one can write

$$\frac{\Delta P}{\Delta t} \approx \frac{dP}{dt}. \quad (\text{V.24})$$

Hence the continuous system turns out to be a cruder approximation of the physical model than the discrete system is, and as such its physical content is lower.

B) Similar to this is the problem of the form of the diffusion term. The construction of this term starts from considering a volume element in the space of the medium, in a given interval of time  $\Delta t$ . During  $\Delta t$  the incoming and the outgoing flux of particles give rise to an increase of the number of particles that the volume element contains, if the incoming flow is bigger than the outgoing. In the opposite situation there will be a decrease, or there will be no change if incoming and outgoing fluxes are equal. In order for this to be valid, the volume element must be big enough to contain a large number of particles, so that either a statistical approach makes sense or –equivalently– that the flow of particles can be regarded as a continuum, thus permitting the use of classical hydrodynamics. At this point one has a finite difference equation, and it is at this point that it is assumed that such a volume element has negligible dimensions, as compared to the macroscopic scales, so that the differences can be replaced by differentials. Once again, we can conclude that the physical content of the discrete scheme is higher, specially because atoms and molecules have dimensions that when taken in clusters of thousands or tens of thousands may not be completely negligible on a macroscopic scale.

These and other arguments suggest that it is more important to investigate discrete models than continuous ones, as far as the physical content of the theories is concerned. In fact, from this perspective, the continuous models must be regarded as an approximation of the discrete ones and not viceversa. This actually holds for all the classical equations that are derived as a balance on volume elements of the phase space. Among these we find the Boltzmann and Boltzmann-like equations, the Navier-Stokes equation, the Fourier equation of heat, Fick's law, the law of continuity, and so on. The great success of all these equations in providing a description of many physical systems rests on the fact that the characteristic times and lengths of the underlying microscopic phenomena are vanishingly

small on the scales of the macroscopic ones. Moreover, at the times when these equations were constructed, the theory of differential equations was much better developed than that of difference equations. Therefore, it was natural to look at the continuous limit.

Nonetheless, the modern developments of programs for digital computers, and the theory of dynamical systems and chaos, have given a strong impetus to the study of discrete maps. Hence, this may be the right time to divert some of the attention devoted to the study of continuous reaction-diffusion systems towards the analysis of the discrete models. In particular, this is important in some fields of nonequilibrium statistical mechanics, where small scale phenomena seem to produce measurable macroscopic effects. Phase transitions and chaotic behaviour are among such problems. If this program succeeds we would have a better theory. If it doesn't, we would gain some valuable insights into the microscopic models, which have been adopted to describe the macroscopic world.



## CHAPTER VI: CONCLUDING REMARKS

### VI.1 Non-Balanced Reactions and Unequal Rates

Before we conclude Part One, we must make few remarks. First of all, observe that 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, like photons for instance, 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



by adding one photon,  $\gamma$ , in order to get the balanced reaction



This makes perfect sense in classical probability theory provided that the energy of the  $\gamma$  is positive. The occurrence of such  $\gamma$ 's provides us also with a tool for modelling 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 large. This may be interpreted as a temperature-dependence of the rate constants. Thus, what seemed to be a limit of the theory presented here turns out to be one of its strong points. In fact, besides allowing us to balance reactions, and to model unequal rates, the use of extra photons also provides us with a tool for describing some features currently regarded as embarrassing in the chemistry literature. In particular, a bistochastic model can be constructed so that the three steps that determine the law of mass action –as described in section I.3– naturally give rise to reactions with unequal

rates, notwithstanding the microscopic reversibility of the underlying scattering processes. Such a model can also be used to derive the principle of detailed balance at the fixed points, from the principle of microscopic reversibility. Hence, a further agreement is found between this theory and equilibrium thermodynamics, [42].

## VI.2 The Choice of the Time-Step and of the Spatial Mesh

One aspect worth noting is the bounds that the bistochasticity limit imposes on the choice of the time step  $\Delta t$ . In particular, for single reactions in space independent problems, it is required that  $\eta\Delta t \leq L_B$ , where  $\eta$  is the rate constant for the associated continuous dynamical system, and  $L_B$  is the corresponding bistochasticity limit. We have seen that  $L_B$  may be as small as  $1/n_{\max}$ , where  $n_{\max}$  is the highest stoichiometric coefficient in the reaction, and we know that extremely fast reactions appear in many models. It follows that the choice of  $\Delta t$  is especially critical in certain cases, and it may have happened that some of the oscillations presented in the specialized literature were due to too large values of the time step, rather than to the dynamics of the systems. This fact, in turn, may have been neglected because of the apparently “nice” behaviour of the numerical scheme. In fact, for values of  $\eta_i\Delta t$  several order of magnitudes higher than the bistochasticity limits  $L_i$ , particular choices of the initial conditions may avoid negative and divergent probabilities, and the halving of the time step may not reveal any substantial change in the overall behaviour of the system. Thus, the programmer is led to believe that convergence to the real solution has been achieved, even if this is completely false.

Concerning systems in which diffusion only takes place, section IV.5 has shown that a relation between  $\Delta t$  and the size  $h$  of the spatial step is imposed by the bistochasticity limit. Such a relation turns out to be the very well known bound in numerical analysis, for the convergence of the discrete schemes to the solution of partial differential equations.

Nonetheless, the derivation of section IV.5 is based on apparently totally different grounds. The numerical analysis approach assumes, in fact, that a unique solution to the parabolic equation (IV.31) exists, and, through estimates of its Taylor expansion, the relation  $\Delta t \leq h^2/2D$  is found as a bound for the non-divergence of the numerical solution from the real one. On the other hand, the argument of section IV.5 has nothing to do with the solution of (IV.31): it simply is a consequence of the requirement that the map be bistochastic. It is likely that an investigation of the possible deeper connections between the two approaches will yield some interesting insights. The question now arises on whether the bistochasticity limit has something to say about the time and space steps of a discrete reaction-diffusion system. In this case the map must be the convex combination of the reaction term, ( $R$ ) say, and of the diffusion one, ( $DIFF$ ) say. Then, the overall map looks like

$$\tau = \lambda \Delta t \eta (R) + (1 - \lambda) \frac{D \Delta t}{h^2} (DIFF), \quad (\text{VI.3})$$

and so one extra degree of freedom is introduced by the arbitrariness of the choice of  $\lambda \in (0, 1)$ . In fact, assume that  $\Delta t = \min(h^2/2D, L_B)$ , and choose now a different set of parameters  $\lambda', \Delta t'$ , and  $h'$ . Then, if we take

$$\begin{aligned} \lambda' \Delta t' &= \lambda \Delta t, & \text{and} \\ \frac{(1 - \lambda') \Delta t'}{h'^2} &= \frac{(1 - \lambda) \Delta t}{h^2}, \end{aligned} \quad (\text{VI.4})$$

we have

$$\tau = \lambda' \Delta t' \eta (R) + (1 - \lambda') \frac{D \Delta t'}{h'^2} (DIFF). \quad (\text{VI.5})$$

Is it possible to violate bistochasticity, in this case, without producing any observable effect? The answer is affirmative. The fact is that, for convex combinations of maps, we need not look at each single map any more, and a new definition of the bistochasticity range must be adopted. To see this, consider that  $\lambda$  lies in  $(0, 1)$ , and that (VI.4) yields

$$\begin{aligned} \lambda' &= \frac{\Delta t}{\Delta t'} \lambda, & \text{and} \\ \left(1 - \frac{h'^2}{h^2}\right) \lambda &= \frac{\Delta t'}{\Delta t} - \frac{h'^2}{h^2}. \end{aligned} \quad (\text{VI.6})$$

Therefore we have three possible cases:

- i. if we choose  $h' = h$ , then we must have  $\Delta t' = \Delta t$  as well, and nothing has been changed.
- ii. If we choose  $h' < h$ , then we have

$$\lambda = \frac{(\Delta t'/\Delta t) - (h'/h)^2}{1 - (h'/h)^2} \in (0, 1), \quad (\text{VI.7})$$

which implies  $\Delta t' < \Delta t$ , and so the bistochasticity of the reaction term is preserved in the primed case. But the fact that  $\lambda$  is bigger than zero also requires that  $\Delta t'/h'^2 > \Delta t/h^2$ , from which we have that the bistochasticity of the diffusion term could be violated.

- iii. Similarly, if we choose  $h' > h$ , we end up with a condition that preserves the bistochasticity of the diffusion term, but does not forbid the violation of that of the reaction term.

This shows that the arbitrariness in the choice of the coefficients of a convex combination of maps, like

$$\tau = \sum_i \lambda_i \tau_i, \quad (\text{VI.8})$$

gives the possibility for the time and space steps to vary in a wider range than in the case of a single map. Therefore, as it was reasonable to assume, the definition to be adopted for the bistochasticity range of  $\tau$  is the following:

*$\Delta t$  and  $h$  belong to the bistochasticity range of  $\tau$  in (VI.8), if and only if a finite set of Boltzmann maps can be found so that  $\tau$  can be expressed as a convex combination of such maps.*

Clearly, if the parameters of all the maps in (VI.8) lie in their bistochasticity ranges, there is at least one set of Boltzmann maps such that  $\tau$  is equal to their convex combination, and so the corresponding time and space steps are in the bistochasticity range of  $\tau$ .

### VI.3 An Overview

In this thesis we have analyzed some aspects of reaction-diffusion systems, both for the discrete and for the continuous case. We have seen that there is a range in which the parameters of the maps make no physical sense, and that there is a proper way of combining maps together. Within the physically meaningful range all the maps relative to single reactions converge to a fixed point that is determined by the initial conditions. This feature is shared by the related continuous dynamical systems, which happen to be just limiting cases of the maps.

The combinations of more reactions give rise to more complex systems, but it is still possible to prove the convergence to the manifold of fixed points, for the discrete case. The continuous problems appear to be more difficult to analyze, but some criteria can be given to investigate the different cases. In particular, it has been shown how to draw conclusions about them, once the associated discrete systems are understood, thus reversing the usual direction of study. We have also seen that the continuous systems, although mathematically extremely interesting, have less physical content than their discrete counterparts.

All the reactions that have been treated here were balanced and they obeyed the principle of microscopic reversibility. These two hypothesis have turned out to be strong points of the theory rather than limitations, as compared to the current theories of chemical kinetics. Also, all the systems studied in this thesis were related to “isolated” reactors, which do not exchange matter or energy with the rest of the universe. Because of this, the use of entropy as a Liapunov function has proved succesful in analyzing the maps. The result is that all the examples that have been examined do not show any complex behaviour. Nonetheless, we must observe that Theorem IV.2 does not cover all the possible cases, and Conjecture IV.1 has not been proven yet. Thus, we cannot exclude the existence of systems whose evolution approaches closer and and closer the manifold of the equilibria, but does not converge to a

specific point. However, work is currently being done, and the preliminary results are along the lines of proving that the iterations of every generalized Boltzmann map converge to a fixed point. Moreover, even in the case that a non-convergent example is found, it is difficult to believe that it will show any chaos. In fact, we know that our maps have no orbits with period longer than 1, due to the fact that the entropy increases a positive amount at every step unless a fixed point has been reached. Therefore, we conclude that the search for complex behavior in chemical reactors is more likely to be successful in systems that have some exchange with the outer environment. For instance, one could consider “closed” systems, which do exchange heat with the rest of the universe, and which are likely to be understood through a similar analysis to that of this thesis, provided that the entropy is replaced by the free energy.

Our final remark regards the study of maps and chaos. Although a lot has been done about maps on the interval, as well as about higher dimensional maps, there is a big difference between our current understanding of the first ones and that of the second ones. Even the simplest and most studied examples, like the Hénon map, very reluctantly uncover their secrets, as the recent paper of Benedicks and Carleson shows [43]. The form of this two-dimensional map is the following:

$$\begin{pmatrix} x \\ y \end{pmatrix} \mapsto \begin{pmatrix} 1 - ax^2 + y \\ bx \end{pmatrix}, \quad (\text{VI.9})$$

where  $a$  and  $b$  are fixed parameters. [43] proves that for every sufficiently small  $b$ , there is a set of values for  $a$ , of positive measure, such that an initial condition can be found whose orbit under the map is chaotic. However, no explicit parameter values for which chaos occurs are given. This indeed seems to be too hard a task, for the time being. Even more confused is the situation of higher dimensional maps.

Of course, the question of where chaos exists is complementary to that of where chaos does not exist. From this point of view, the maps that have been discussed in this thesis may

be of some interest, in the study of the regions where there is no chaos, for particular classes of maps of all dimensionalities. In fact, assume that a given map  $\sigma$  can be transformed by a sufficiently smooth one-valued function into a generalized Boltzmann map  $\tau$ . Then,  $\sigma$  will show no chaotic behaviour in the range of parameters for which  $\tau$  is proved not to be chaotic. As the analysis of  $\tau$  within the bistochasticity range is rather easy, this may be a way of studying the non chaotic regimes of many maps of any finite dimension.

## **CHAPTER VII: COLLIDED FLUX EXPANSION FOR THE TRANSPORT OF MUONIC DEUTERIUM IN FINITE MEDIA**

### **I.1 Introduction**

In modern times, the problem of energy production has become so important that experts of all sciences have been involved in it. This has prompted considerable progress in many research areas of Physics, Engineering, Chemistry, Biology, etc. Of particular interest is the case of nuclear energy, of which two different kinds are used and studied today. The first, known as "fission", is produced by bombarding heavy nuclei with neutrons, so to break them into smaller nuclei. Commercial power plants that work in this way are currently in operation in most of the world (with a few exceptions like Italy, for instance). The fuels that are usually used are uranium,  $U^{235}$ , and plutonium,  $Pu^{239}$ . This form of energy was developed as a consequence of the studies that led to the construction of the first atomic bomb, in the 40's.

The other form of nuclear energy is called "fusion", and uses the opposite principle, that is to say it is produced by letting two light nuclei join together to form a heavier one. The fuel consists of deuterium,  $H^2$ , and of tritium  $H^3$ . As for fission, nuclear fusion energy is a side effect of military studies; in particular, of those studies that made possible the construction of the H-bomb, in the 50's. However, to date there is no commercially operating fusion power plant, despite the great advantages that are expected from this source, as compared to fission. Among the relevant features, we should quote the following at least: a) the curve of nuclear binding energy versus atomic number shows that fusion is energetically much more "generous" than fission; b) the fuel for fusion is much more widely available on the Earth's surface and cheaper than that for fission; c) the ecological impact



of fusion power plants is expected to be smaller than that of fission plants, also because fusion plants are supposed to be intrinsically safe.

Unfortunately, the most studied way of producing nuclear fusion is that of heating the fuel up to  $10^7 - 10^8$  K, a range which includes temperatures somewhat higher than those at the center of the Sun. There are two main ways of achieving this: one that leads to the concept of magnetically confined plasmas, and another one related to inertially confined plasmas. Neither of these concepts has yet reached the point of permitting the commercial use of fusion energy. In fact, because of those temperatures, it is clear that enormous difficulties are encountered in achieving the desired values of the main control parameter, which is  $n\tau = (\text{fuel density}) \times (\text{confinement time})$ . Note that in the Sun the value of  $n$  is so high that self sustained fusion is achieved at lower temperatures.

On the other hand, a different idea of producing nuclear fusion was developed, in the 60's, and it is still gaining popularity among the specialists. The concept is based on the use of "muonic" atoms, instead of the usual ones, from which one electron has been stripped away and replaced by a muon. The result is an atom about 207 times smaller than usual, as a consequence of the fact that muons are about 207 times heavier than electrons, and of the fact that the radius of the orbit of a lepton around a nucleus is inversely proportional to its mass, according to the planetary model of the atom. This fact allows the muonic atoms to come closer than the usual atoms, before they can feel any repulsive force, thus greatly enhancing the probability of nuclear fusion by the tunnel effect. It turns out that the optimum temperature for muon-catalyzed fusions is around 1200 K, which is also about the optimum temperature for the operation of conventional modern power plants. Note that this is the kind of nuclear energy that was first named "Cold Fusion" –for obvious reasons– and it is not to be confused with the much more recent experiments that were named in the same way, but whose scientific foundations do not appear to be very solid at present.

Together with the many good reasons to pursue the study of muon-catalyzed fusion, there are also some problems. Among these is the fact that a muon has a short lifetime ( $\approx 2 \cdot 10^{-6}$  seconds), and so it can catalyze only few reactions. However, the way in which the experiment is run affects the number of fusions that one muon can catalyze. Thus, it becomes necessary to study certain features of these experiments, like the transport of muonic atoms in molecular media, so that they may be performed with the best results.

## VII.2 Statement of the Problem

In this work we investigate the efficiency of the multiple-collision expansion, [44], [45] and Refs. therein, as a tool for modeling the transport of muonic atoms in a molecular gas. The multiple collision expansion is nothing other than a Neumann series solution of the integral form of the transport equation [49] and may thus be considered a perturbation series, analogue to the Dyson series of QED. This series converges rapidly when the optical thickness of the medium being studied is small. As discussed in Ref. [46], a diffusion approximation can be applied to optically thick media (optical thickness = cross section  $\times$  thickness). Our work is intended to extend the transport calculations presented in section V of [46] to include certain anisotropy effects and energy dependent cross sections [47],[48].

In [45], multiple collision theory has been used to describe neutron transport in infinite media. An essential feature in the successful application of this method to infinite geometry is the fact that the solution is factorizable in the form of a function of  $t$  multiplied by a function of  $\mu$  and  $x/vt$ . Although this property does not carry over to finite geometry, our physical intuition would suggest that the multiple collision expansion theory is perfectly applicable to problems involving finite media of moderate thickness, as pointed out by K.M. Case and P.F. Zweifel, [49], since the streaming out of particles should leave inside only low order collided particles and, therefore, only few terms in the collision expansion should

play a significant role. In [46], E. Rusjan and P.F. Zweifel have calculated the emerging flux of muonic deuterium atoms from a slab of molecular deuterium, via multiple collision expansion with a 1-speed approximation. Our purpose is to develop the relevant equations and carry out the numerical analysis in order to remove certain simplifying assumptions imposed in the quoted reference. In particular, we want to remove the assumption that all atoms contributing to the once-collided particle flux travel with the same speed, the assumption that the once-collided particles are generated by an isotropic source, the assumption of isotropic scattering in the Center of Mass reference frame, and we want also to take the scattering cross sections to be continuously dependent on the energy. Our goal is to evaluate the effectiveness of the approximations made in [46], considering both the accuracy that can be reached in the calculation of the emerging flux and the computer resources needed by such a work. This investigation is required because for many cases of practical interest high order collision terms need to be evaluated, but there is no hope to perform the relevant numerical calculations without certain appropriate simplifying assumptions.

Here we address these questions for cases of particular interest to us, in particular we study cases under experimental investigation as kindly pointed out to us by Prof. R. Siegel [50]. In section VII.3 we develop the relevant mathematical framework, following the standard prescriptions of particles transport theory. We conclude, in section VII.4, that modern computers can successfully tackle such complicated problems, because the simplifying assumptions of [46], required to render the method practical, are vindicated.

### VII.3 Application to Thin Media

Let us concentrate first on optically thin media, from which most atoms escape without suffering a single collision.

Let us consider a slab of thickness " $d$ " filled with molecular deuterium at a temperature

“ $T$ ” and at a pressure “ $p$ ”, and assume there is a source of muonic deuterium atoms of the form  $S(E, t) = S_0\delta(t)\delta(E - E_0)$ . Assume also that the muonic atoms are produced in such a way as to respect the statistical mixture of duplet ( $D$ ) and quadruplet ( $Q$ ) states, i.e.  $S_0 = S_{0D} + S_{0Q}$  and  $S_{0D} = S_{0Q}/2$ . This models the experimental setup for muon experiments, and is also of interest for the study of muon catalyzed fusion: [51] – [58].

Expanding the angular flux  $\phi_a$  for  $a = D, Q$  as

$$\phi_a = \sum_{m=0}^{\infty} \phi_a^{(m)}, \quad (\text{VII.1})$$

where  $\phi_a^{(m)}$  is the flux of particles of species “ $a$ ” which have undergone  $m$  collisions, we have

$$\phi_a^{(m)}(t, \mathbf{x}, \mu, E) = \int_0^t v \exp[-v\Sigma_a(E, \mathbf{x} - \mu v(t - \tau))(t - \tau)] S_a^{(m-1)}(\tau, \mathbf{x} - \mu v(t - \tau), \mu, E) d\tau. \quad (\text{VII.2})$$

This can be viewed either as the solution to the transport equation

$$\frac{1}{v} \frac{\partial \phi_a^{(m)}}{\partial t} + \mu \frac{\partial \phi_a^{(m)}}{\partial x} + \Sigma_a \phi_a^{(m)} = S_a^{(m-1)} \quad (\text{VII.3})$$

via integration along the characteristics [49], or as a balance equation in the phase space of the system [59], [60]. In turn  $S_a^{(m)}$  is expressed as:

$$\begin{aligned} S_a^{(m)}(t, \mathbf{x}, \mu, E) = & \int_0^\infty dE' \int_{-1}^1 d\mu' \Sigma_{aa}(E' \rightarrow E, \mu' \rightarrow \mu; \mathbf{x}) \phi_a^{(m)}(t, \mathbf{x}, \mu', E') \\ & + \int_0^\infty dE' \int_{-1}^1 d\mu' \Sigma_{ba}(E' \rightarrow E, \mu' \rightarrow \mu; \mathbf{x}) \phi_b^{(m)}(t, \mathbf{x}, \mu', E') \end{aligned} \quad (\text{VII.4})$$

where  $\Sigma_a(E, \mathbf{x})$  is the total macroscopic cross section for atoms of species “ $a$ ” and  $v$  is their speed.  $S_a^{(m)}(t, \mathbf{x}, \mu, E)$  represents the number of  $m$ -collided particles with energy  $E$  and direction  $\mu$  that are produced in the unit volume around  $\mathbf{x}$  at the time  $t$ , by collisions suffered by the  $(m - 1)$ -collided particles.  $\Sigma_{aa}(E' \rightarrow E, \mu' \rightarrow \mu; \mathbf{x})$  is the transfer function for collisions of particles “ $a$ ” to remain particles “ $a$ ” and to change energy from  $E'$  to  $E$  and direction from  $\mu'$  to  $\mu$  at the position  $\mathbf{x}$ .  $\Sigma_{ba}(E' \rightarrow E, \mu' \rightarrow \mu; \mathbf{x})$  has the same meaning but for inelastic collisions that change particles “ $b$ ” into particles “ $a$ ”.

Let us assume, now, that our slab is homogeneous and isotropic. Then we can perform the standard analysis of those functions via orthogonal polynomials (see [49], [61], [62] for instance) and write:

$$\Sigma(E' \rightarrow E, \mu' \rightarrow \mu; \mathbf{x}) = H(d/2 - |\mathbf{x}|) \Sigma(E' \rightarrow E, \mu' \rightarrow \mu) \quad (\text{Homogeneous medium}) \quad (\text{VII.5})$$

$$\Sigma(E' \rightarrow E, \mu' \rightarrow \mu) = \sum_{l=0}^{\infty} \frac{2l+1}{2} P_l(\mu) P_l(\mu') \Sigma^l(E' \rightarrow E) \quad (\text{Isotropic medium}) \quad (\text{VII.6})$$

$$\Sigma^l(E' \rightarrow E) = \int_{-1}^{-1} \Sigma(E' \rightarrow E, \mu) P_l(\mu) d\mu \quad (\text{VII.7})$$

$$\phi_{al}^{(m)}(t, \mathbf{x}, E) = \int_{-1}^1 \phi_a^{(m)}(t, \mathbf{x}, \mu, E) P_l(\mu) d\mu \quad (\text{VII.8})$$

where  $H$  is the Heaviside function. Substituting into equation (VII.4) we get

$$\begin{aligned} S_a^{(m)}(t, \mathbf{x}, \mu, E) = & \int_0^{\infty} dE' \int_{-1}^1 d\mu' \phi_a^{(m)}(t, \mathbf{x}, \mu', E') \sum_{l=0}^{\infty} \frac{2l+1}{2} \Sigma_{aa}^l(E' \rightarrow E; \mathbf{x}) P_l(\mu) P_l(\mu') \\ & + \int_0^{\infty} dE' \int_{-1}^1 d\mu' \phi_b^{(m)}(t, \mathbf{x}, \mu', E') \sum_{l=0}^{\infty} \frac{2l+1}{2} \Sigma_{ba}^l(E' \rightarrow E; \mathbf{x}) P_l(\mu) P_l(\mu'). \end{aligned} \quad (\text{VII.9})$$

If we go one step beyond the assumption of isotropic scattering and stop our sums at  $l = 1$ , then  $S_a^{(m)}$  is the sum of four terms only, namely:

$$S_a^{(m)} = \int_0^{\infty} dE' \left\{ \frac{1}{2} \left[ \Sigma_{aa}^0 \phi_{a0}^{(m)} + \Sigma_{ba}^0 \phi_{b0}^{(m)} \right] + \frac{3}{2} \mu \left[ \Sigma_{aa}^1 \phi_{a1}^{(m)} + \Sigma_{ba}^1 \phi_{b1}^{(m)} \right] \right\}. \quad (\text{VII.10})$$

We need to know the form of the transfer functions that appear in (VII.9). Through a classical procedure, [61], [63], assuming stationary scattering centers and defining the function  $\Lambda$  as  $\Lambda(E, E') = H(E - E^-(E')) - H(E - E^+(E'))$ , we get

$$\Sigma_{aa}^0(E' \rightarrow E; \mathbf{x}) = H(d/2 - |\mathbf{x}|) \frac{\Sigma_{aa}(E')}{(1 - \alpha)E'} [H(E' - E) - H(E' - E/\alpha)] \quad (\text{VII.11})$$

where  $\alpha = \left( \frac{A-1}{A+1} \right)^2$ ,  $1 =$  projectile mass,  $A =$  target mass,  $E^{\pm} = E' \left( \frac{A\beta(E') \pm 1}{A+1} \right)^2$ , and  $\beta(E') = \sqrt{1 + \frac{A+1}{A} \frac{U}{E'}}$ , where  $U =$  projectile potential energy change in the inelastic

collision, and

$$\Sigma_{QD}^0(E' \rightarrow E; \mathbf{x}) = H(d/2 - |\mathbf{x}|) \frac{\Sigma_{QD}(E')}{(1 - \alpha)E'\beta(E')} \Lambda(E, E') \quad (\text{VII.12})$$

$$\Sigma_{DQ}^0(E' \rightarrow E; \mathbf{x}) = H(d/2 - |\mathbf{x}|) \begin{cases} 0 & \text{if } 0 \leq E' < -\frac{A+1}{A}U \\ \frac{\Sigma_{DQ}(E')}{(1 - \alpha)E'\beta(E')} \Lambda(E, E') & \text{if } E' \geq -\frac{A+1}{A}U \end{cases} \quad (\text{VII.13})$$

$$\Sigma_{ac}^1(E' \rightarrow E; \mathbf{x}) = \frac{1}{2} \Sigma_{ac}^0(E' \rightarrow E; \mathbf{x}) \left[ (A+1) \sqrt{\frac{E'}{E}} - (A-1) \sqrt{\frac{E}{E'}} \right] \quad (\text{VII.14})$$

for  $c = b$  and  $c = a$ . Note that in [46] the  $U_{eff}$  term given in [63] was used for the calculations relevant to the transport of muonic hydrogen, instead of  $U$ . Here we are not going to make that correction to the value of  $U$ , because the difference is negligible when muonic deuterium is considered.

In order to have an analytical expression for  $S_a^{(m)}$  in (VII.10), we need to know the form of  $\phi_{D0}^{(m)}, \phi_{Q0}^{(m)}, \phi_{D1}^{(m)}, \phi_{Q1}^{(m)}$ , which are known if  $S_a^{(m-1)}$  is known. Then we may start from  $\phi_a^{(0)}(t, \mathbf{x}, \mu, E)$  and its 0th and 1st moments, and iteratively construct all the others. This can be done by first solving

$$\frac{1}{v_0} \frac{\partial \phi_a^{(0)}}{\partial t} + \mu \frac{\partial \phi_a^{(0)}}{\partial \mathbf{x}} + \Sigma_a \phi_a^{(0)} = S_{0a} \delta(t) \delta(E - E_0). \quad (\text{VII.15})$$

In [46] equation (VII.15) was solved with  $S_0 = 1/2d$  and  $\phi_{a0}^{(0)}(t, \mathbf{x}, E)$  and  $\phi_{a1}^{(0)}(t, \mathbf{x}, E)$  were given analytically. This allows us to compute the emerging uncollided flux  $X_a^{(0)}(t, E_0) = 2\phi_{a1}^{(0)}(t, d/2, E_0)$ , which agrees with that in [46], and it yields an analytical expression for  $S_a^{(0)}$ :

$$S_a^{(0)}(t, \mathbf{x}, \mu, E) = H(d/2 - |\mathbf{x}|) \left\{ \frac{1}{2} \left[ \Sigma_{aa}^0(E_0 \rightarrow E) \phi_{a0}^{(0)}(t, \mathbf{x}, E_0) + \Sigma_{ba}^0(E_0 \rightarrow E) \phi_{b0}^{(0)}(t, \mathbf{x}, E_0) \right] + 3 \left[ \Sigma_{aa}^1(E_0 \rightarrow E) \phi_{a1}^{(0)}(t, \mathbf{x}, E_0) + \Sigma_{ba}^1(E_0 \rightarrow E) \phi_{b1}^{(0)}(t, \mathbf{x}, E_0) \right] \frac{\mu}{2} \right\}. \quad (\text{VII.16})$$

Substituting (VII.16) into (VII.2) we derive an analytical expression for  $\phi_a^{(1)}(t, d/2, \mu, E)$ , namely:

$$\begin{aligned} \phi_a^{(1)}(t, d/2, \mu, E) &= \\ &= \frac{ve^{v\Sigma_a(E)t}}{2} \left\{ \left[ \Sigma_{aa}^0(E_0 \rightarrow E) I_0^{aa}(t, d/2, \mu, E) + \Sigma_{ba}^0(E_0 \rightarrow E) I_0^{ba}(t, d/2, \mu, E) \right] \right. \\ &\quad \left. + \frac{3\mu v}{2} \left[ \Sigma_{aa}^1(E_0 \rightarrow E) I_1^{aa}(t, d/2, \mu, E) + \Sigma_{ba}^1(E_0 \rightarrow E) I_1^{ba}(t, d/2, \mu, E) \right] \right\} \end{aligned} \quad (\text{VII.17})$$

for  $a \neq b$ , where

$$\begin{aligned} I_0^{ca}(t, d/2, \mu, E) &= \int_0^t H \left( \frac{d}{2} - \left| \frac{d}{2} - \mu v(t - \tau) \right| \right) \phi_{c0}^{(0)} \left( \tau, \frac{d}{2} - \mu v(t - \tau), E_0 \right) e^{v\Sigma_a(E)\tau} d\tau \\ &= S_0 \left\{ \frac{2v_0}{L_{ca}(E, E_0)} \left[ e^{L_{ca}(E, E_0)t} - e^{L_{ca}(E, E_0)T'_i} \right] \right. \\ &\quad - \frac{v_0 + \mu v}{L_{ca}(E, E_0)} \left[ e^{L_{ca}(E, E_0)T_{f1}} - e^{L_{ca}(E, E_0)T_{i1}} \right] \\ &\quad + \frac{v_0 - \mu v}{L_{ca}(E, E_0)} \left[ e^{L_{ca}(E, E_0)T_{f2}} - e^{L_{ca}(E, E_0)T_{i2}} \right] \\ &\quad + \mu vt \left[ E_1(-L_{ca}(E, E_0)T_{i1}) - E_1(-L_{ca}(E, E_0)T_{f1}) \right] \\ &\quad \left. - (d - \mu vt) \left[ E_1(-L_{ca}(E, E_0)T_{i2}) - E_1(-L_{ca}(E, E_0)T_{f2}) \right] \right\} \end{aligned} \quad (\text{VII.18})$$

where  $T'_i = 0$  if  $t \leq d/(2\mu v)$  and  $T'_i = \max[0, t - d/(\mu v)]$  if  $t > d/(2\mu v)$ , and

$$\begin{aligned} I_1^{ca}(t, d/2, \mu, E) &= \int_0^t H \left( \frac{d}{2} - \left| \frac{d}{2} - \mu v(t - \tau) \right| \right) \phi_{c0}^{(1)} \left( \tau, \frac{d}{2} - \mu v(t - \tau), E_0 \right) e^{v\Sigma_a(E)\tau} d\tau \\ &= \frac{S_0}{v_0} \left\{ \frac{v_0^2 - \mu^2 v^2}{2L_{ca}(E, E_0)} \left[ e^{L_{ca}(E, E_0)T_{f1}} - e^{L_{ca}(E, E_0)T_{i1}} - e^{L_{ca}(E, E_0)T_{f2}} + e^{L_{ca}(E, E_0)T_{i2}} \right] \right. \\ &\quad + \mu^2 v^2 t \left[ E_1(-L_{ca}(E, E_0)T_{i1}) - E_1(-L_{ca}(E, E_0)T_{f1}) \right] \\ &\quad + \mu v(d - \mu vt) \left[ E_1(-L_{ca}(E, E_0)T_{i2}) - E_1(-L_{ca}(E, E_0)T_{f2}) \right] \\ &\quad - \frac{(\mu vt)^2}{2} \left[ \frac{E_2(-L_{ca}(E, E_0)T_{i1})}{T_{i1}} - \frac{E_2(-L_{ca}(E, E_0)T_{f1})}{T_{f1}} \right] \\ &\quad \left. + \frac{(d - \mu vt)^2}{2} \left[ \frac{E_2(-L_{ca}(E, E_0)T_{i2})}{T_{i2}} - \frac{E_2(-L_{ca}(E, E_0)T_{f2})}{T_{f2}} \right] \right\}. \end{aligned} \quad (\text{VII.19})$$

for  $c = b$  and  $c = a$ . Here  $L_{ca}(E, E_0) = v\Sigma_a(E) - v_0\Sigma_c(E_0)$ ,

$$E_n(x) = \int_1^\infty \frac{e^{-xt}}{t^n} dt \quad \text{for } n = 1, 2 \quad (\text{VII.20})$$

and

$$\left. \begin{aligned} T_{ij} &= T_{ij}(t, \mu, v) = \max \left[ t_{ij}(t, \mu, v), t - \frac{d}{\mu v} \right] \\ T_{fj} &= T_{fj}(t, \mu, v) = \max \left[ t_{fj}(t, \mu, v), t - \frac{d}{\mu v} \right] \end{aligned} \right\} \quad \text{if } t - \frac{t}{2\mu v} \geq t_{fj}(t, \mu, v) \quad (\text{VII.21})$$

$$\left. \begin{aligned} T_{ij} &= T_{ij}(t, \mu, v) = \max \left[ t_{ij}(t, \mu, v), t - \frac{d}{\mu v} \right] \\ T_{fj} &= T_{fj}(t, \mu, v) = t_{fj}(t, \mu, v) \end{aligned} \right\} \quad \text{if } t_{ij}(t, \mu, v) < t - \frac{t}{2\mu v} < t_{fj}(t, \mu, v) \quad (\text{VII.22})$$

$$\left. \begin{aligned} T_{ij} &= T_{ij}(t, \mu, v) = t_{ij}(t, \mu, v) \\ T_{fj} &= T_{fj}(t, \mu, v) = t_{fj}(t, \mu, v) \end{aligned} \right\} \quad \text{if } t - \frac{t}{2\mu v} \leq t_{ij}(t, \mu, v) \quad (\text{VII.23})$$

for  $j = 1, 2$ , where the following must be used:

$$\left. \begin{aligned} t_{i1}(t, \mu, v) &= \min \left( t, \frac{\mu v t}{v_0 + \mu v} \right) \\ t_{f1}(t, \mu, v) &= t \end{aligned} \right\} \quad (\text{VII.24})$$

$$t_{i2}(t, \mu, v) = \left. \begin{aligned} &\left\{ \begin{array}{ll} \min \left[ t, \max \left( 0, \frac{d - \mu v t}{v_0 - \mu v} \right) \right] & v_0 > \mu v \\ t_{f2}(t, \mu, v) & \text{if } d - \mu v t > 0 \\ 0 & \text{if } d - \mu v t \leq 0 \\ 0 & \end{array} \right\} \end{aligned} \right\} \quad \begin{array}{l} v_0 = \mu v \\ v_0 < \mu v \end{array} \quad (\text{VII.25})$$

$$t_{f2}(t, \mu, v) = \left. \begin{array}{l} t \\ \max \left[ 0, \min \left( t, \frac{d - \mu v t}{v_0 - \mu v} \right) \right] \end{array} \right\} \quad \begin{array}{l} v_0 \geq \mu v \\ v_0 < \mu v \end{array} \quad (\text{VII.26})$$

The last step is to compute, with the aid of a computer, the experimentally measurable quantity, that is:

$$X(t) = \sum_{m=0}^{\infty} X^{(m)}(t) = \sum_{m=0}^{\infty} \left[ X_D^{(m)}(t) + X_Q^{(m)}(t) \right], \quad (\text{VII.27})$$



where

$$X_a^{(m)}(t) = 2 \int_0^\infty dE \int_0^1 d\mu \left[ \mu \phi_a^{(m)}(t, d/2, \mu, E) \right]. \quad (\text{VII.28})$$

In our case we determine the contribution of the 0th and 1st order collided particles only, as done in [46], in order to assess the validity of

$$X(t) \simeq X^{(0)}(t) + X^{(1)}(t). \quad (\text{VII.29})$$

#### VII.4 Numerical Results

Numerically we have computed the quantities given in (VII.28), (VII.29) and the integrated flux

$$F(t) = \int_0^t X(s) ds \quad (\text{VII.30})$$

starting from the knowledge of the analytical expression for  $\phi_a^{(0)}, \phi_a^{(1)}$ . Three numerical integrations had to be performed: one over the angle variable, one over the energy variable and one over the time variable, in the given order. For the first integration we performed accuracy tests on several different integration routines, as available to us, which convinced us to choose the routine QDAGS, of the vectorized IMSL-MATH/11 package available on the Pittsburgh CRAY Y-MP, and the routine GAULEG, presented in [64]. Of these, QDAGS is to be preferred on the ground of CPU-time performance, as our program runs about 20 times faster when QDAGS is used as compared to when the same program is run with GAULEG. The integration over energy was performed through a standard but fine ( $\sim 30$  groups) multigroup approximation of the continuous distribution. Note that the integral over the energy only apparently goes from 0 to  $\infty$  since there are no particles of  $0^{th}$  and  $1^{st}$  collision order with energy higher than  $E_0 + U$ . Finally, the integration over the time variable was performed through an integration routine devised by us and based on the trapezoid rule. We observe that the expressions (VII.11), (VII.12), (VII.13) and

(VII.14) assume that the target molecules are at rest, thus they apply strictly only for  $T = 0$ . For  $T > 0$ , the thermal motion of the scattering centers must be taken into account, and two corrections must be introduced: a) the doppler broadening (or Wigner-Wilkins effect), b) the temperature dependent effect of the chemical bond. We have introduced these two corrections by averaging over Maxwellian distributions and by multiplying the free microscopic cross sections by a temperature dependent factor, following the same procedure discussed in [63]. The other obvious effect of the temperature is on the density of the scattering centers, which were assumed to be the constituents of a perfect gas. Some results are given in the figures. Note that in all the figures, with the exception of Figure VII.1, the Y-axis on the left refers to the solid line, i.e. to the emerging flux  $X(t)$ , while the Y-axis on the right refers to the triangles, i.e. to  $F(t)$  which represents the fraction of particles of 0th and 1st order that escaped from the medium in the time interval  $[0, t]$ . Our results show good agreement with the calculations previously published for the optically thin media considered in [46]. For such media, the difference between our calculation and that of Rusjan and Zweifel amounts to about 1% when the emerging flux  $X$  is considered, and about 5% for the integrated emerging flux; see Figure VII.1. This may be taken, then, as a bound on the performance of the simpler scheme outlined by those authors. For increased accuracy and to consider somewhat thicker slabs, it will be necessary to consider higher-order collided fluxes. Here, the inclusion of anisotropy and energy dependence complicates greatly the necessary analytical development and increases the computer resource needs, and so the approach of [46] is likely to be necessary for practical considerations. Indeed, our analysis shows that the approximations of one energy group, isotropic scattering and isotropic source of once collided particles can be made without causing serious errors and with the advantage that calculations can be carried within reasonable time limits, thus making feasible an higher order collision expansion analysis. The method presented in [46] is the only one capable to achieve such results, among those we are currently aware of.

# FIGURES

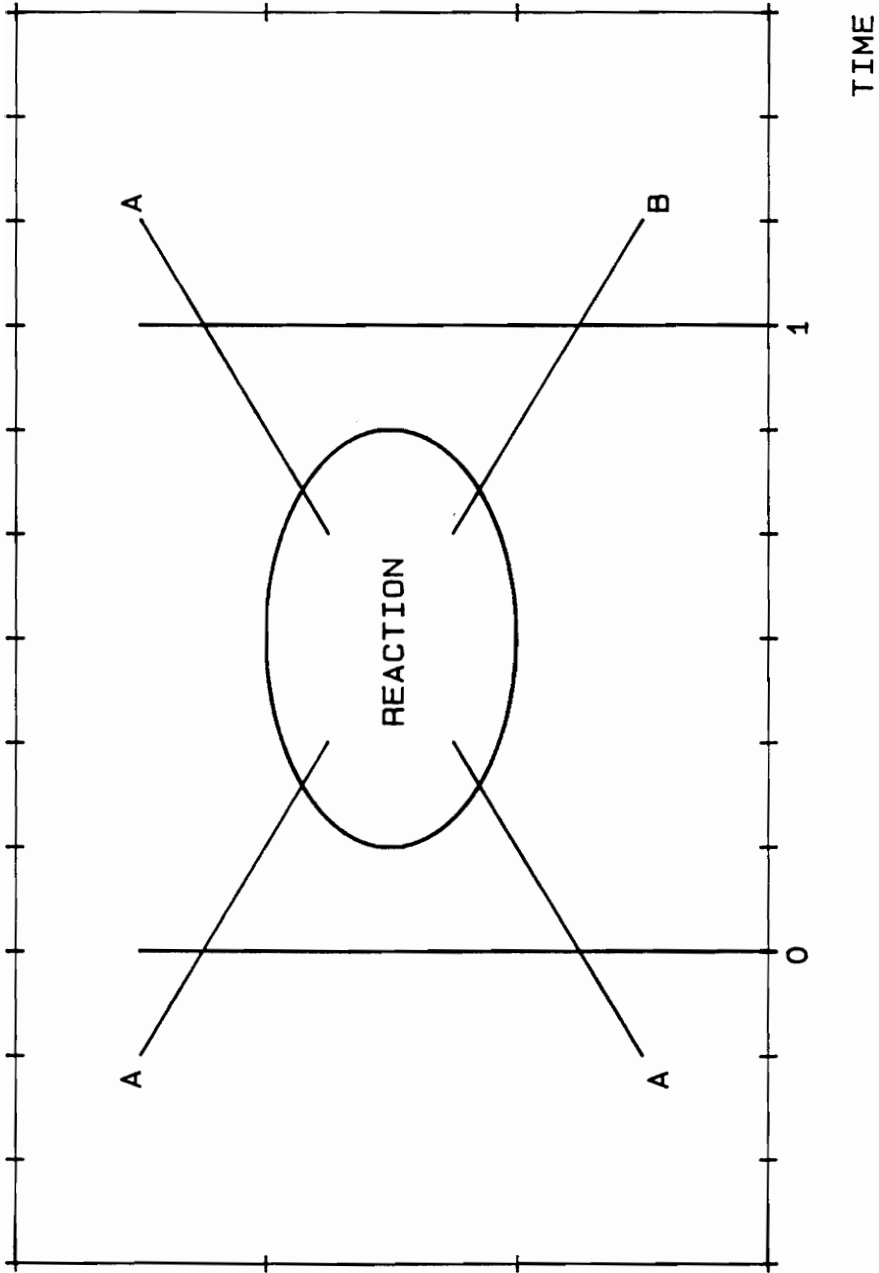


FIG. I.1 The simplest autocatalytic reaction:  $2A \rightarrow A + B$ .

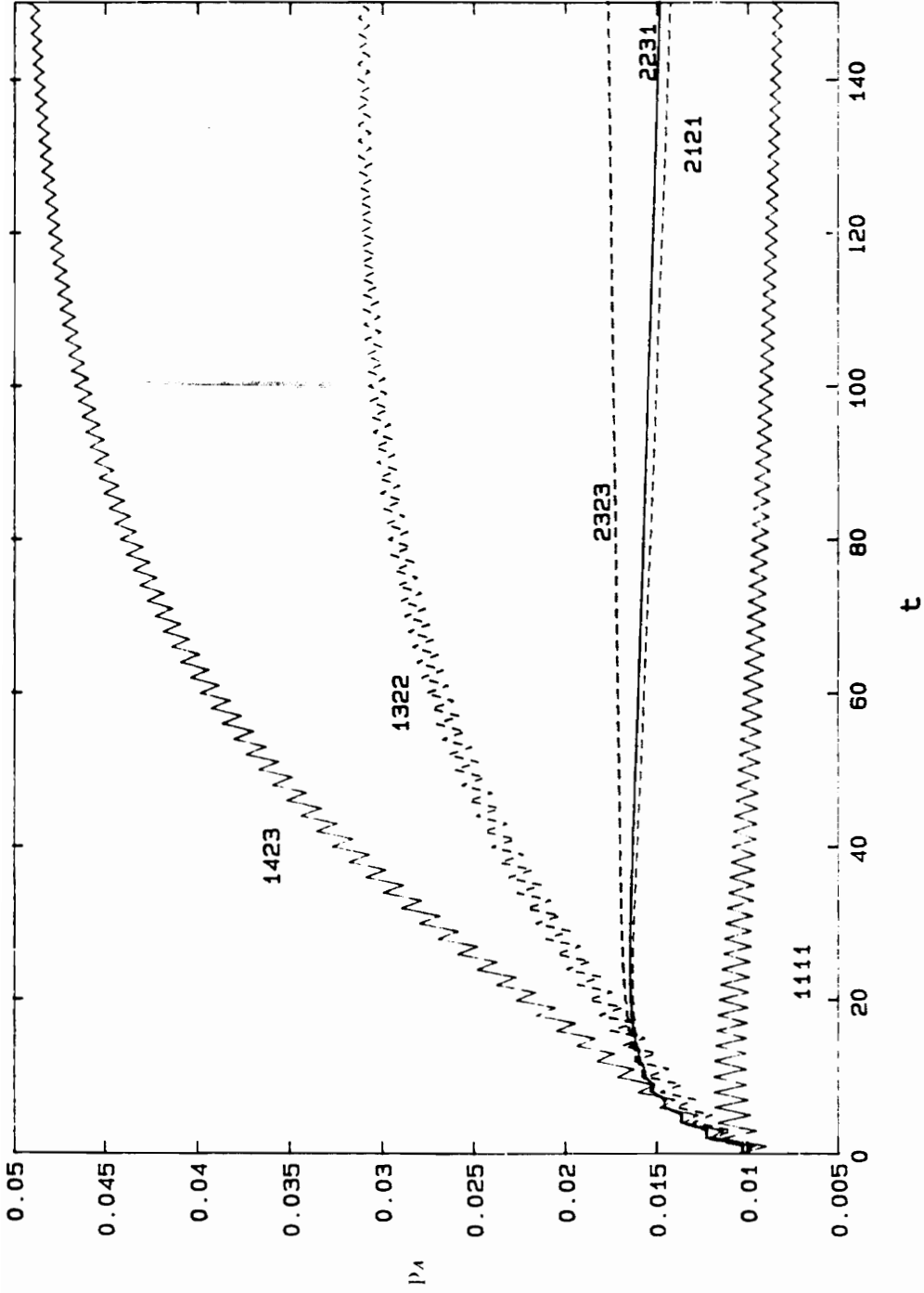


FIG. V.1  $nA + mB = lC + (n+m-l)D$ ;  $D + E = A + C$ . The 6 different curves represent the result of the iteration of maps for 6 different choices of the stoichiometry of the first component.

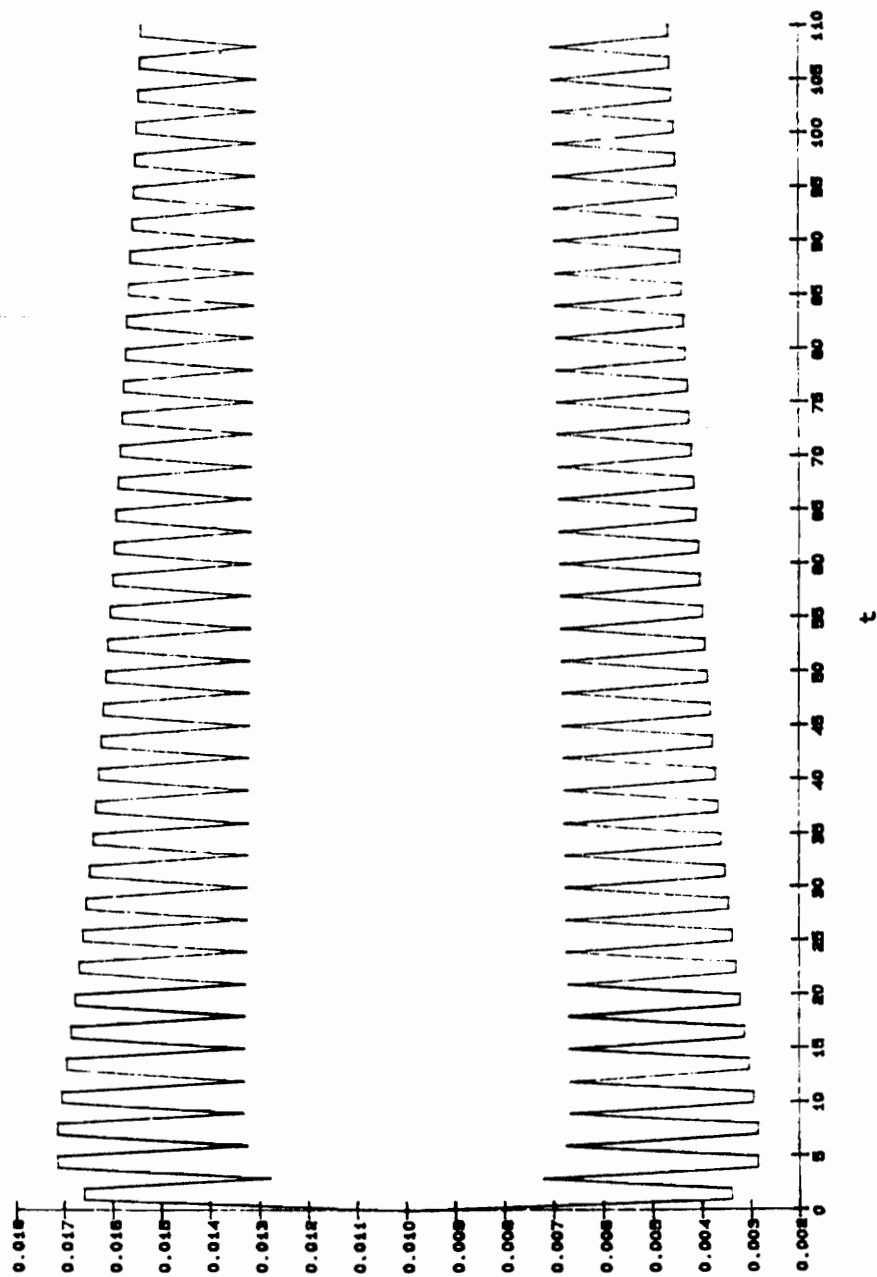


FIG. V.2 The top curve represents  $p_D$ , while the bottom one represents  $p_A$ , for an iteration of maps relative to  $A + B = C + D$ ;  $2C = E + F$ ;  $D + E = A + C$ .

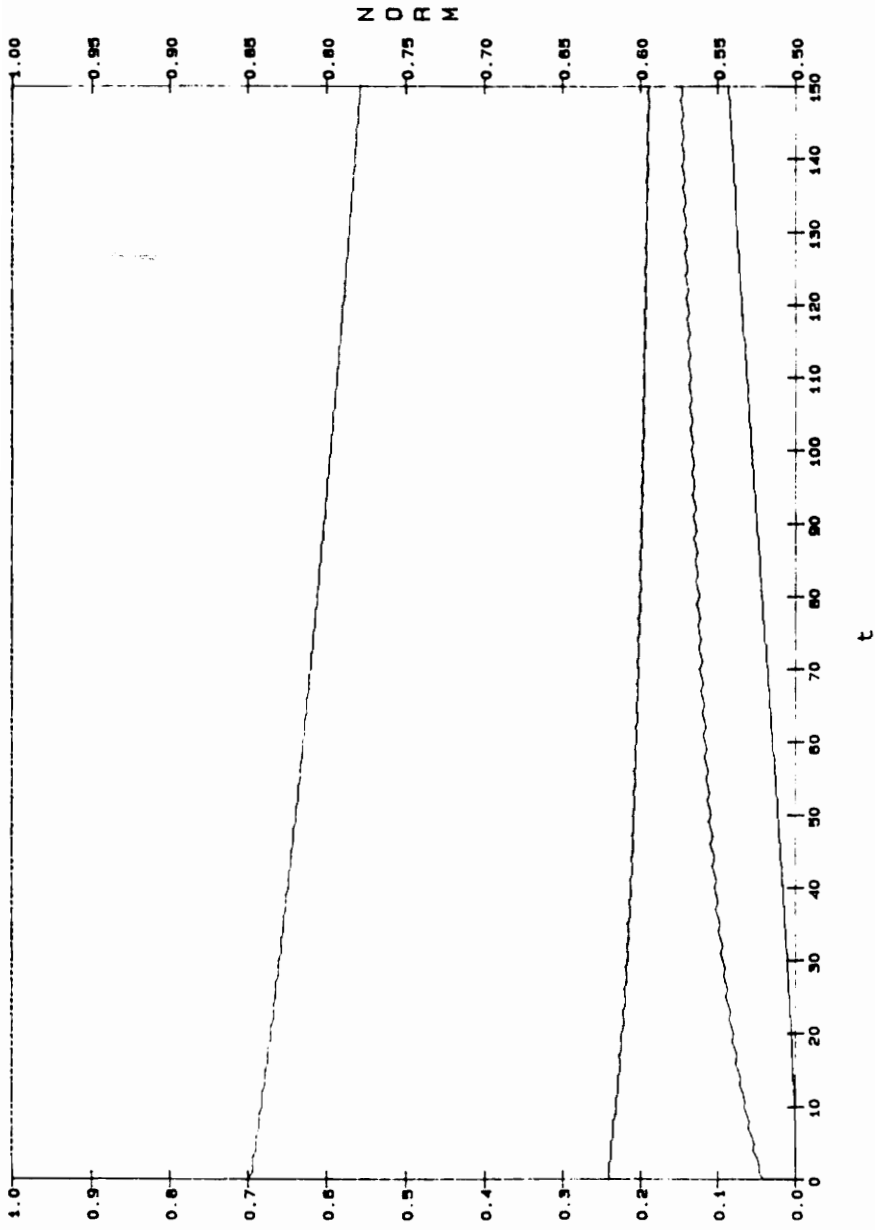


FIG. V.3 From top to bottom we have the curves of  $p_B$ ,  $p_E$ ,  $p_C$  and  $p_F$ , for the same reaction as in FIG. V.2. The vertical axis on the right refers to the sum of all the probabilities.

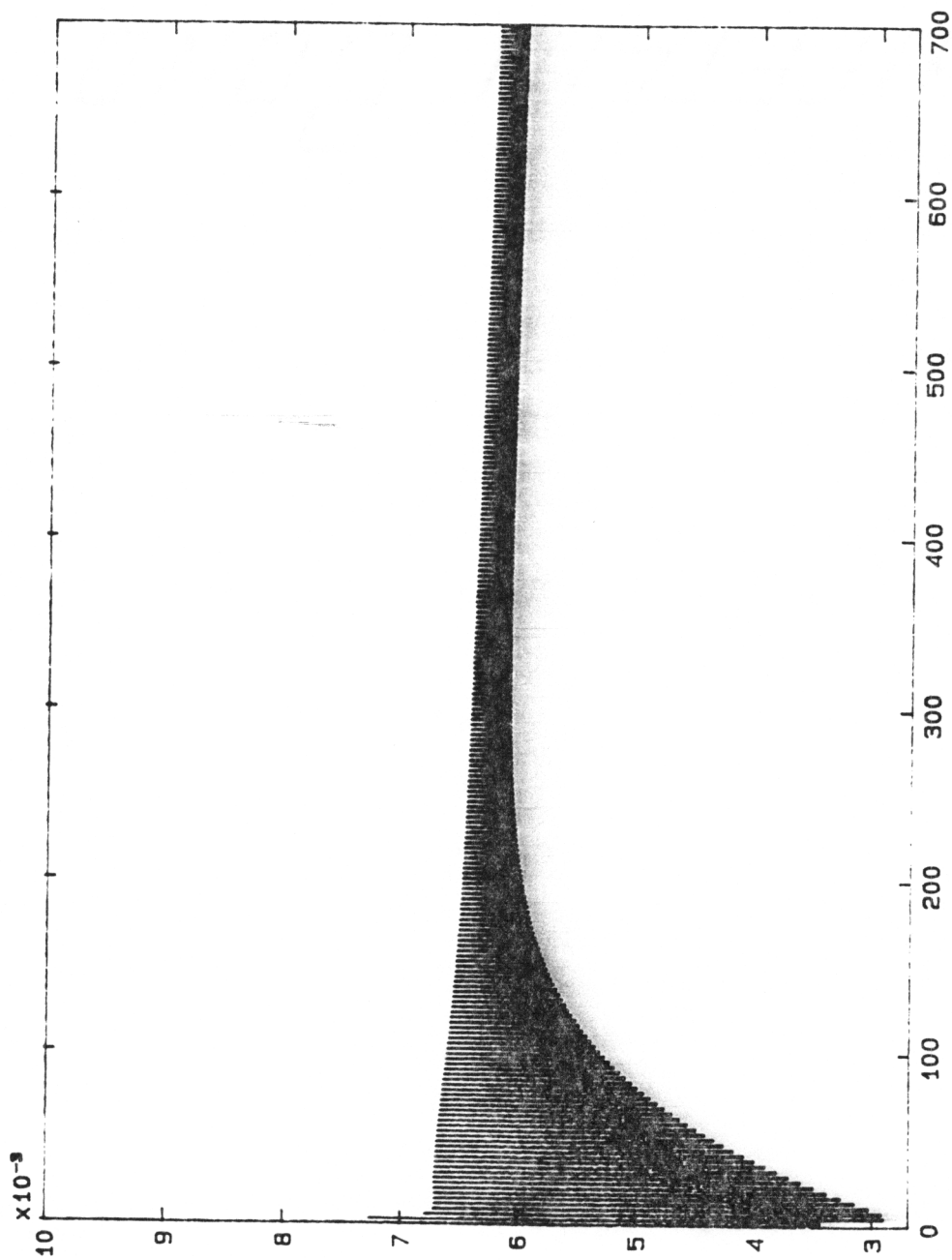


FIG V.4  $p_A$  as given by the iterations of maps for the reaction  $A + B = C + D$ ;  $3C = E + 2F$ ;  
 $D + E = A + C$ .



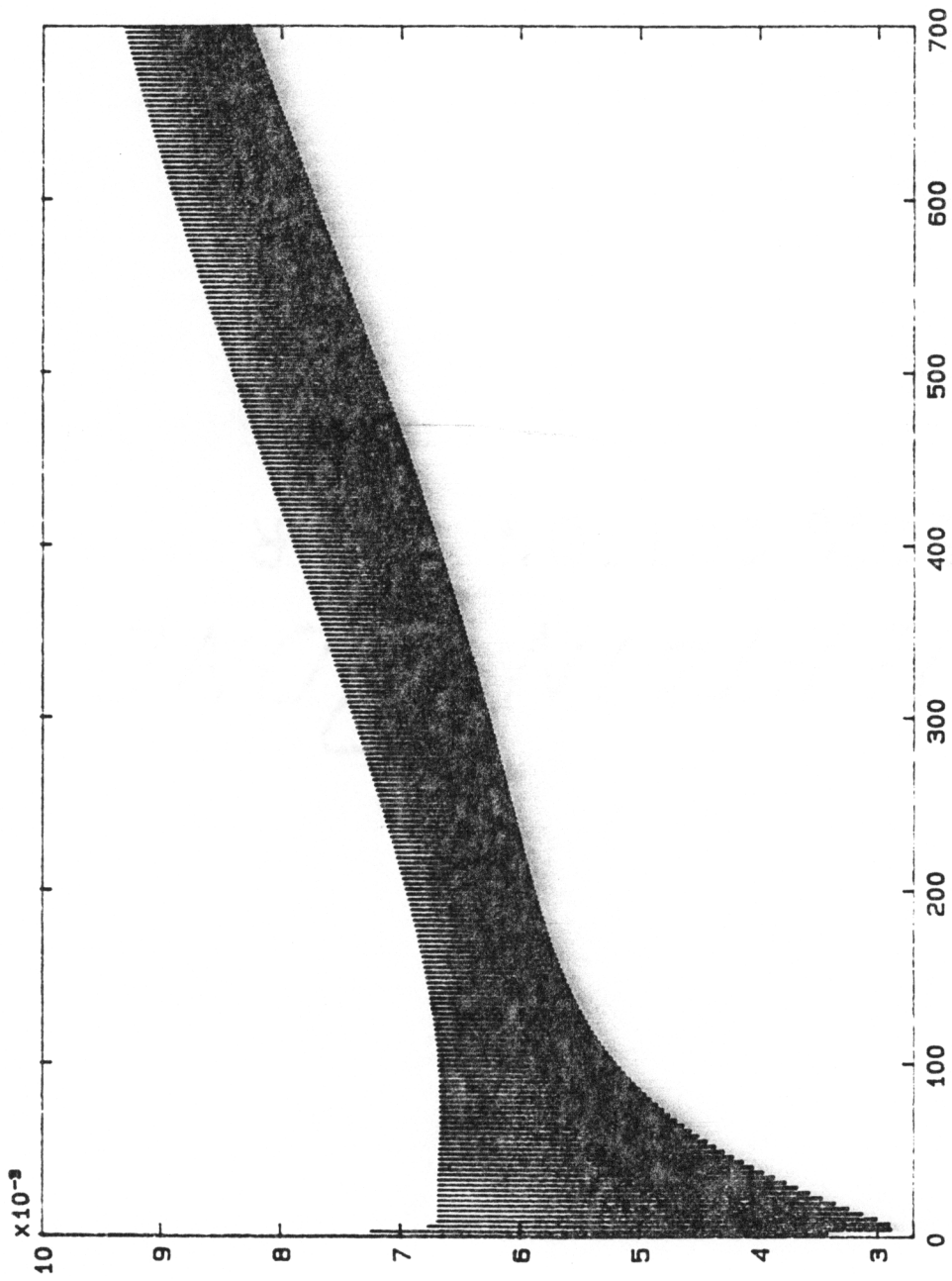
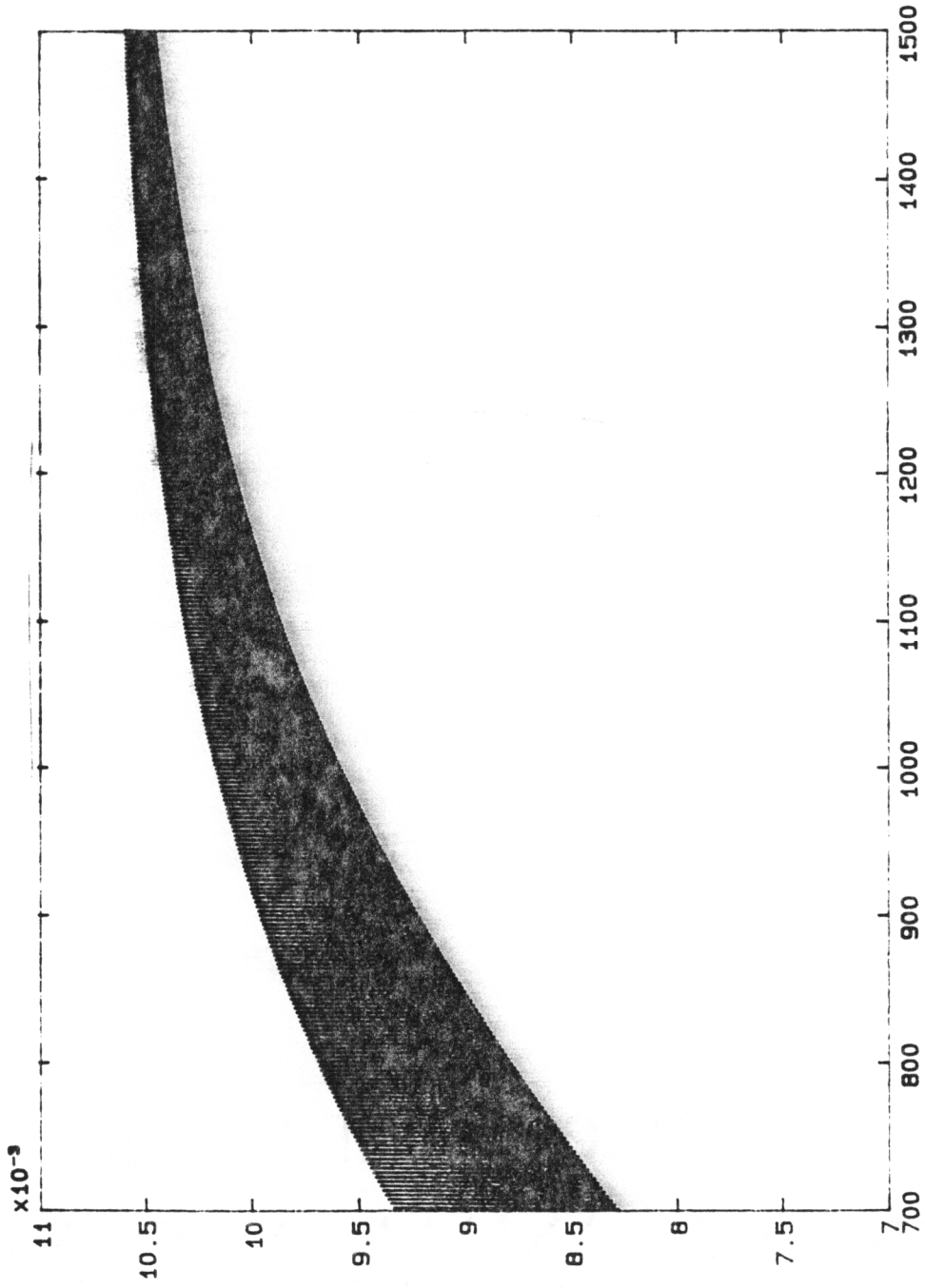


FIG. V.5 First 700 oscillations of  $p_4$  produced by the iteration of maps for the reaction  $A + B = C + D$ ;  
 $5 C = E + 4 F$ ;  $D + E = A + C$ .

FIG. V.6 Following 800 oscillations of  $p_4$  for the scheme of FIG. V.5.

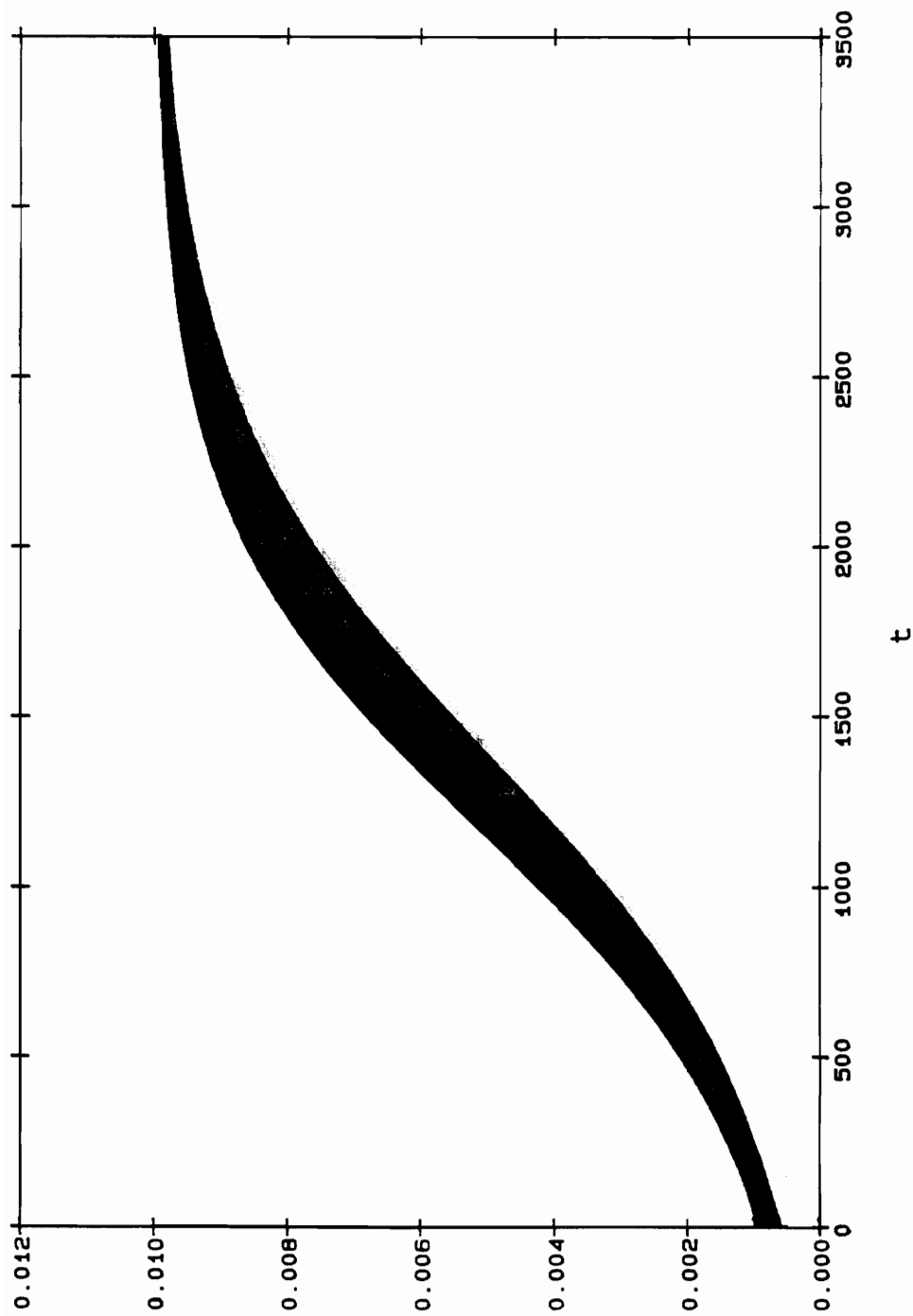


FIG. V.7 3500 oscillations of  $p_A$  produced by the iteration of maps for the reaction (V.4). This figure shows their amplitude only.

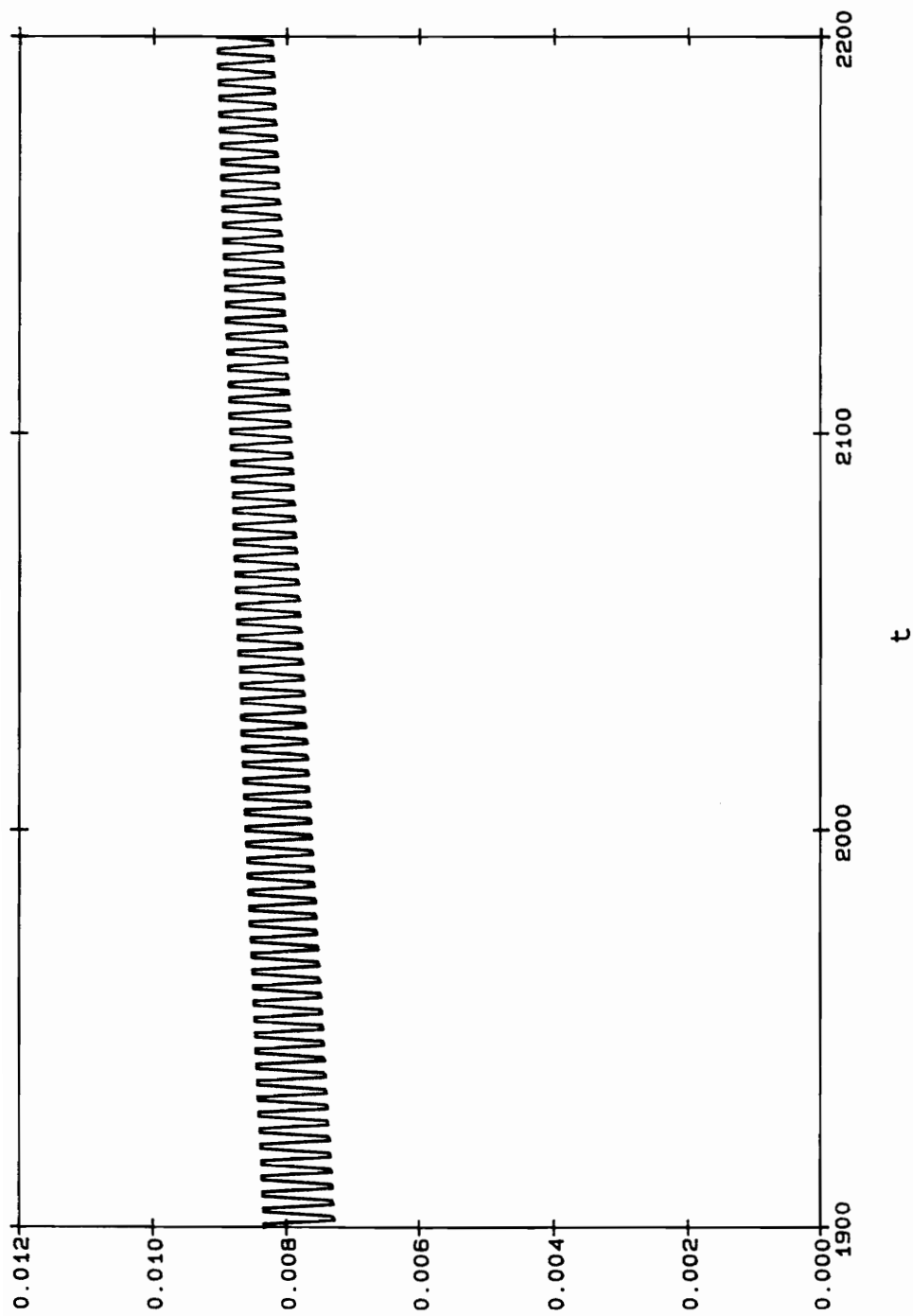


FIG. V.8 A detail of FIG. V.7.

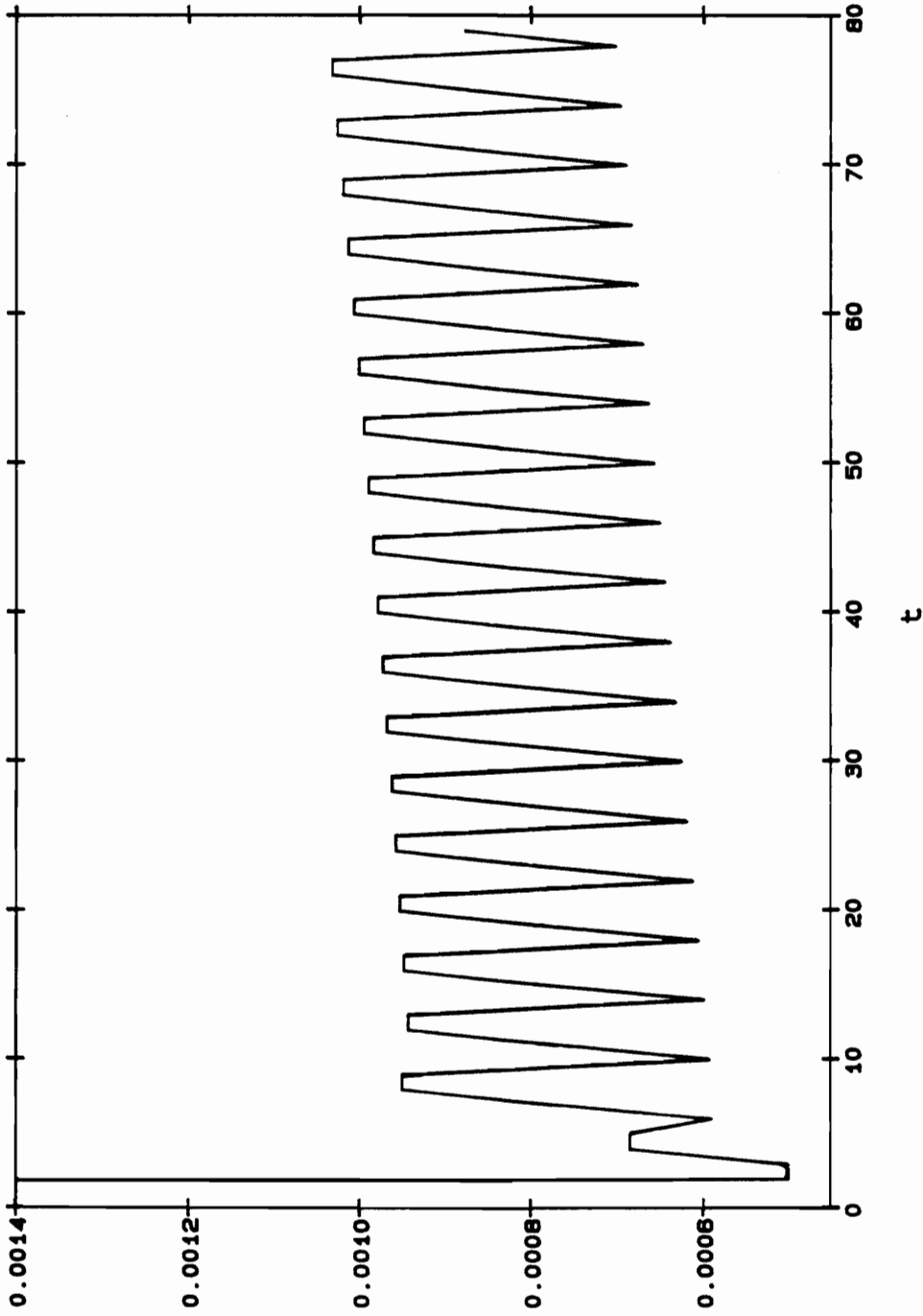


FIG. V.9 First 80 oscillations of  $p_A$  from FIG. V.7. The initial data are  $p_A(0) = p_B(0) = p_C(0) = p_D(0) = 0.1$ . The coupling constants of the second and fourth reaction equal their bistochasticity limit, which is  $1/2$ .

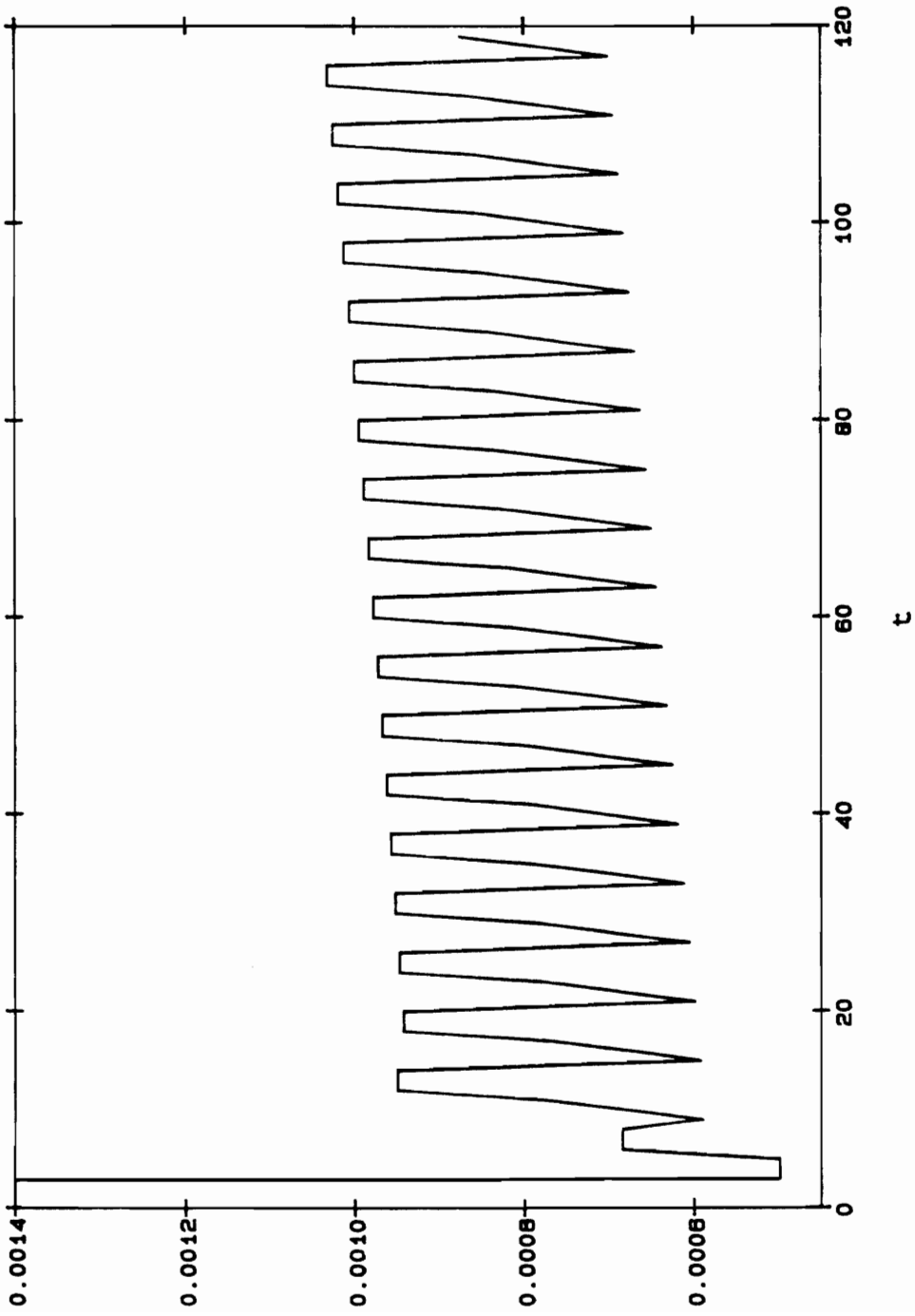


FIG. V.10 Same as FIG. V.9, with coupling constants equal to 0.25.

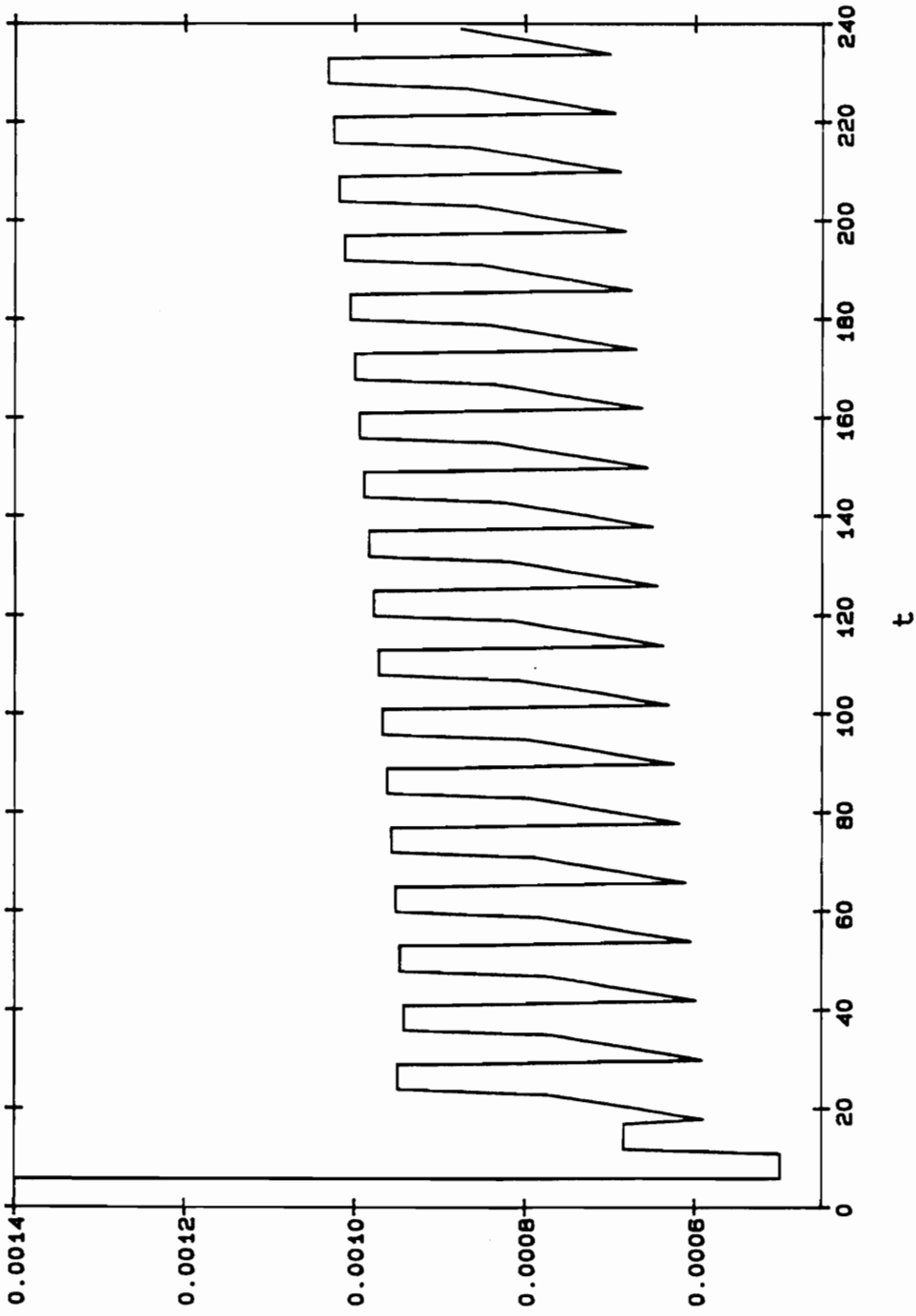


FIG. V.11 Same as FIG. V.9, with coupling constants equal to 0.1.

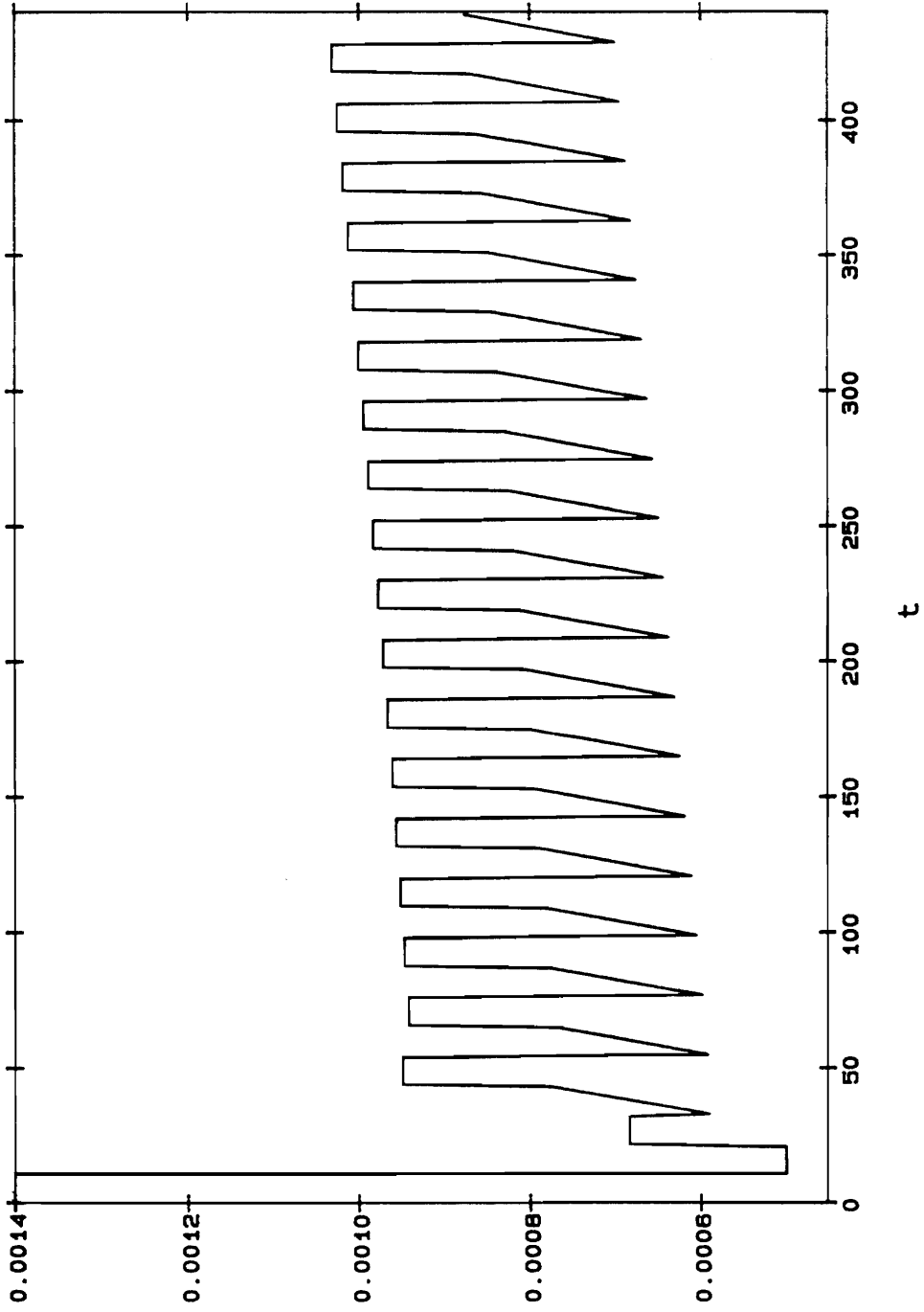


FIG. V.12 Same as FIG. V.9, with coupling constants equal to 0.05.



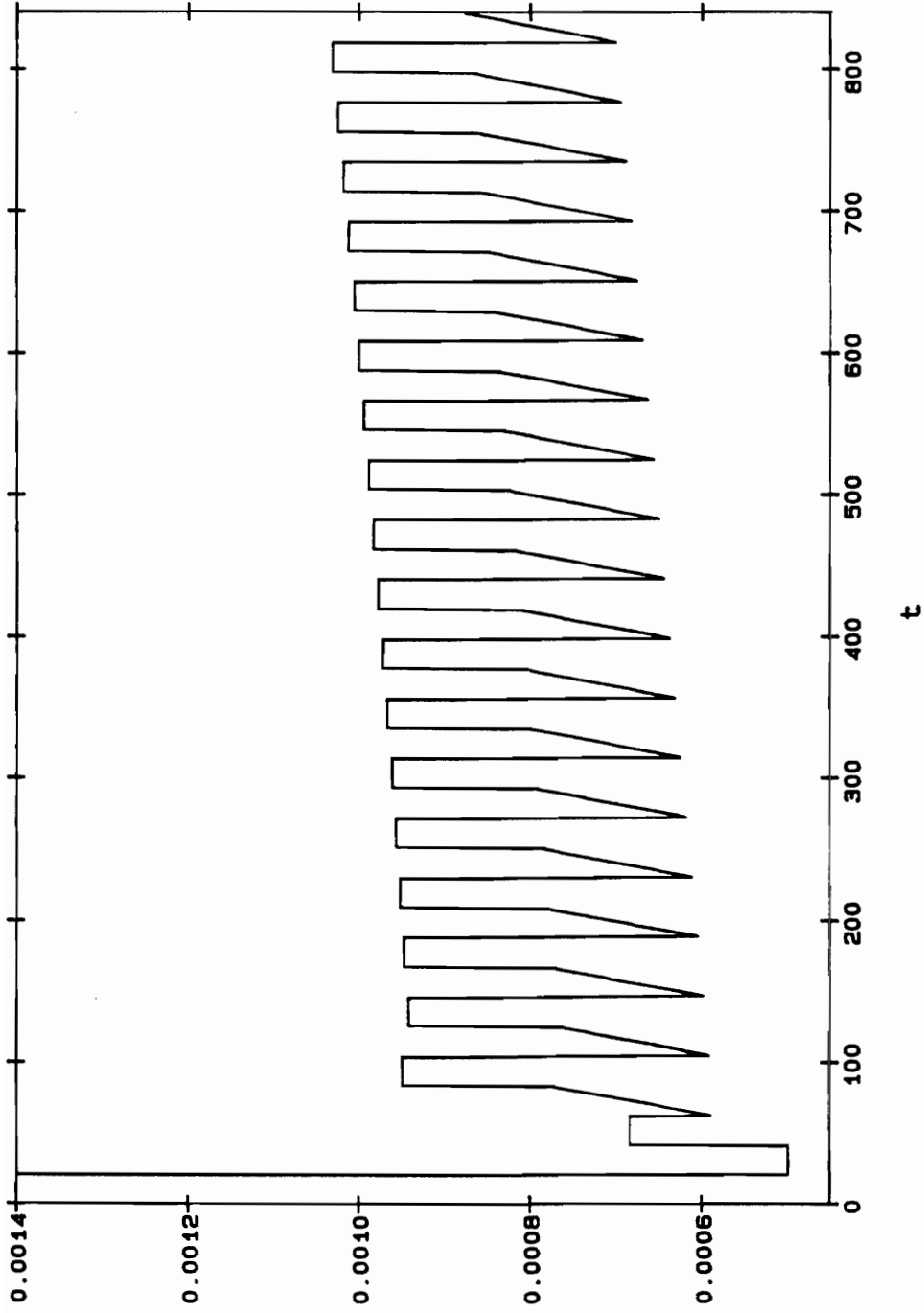


FIG. V.13 Same as FIG. V.9, with coupling constants equal to 0.025.

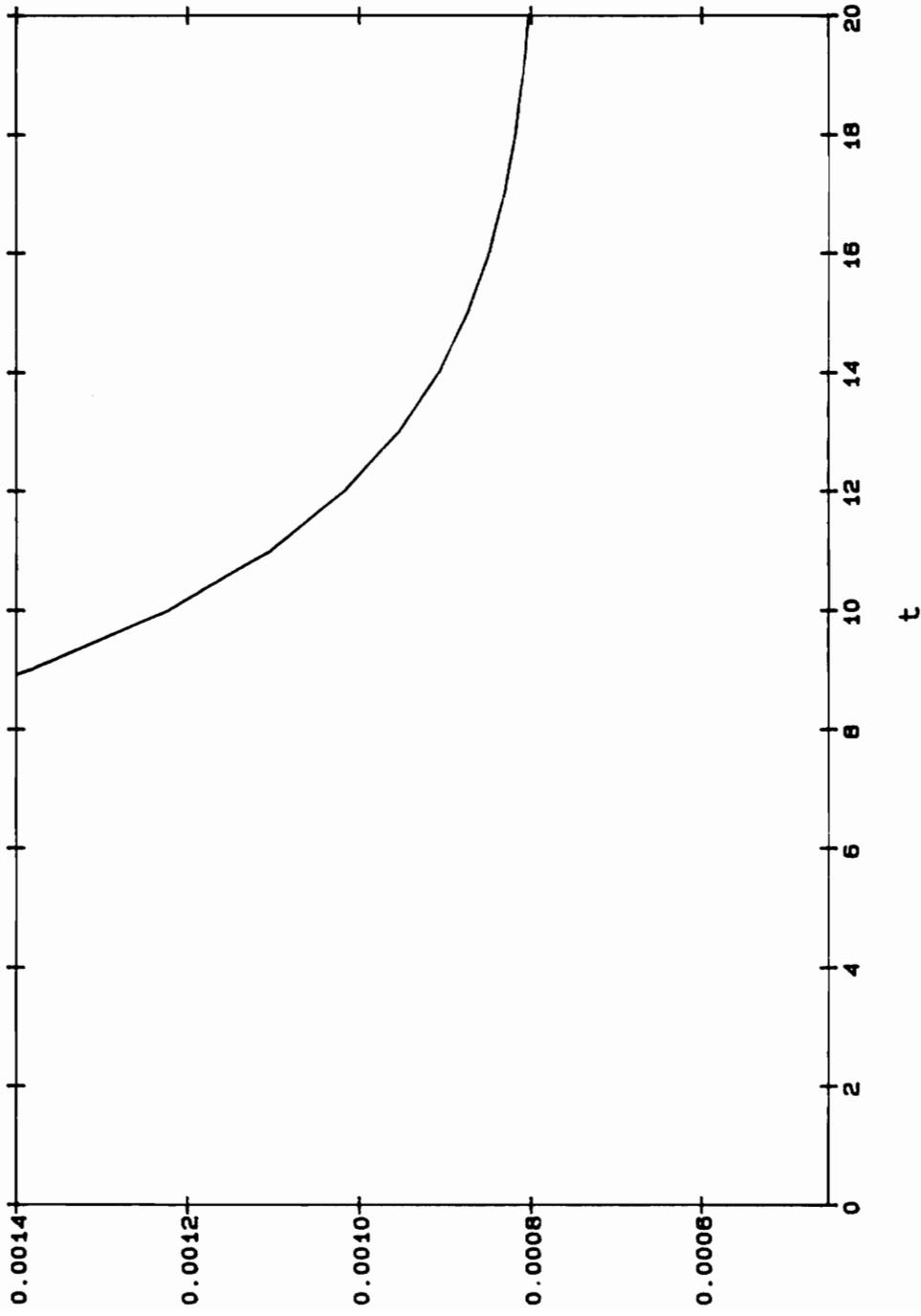


FIG. V.14 Same time interval, same initial data and same coupling constants as in FIG. V.9, for the convex combination relative to reaction (V.4).

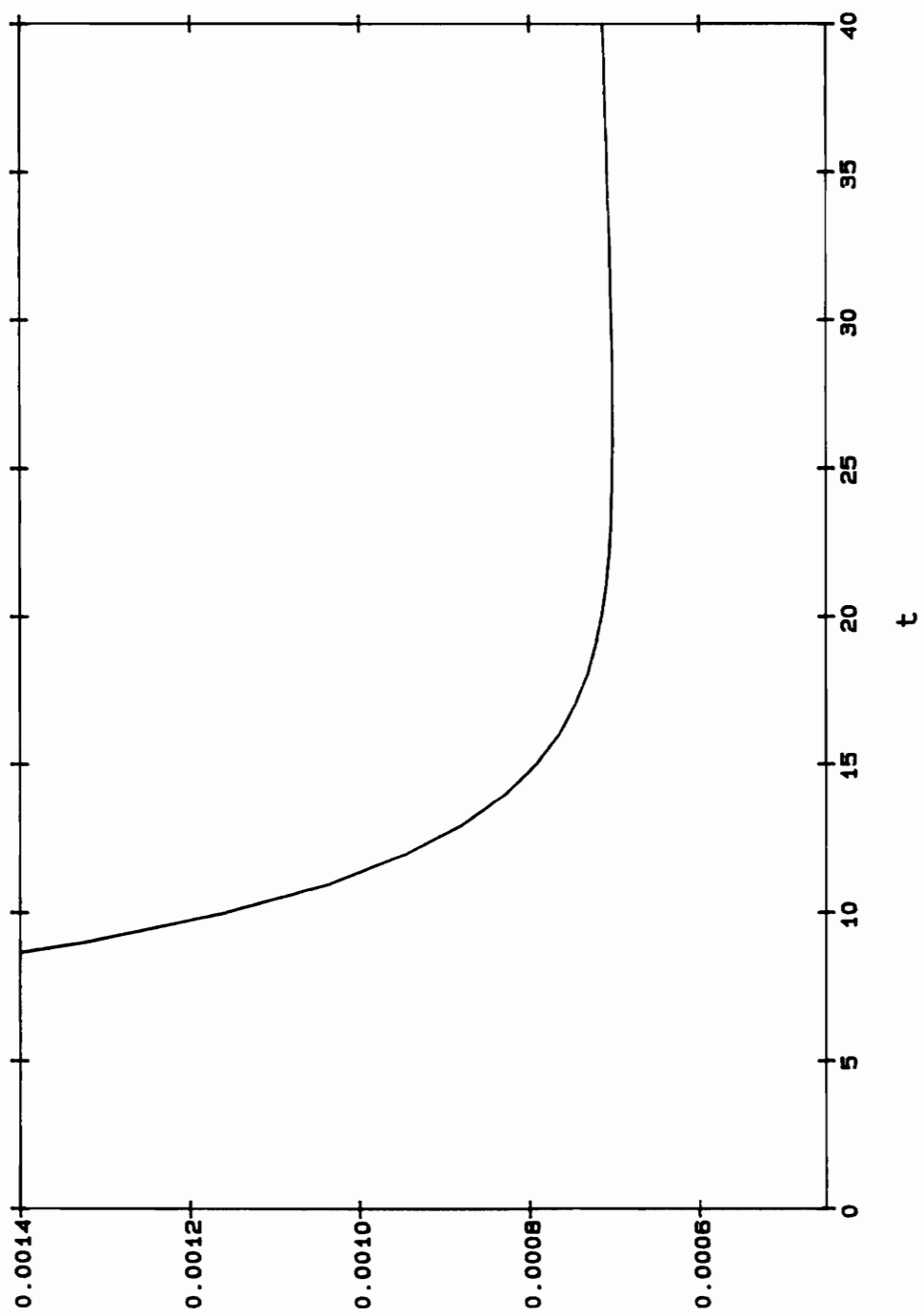


FIG. V.15 Same as FIG. V.14, with coupling constants equal to 0.25.

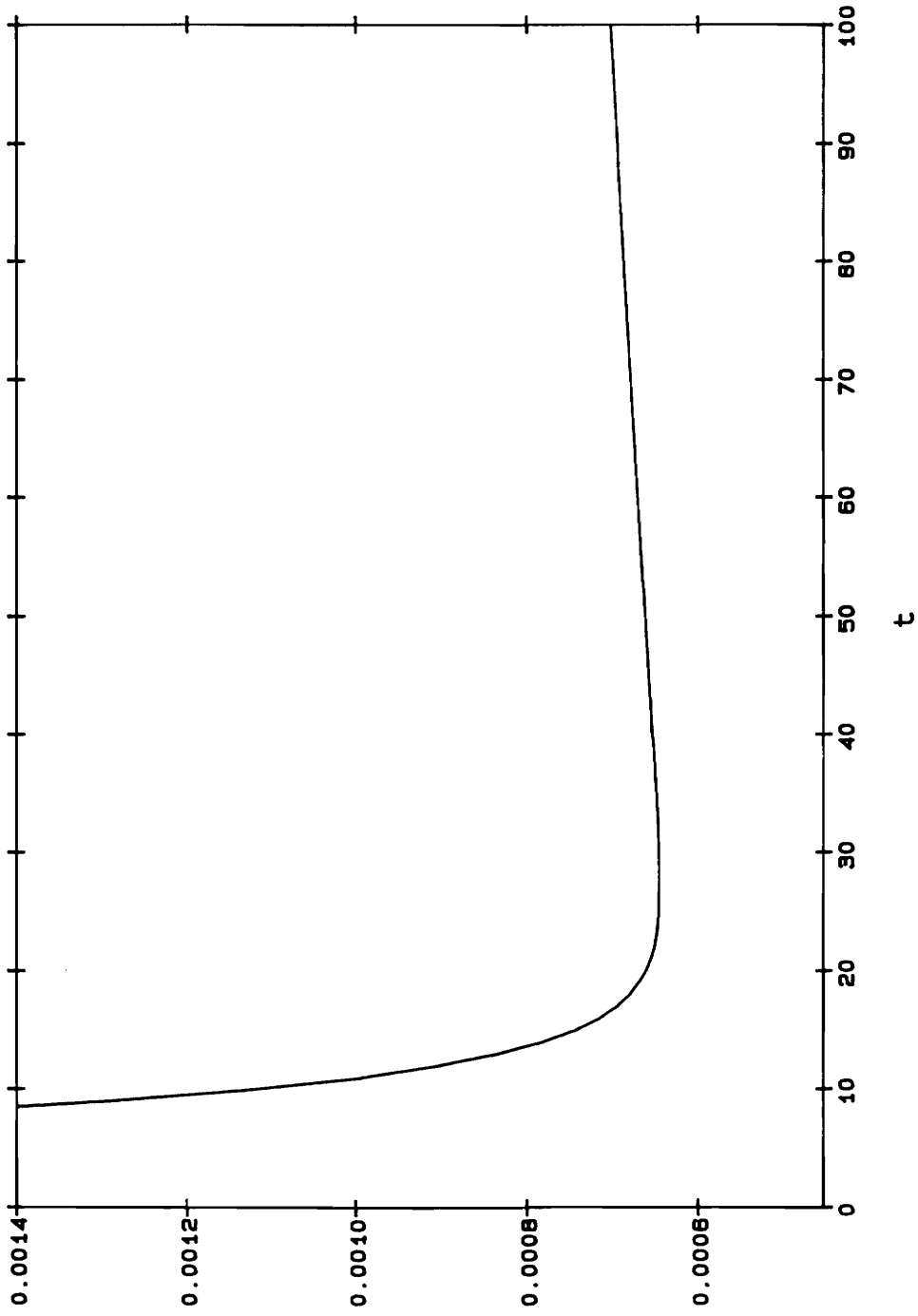


FIG. V.16 Same as FIG. V.14, with coupling constants equal to 0.1.

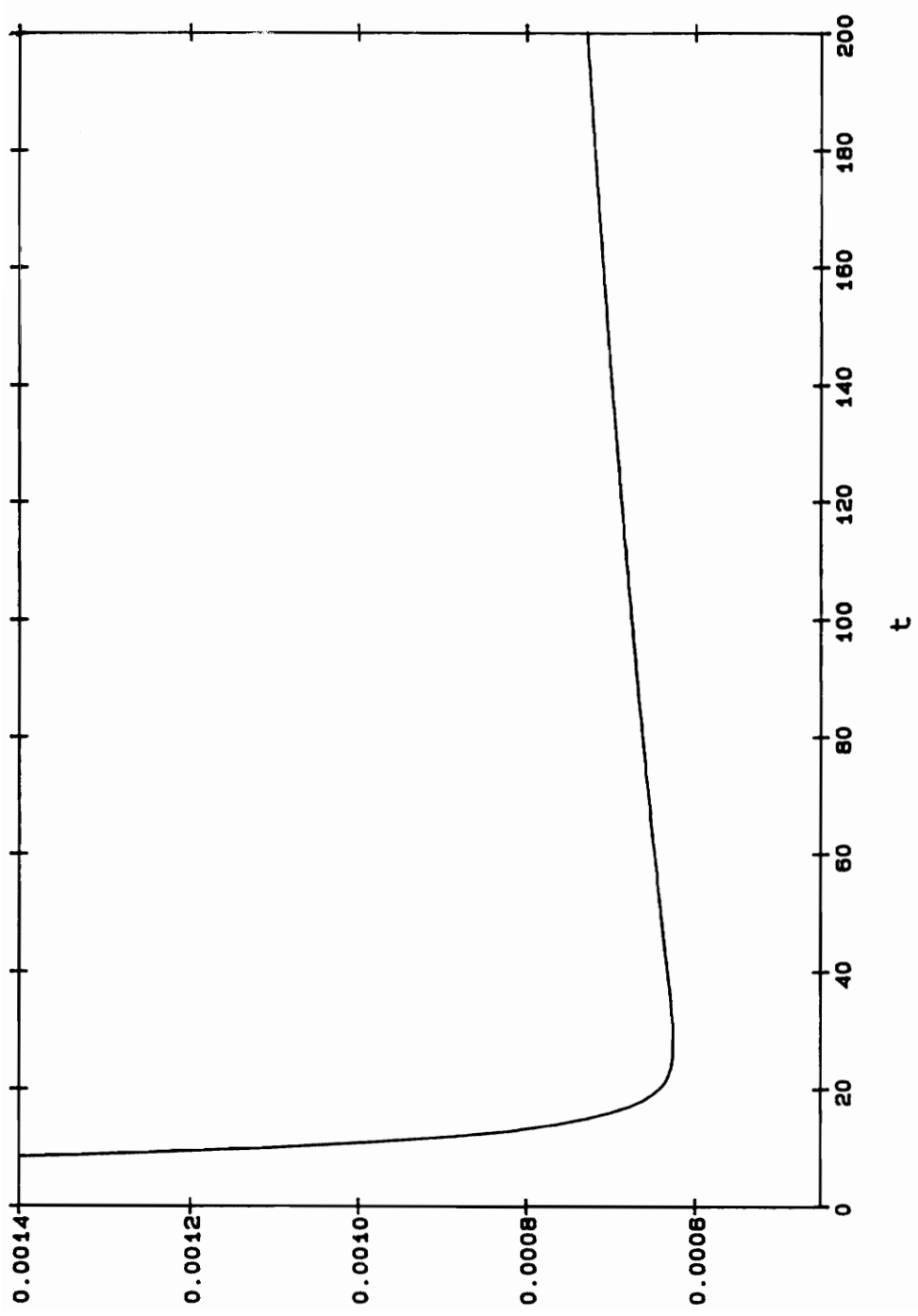


FIG. V.17 Same as FIG. V.14, with coupling constants equal to 0.05.

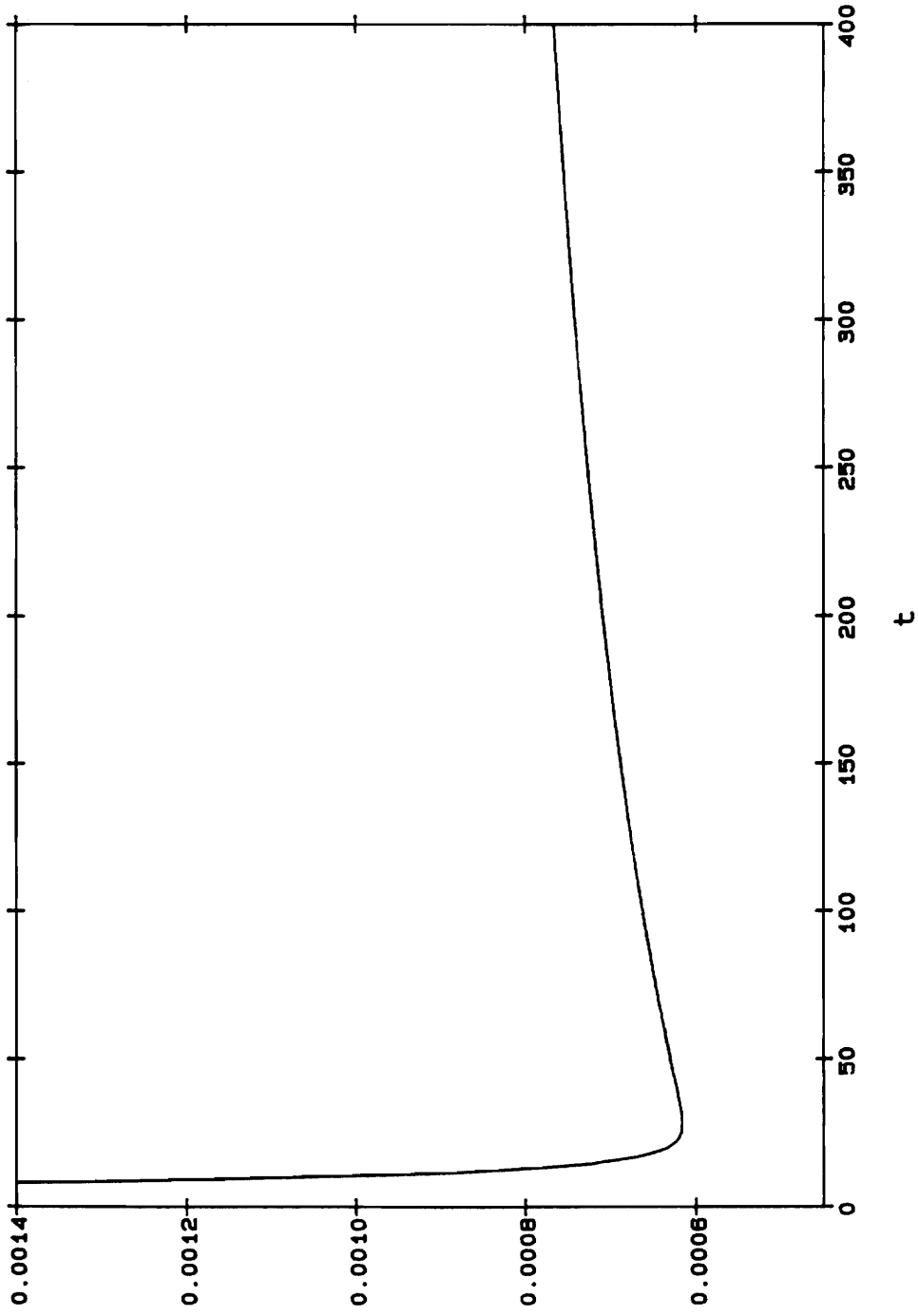


FIG. V.18 Same as FIG. V.14, with coupling constants equal to 0.025.

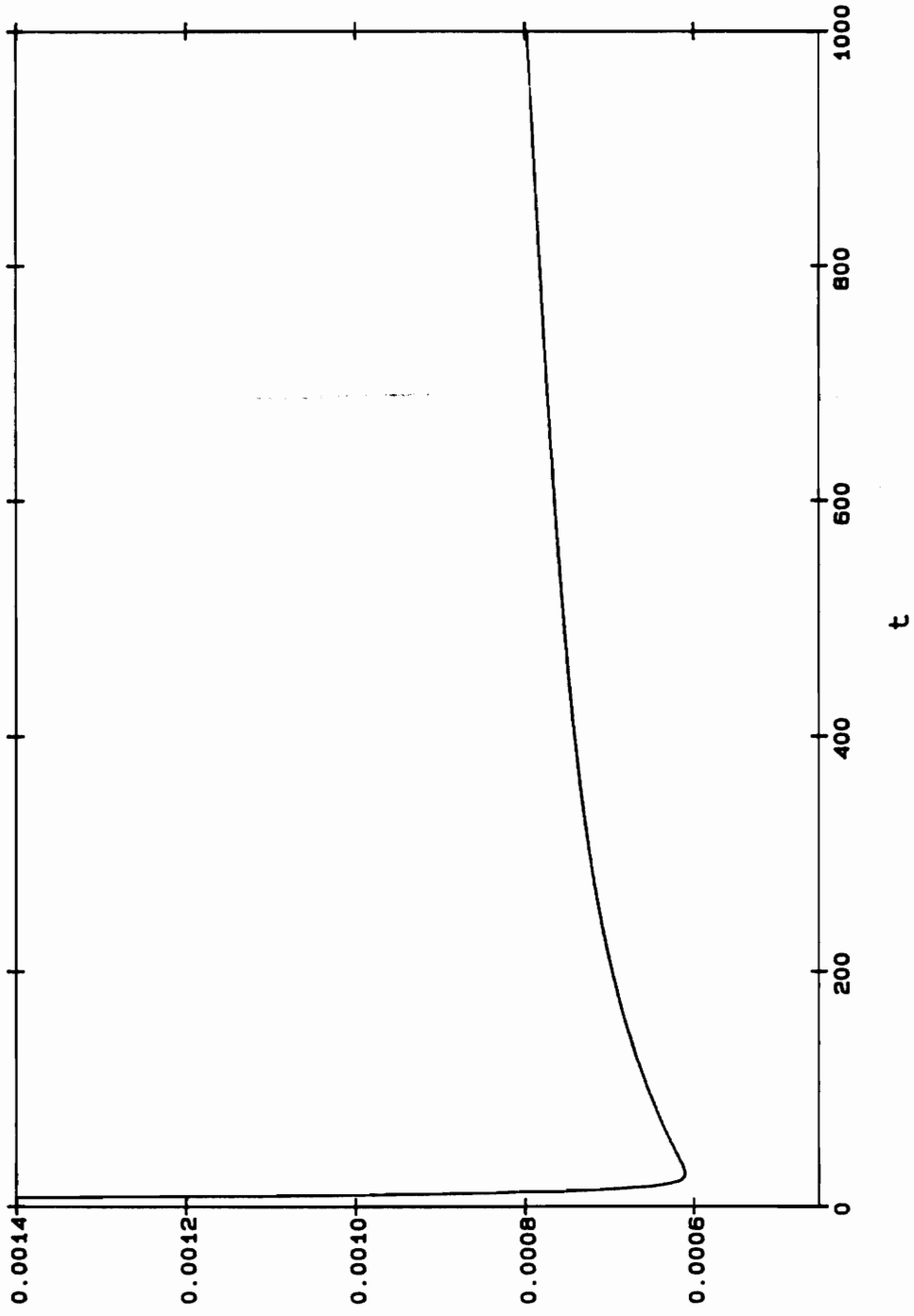


FIG. V.19 Same as FIG. V.14, with coupling constants equal to 0.01.

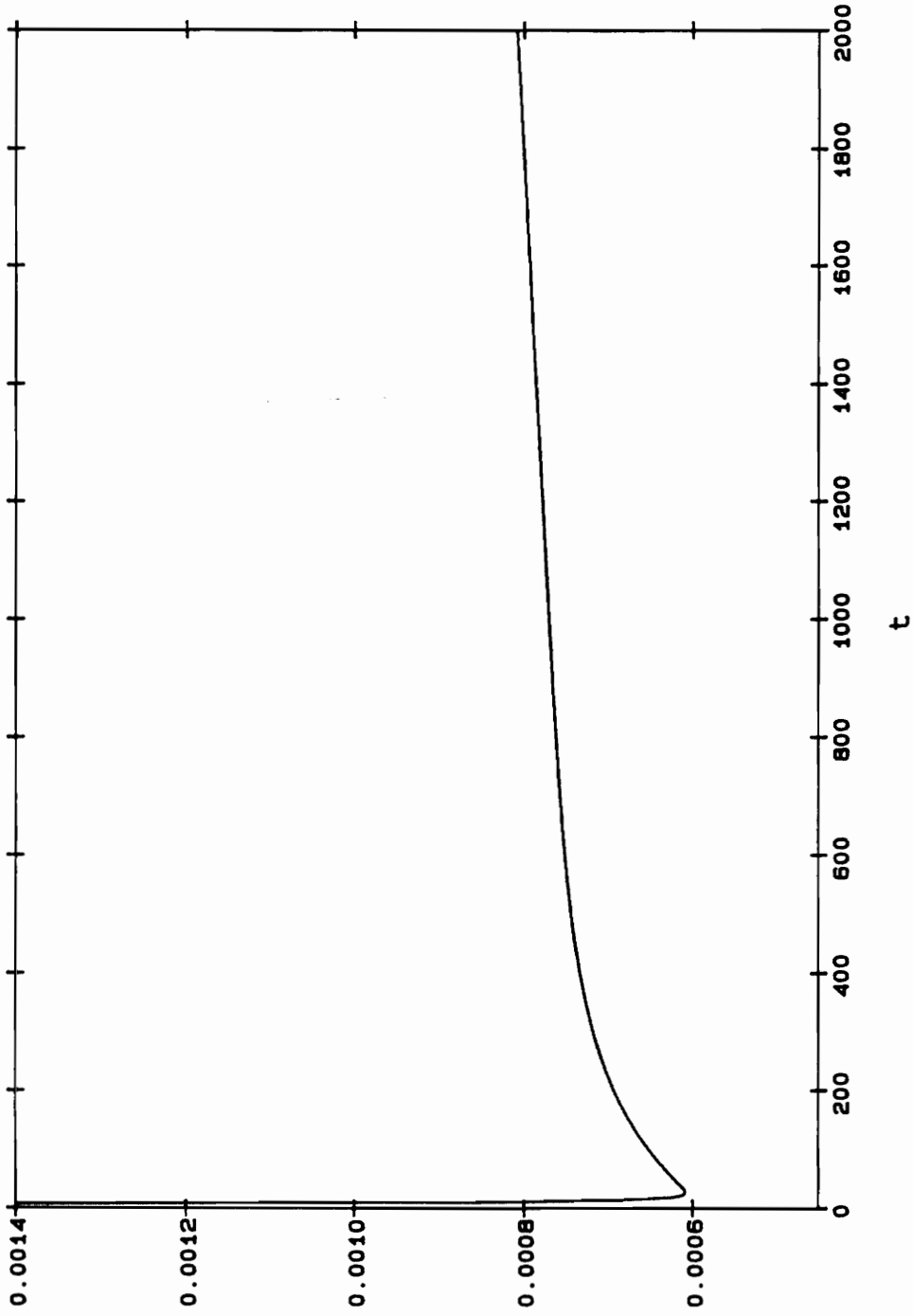


FIG. V.20 Same as FIG. V.14, with coupling constants equal to 0.005.



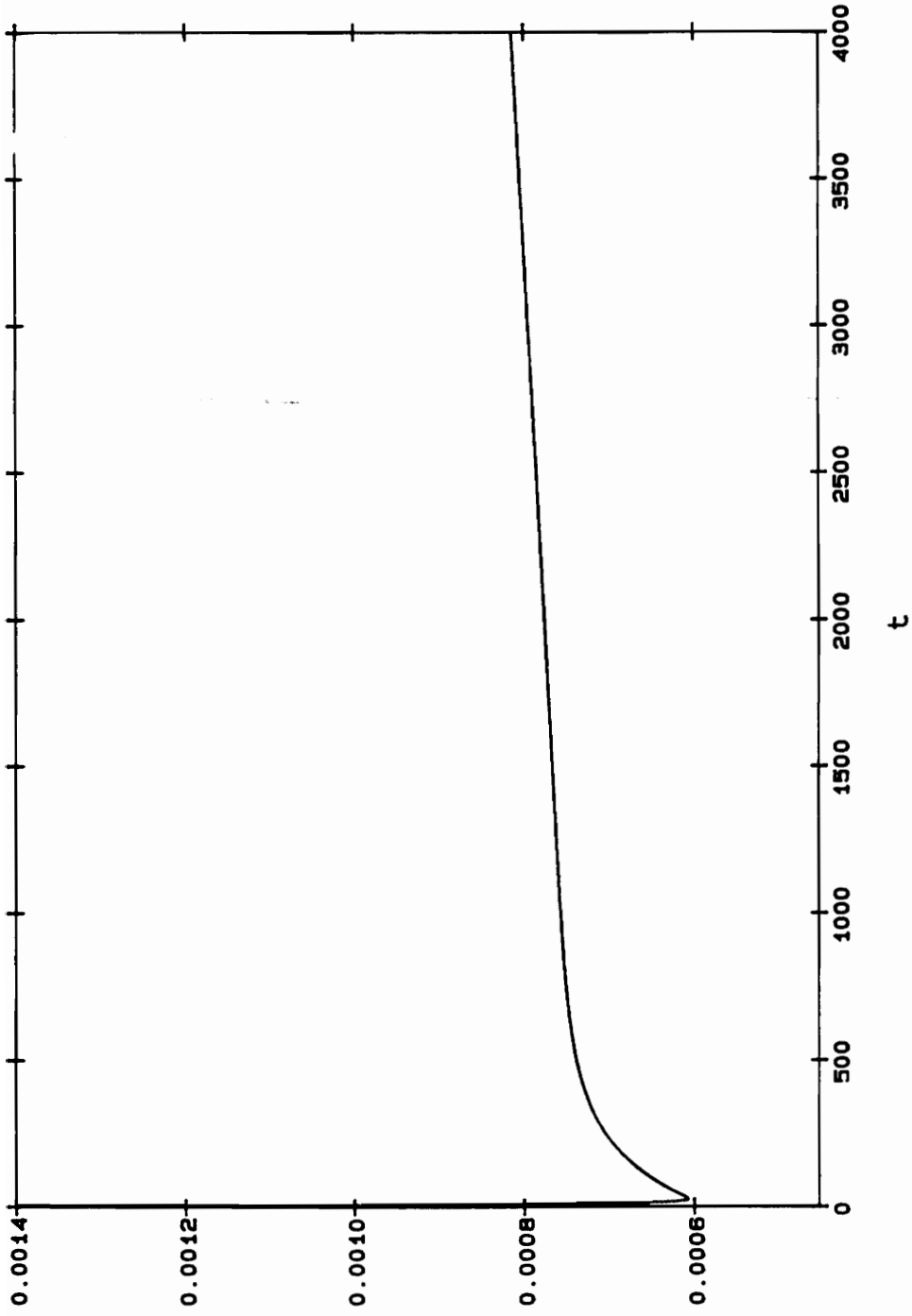


FIG. V.21 Same as FIG. V.14, with coupling constants equal to 0.0025.

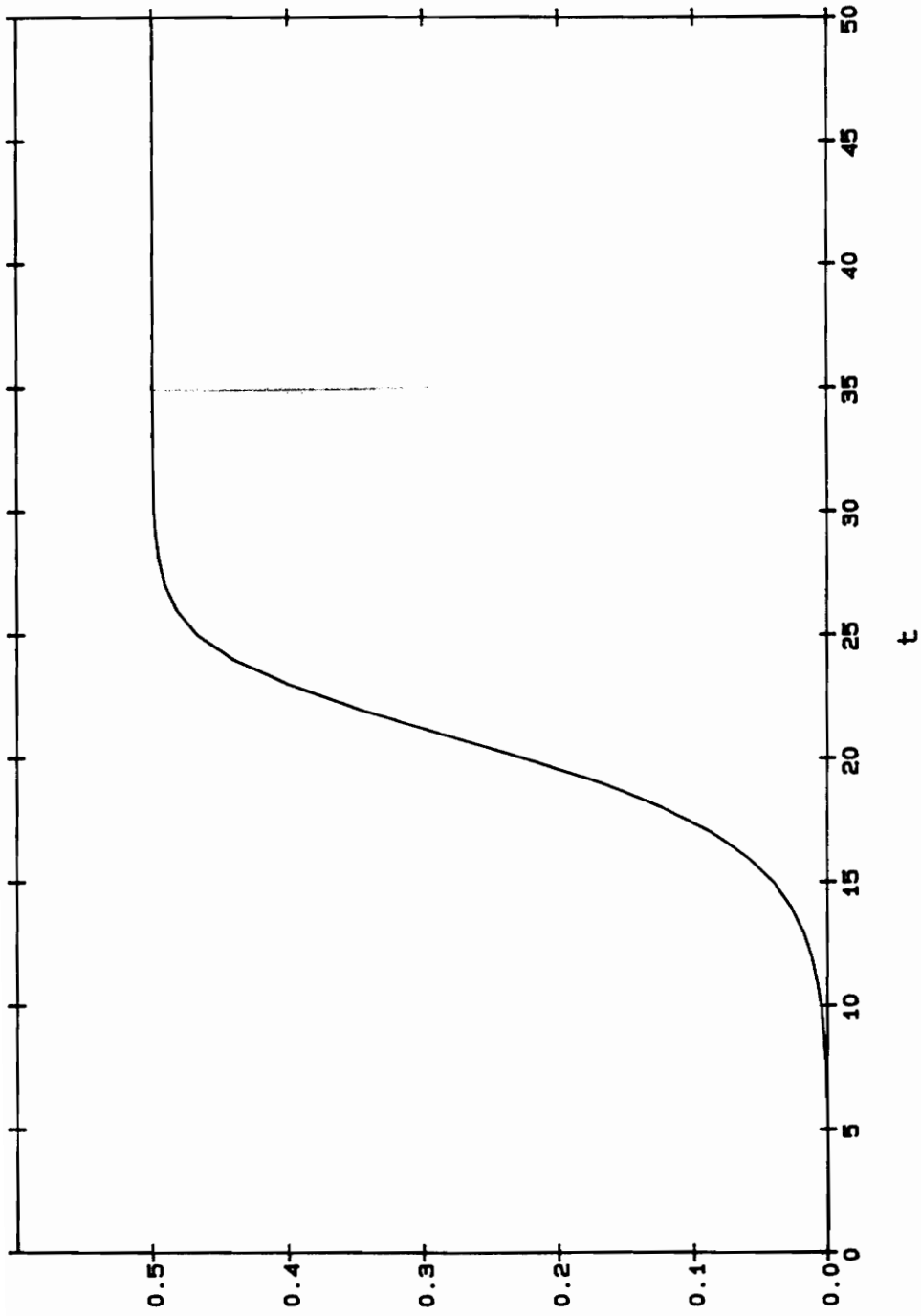


FIG. V.22 Result of 50 iterations of the map defined by (V.5), for  $p=0.00015$  and coupling constant equal to 0.5 (the bistochasticity limit).

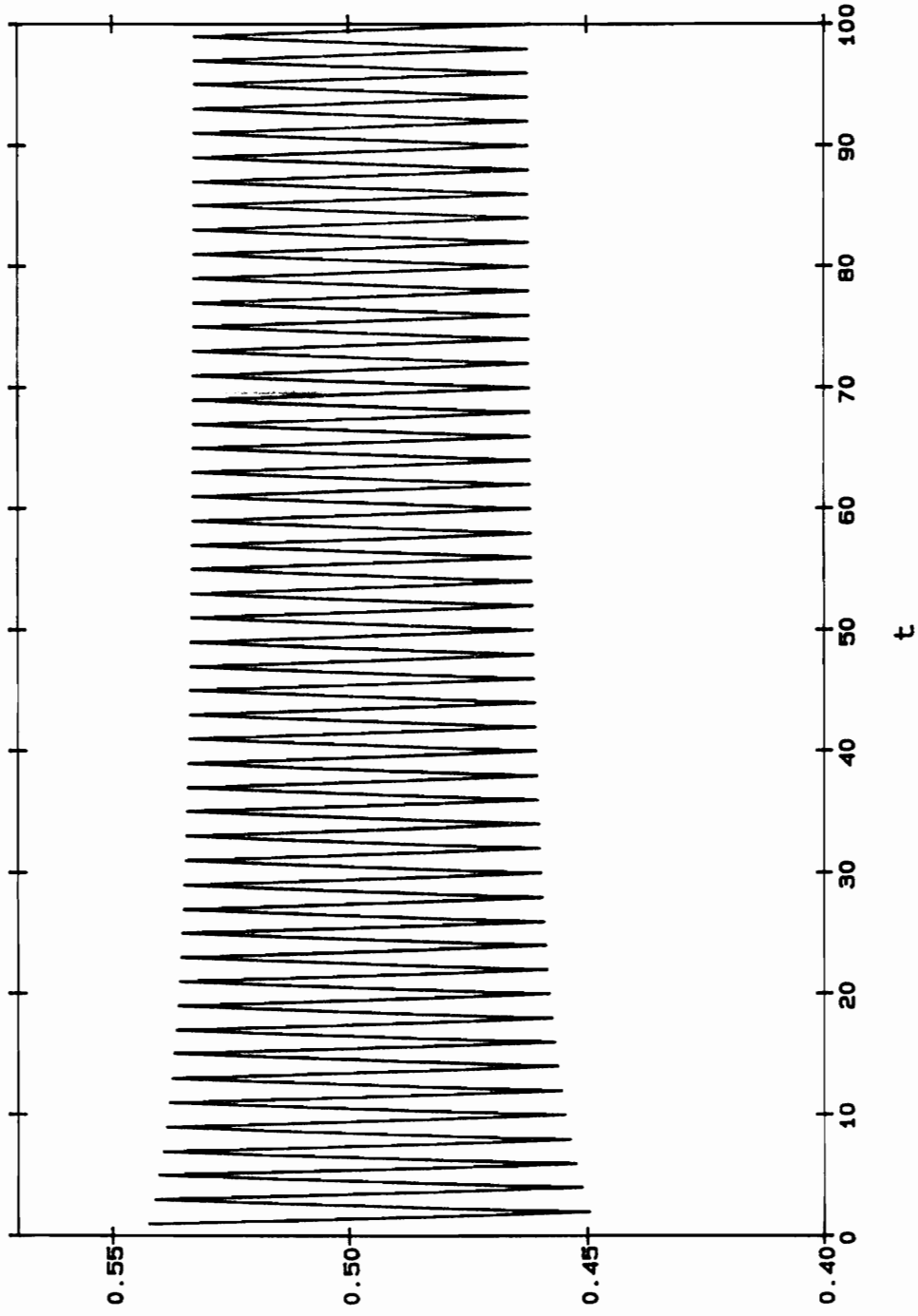


FIG. V.23 100 iterations of the same map as in FIG. V.22, with coupling constant equal to 2.02. A period 2 orbit is rapidly reached.

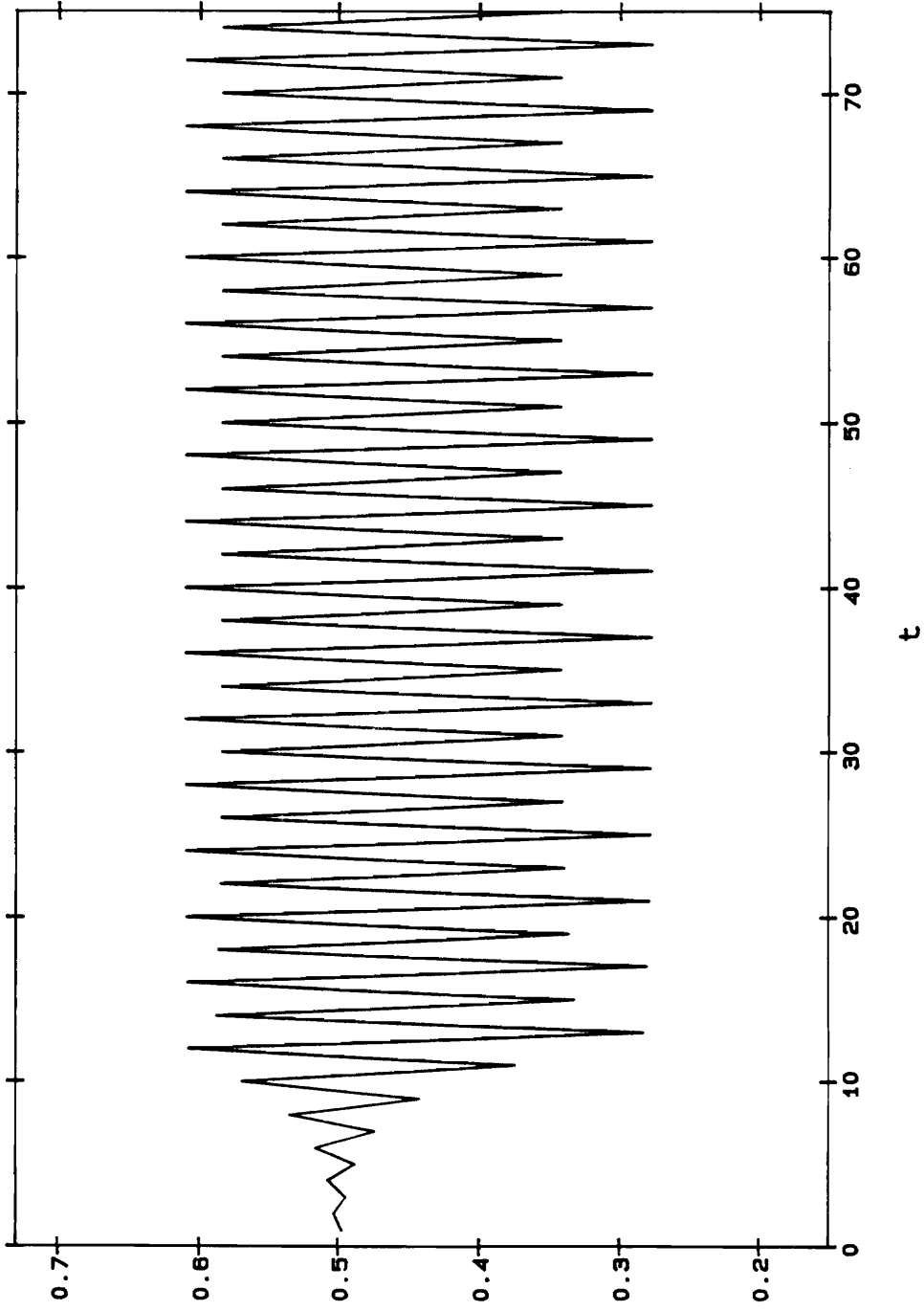


FIG. V.24 80 iterations of the same map as in FIG. V.22, with coupling constant equal to 2.48. A period 4 orbit is rapidly reached.

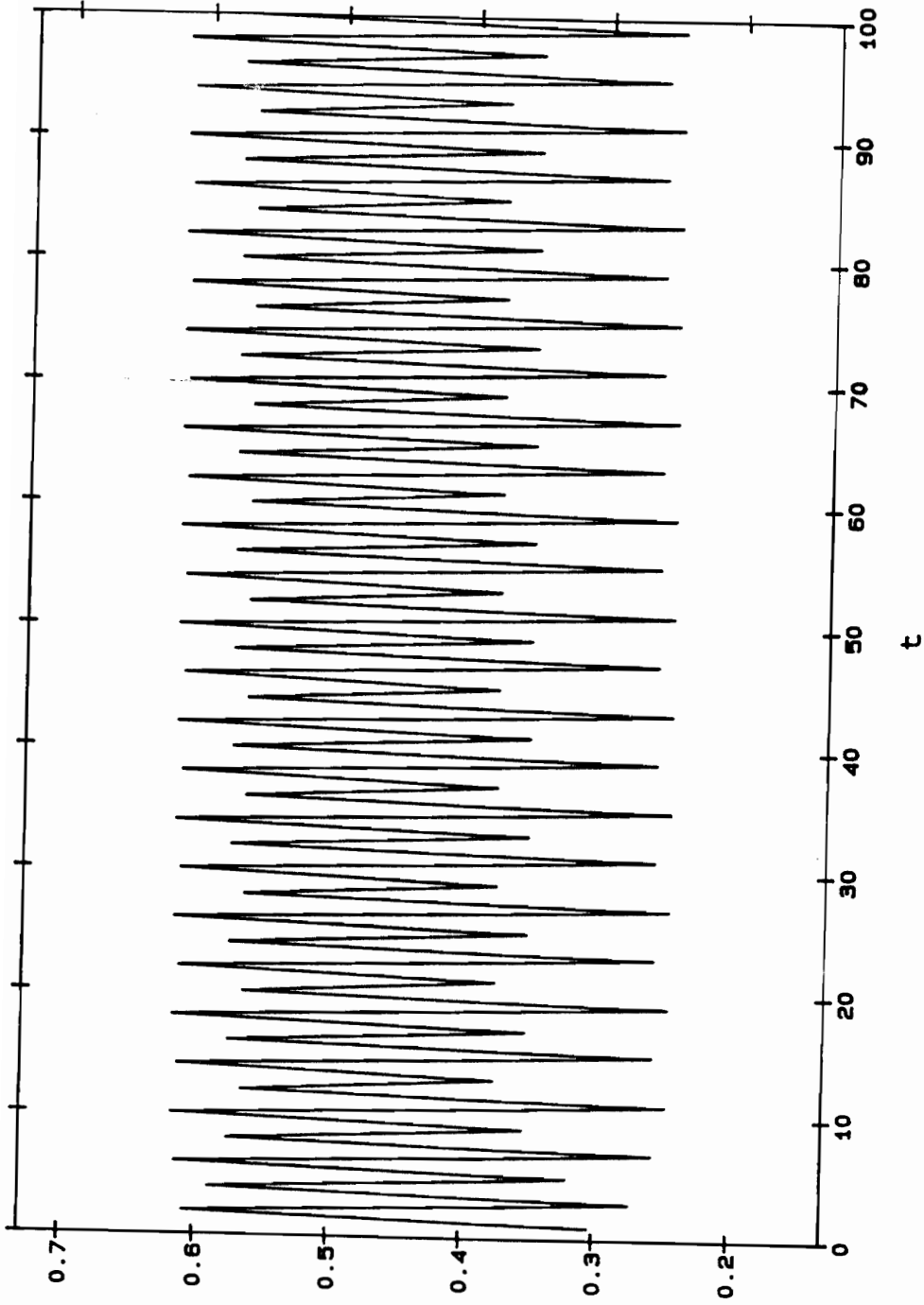


FIG. V.25 100 iterations of the same map as in FIG. V.22, with coupling constant equal to 2.55. A period 8 orbit is rapidly reached.

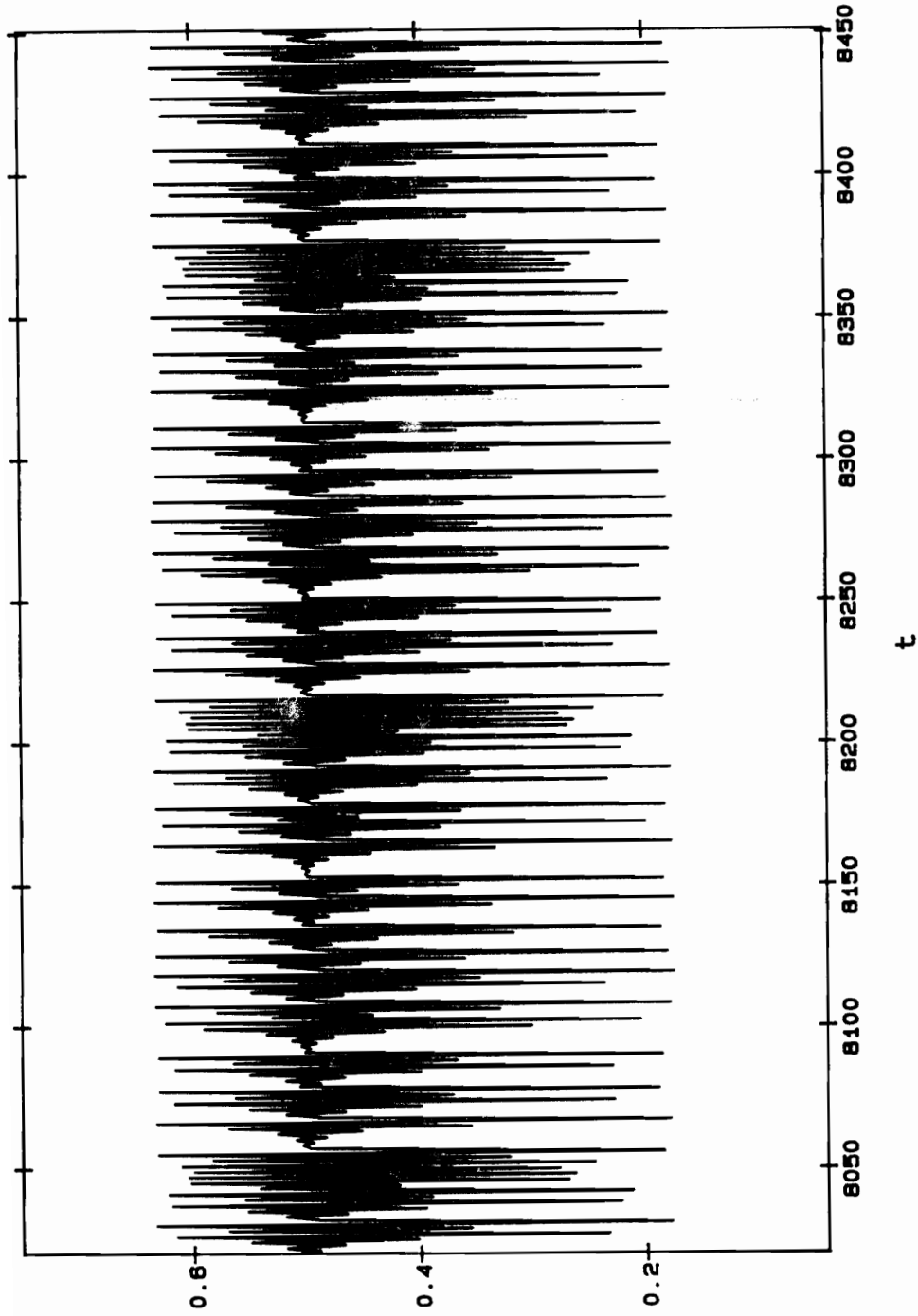


FIG. V.26 Chaos from the same map as in FIG. V.22, with coupling constant equal to 2.7. After 8000 iterations no periodic orbit is observed.

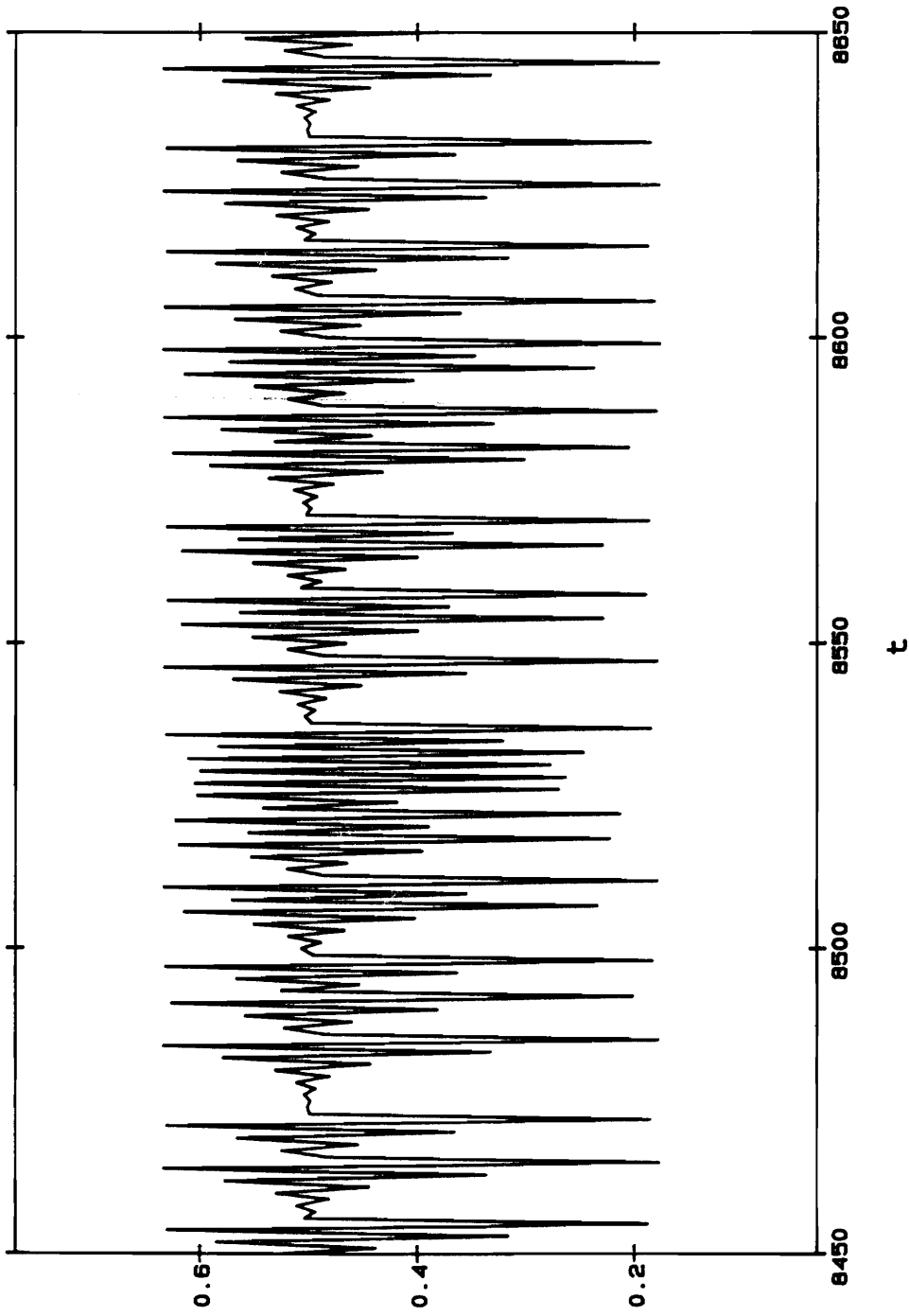


FIG. V.27 More iterations of the same map as in FIG. V.22, with coupling constant equal to 2.7.

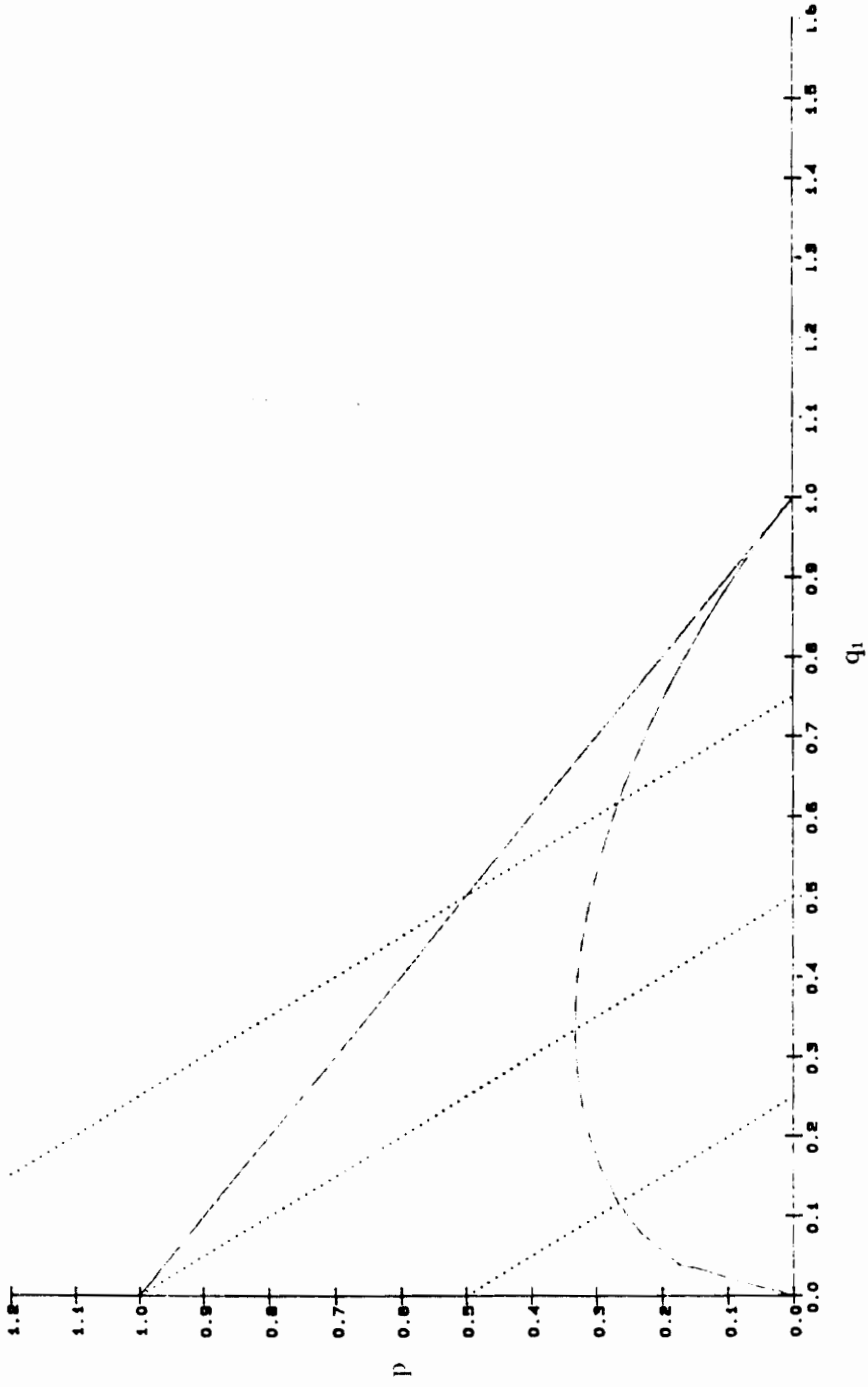


FIG. V.28 Manifold of the fixed points of  $2A = B + C$  (the curved line) in the  $q_1p$ -plane. The dotted lines represent three planes of the motion. The line joining  $(0,1)$  to  $(1,0)$  is the line where  $q_2$  is zero.



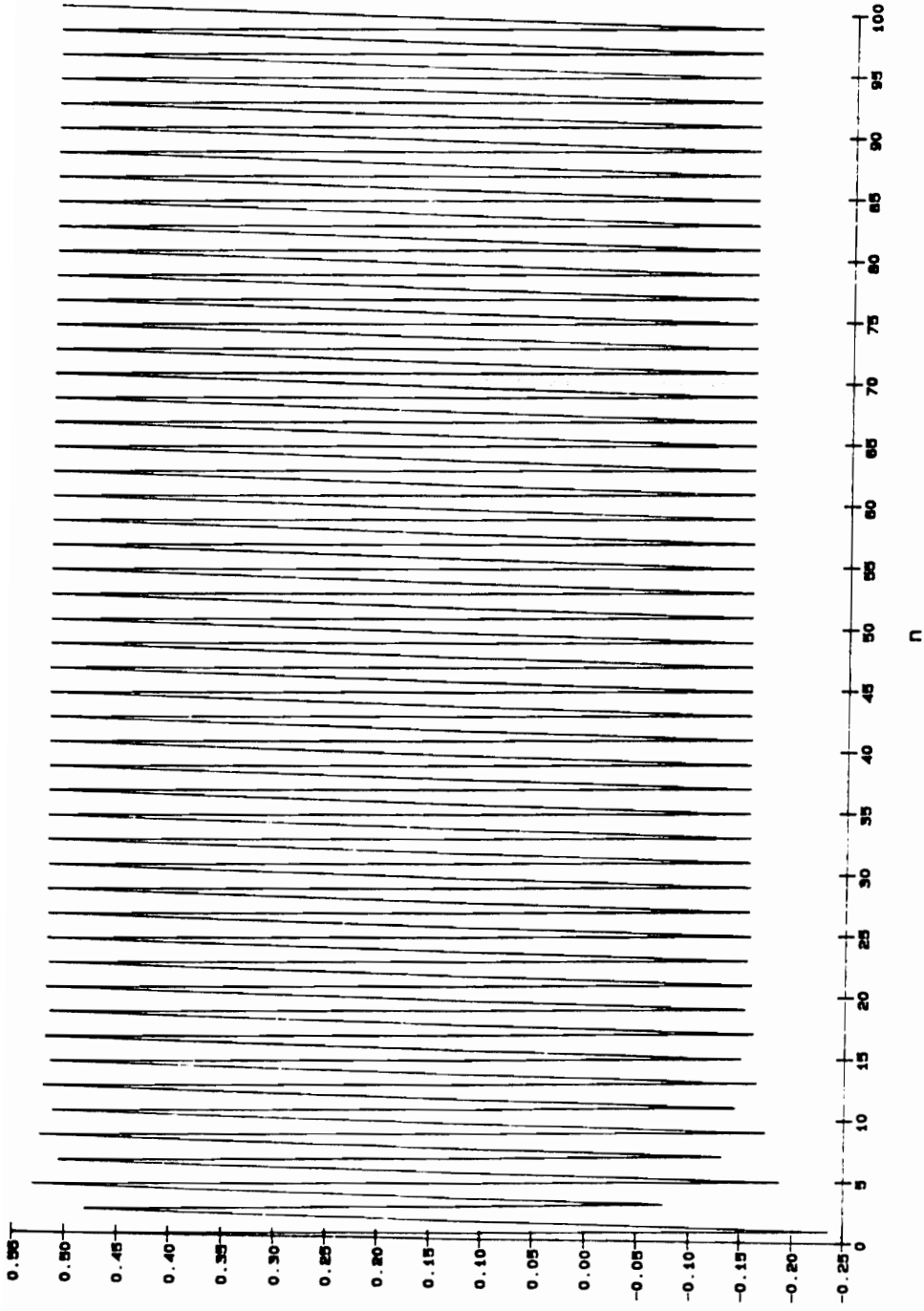


FIG. V.29 Period 2 for the map (V.6). Here  $p=0.55$ ,  $q_2=0.005$  and the coupling constant equals 1.3. Note the negative values of the iterates of  $p$ .

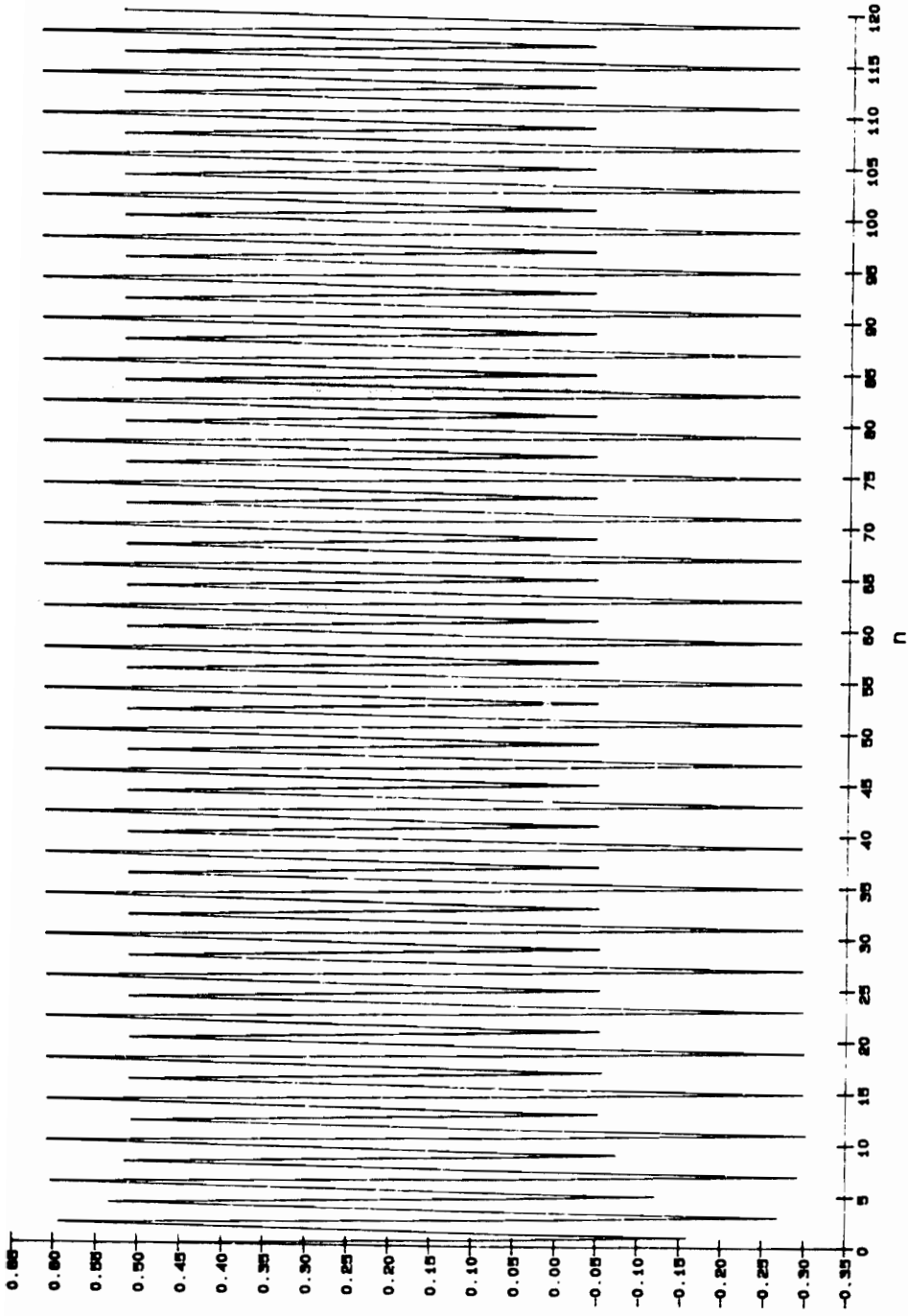


FIG. V.30 Period 4 for the map (V.6), with  $p=0.55$ ,  $q_2=0.02$ , and coupling constant equal to 1.3.

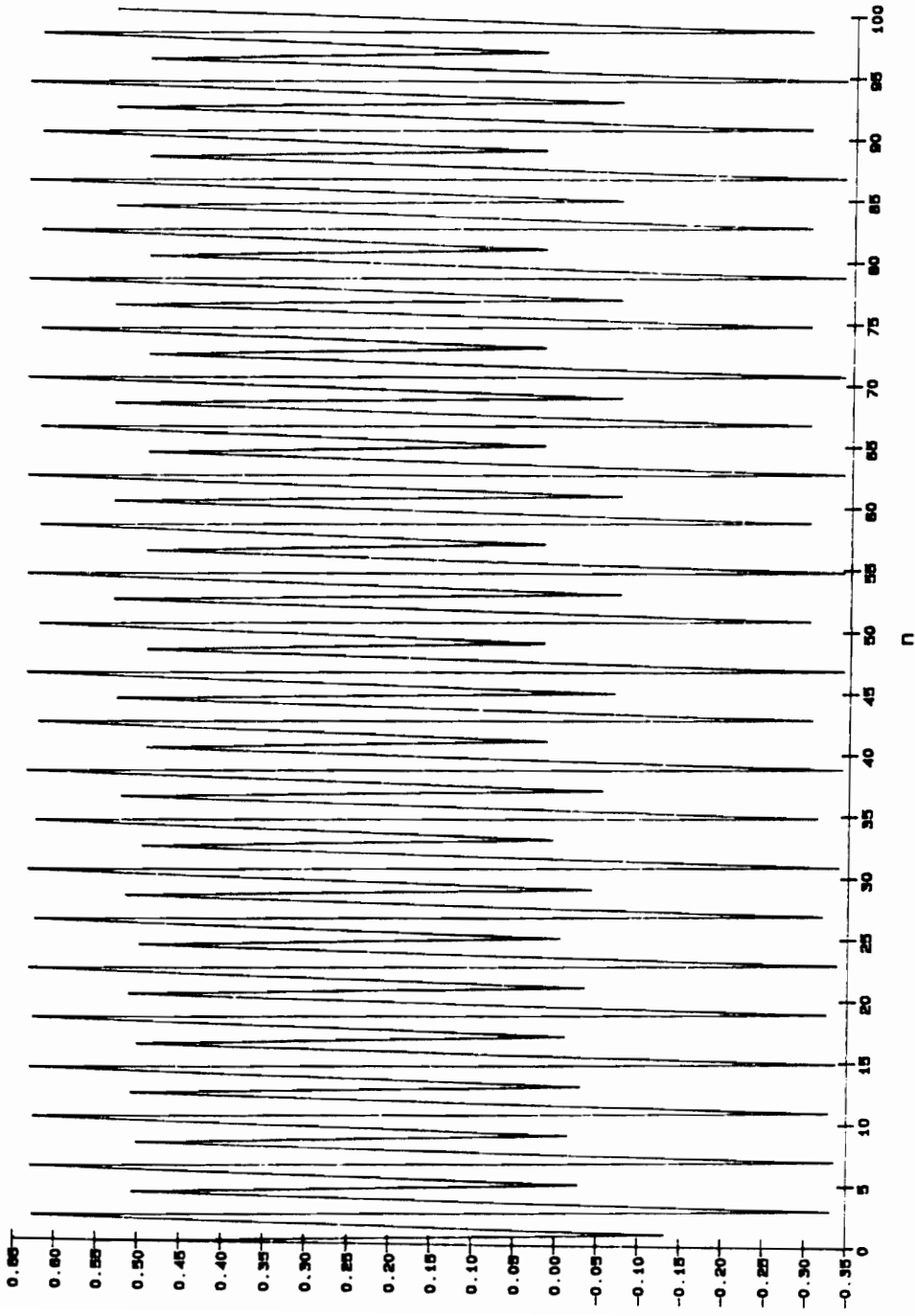


FIG. V.31 Period 8 for the map (V.6), with  $p=0.55$ ,  $q_2=0.1285$ , and coupling constant equal to 1.3.

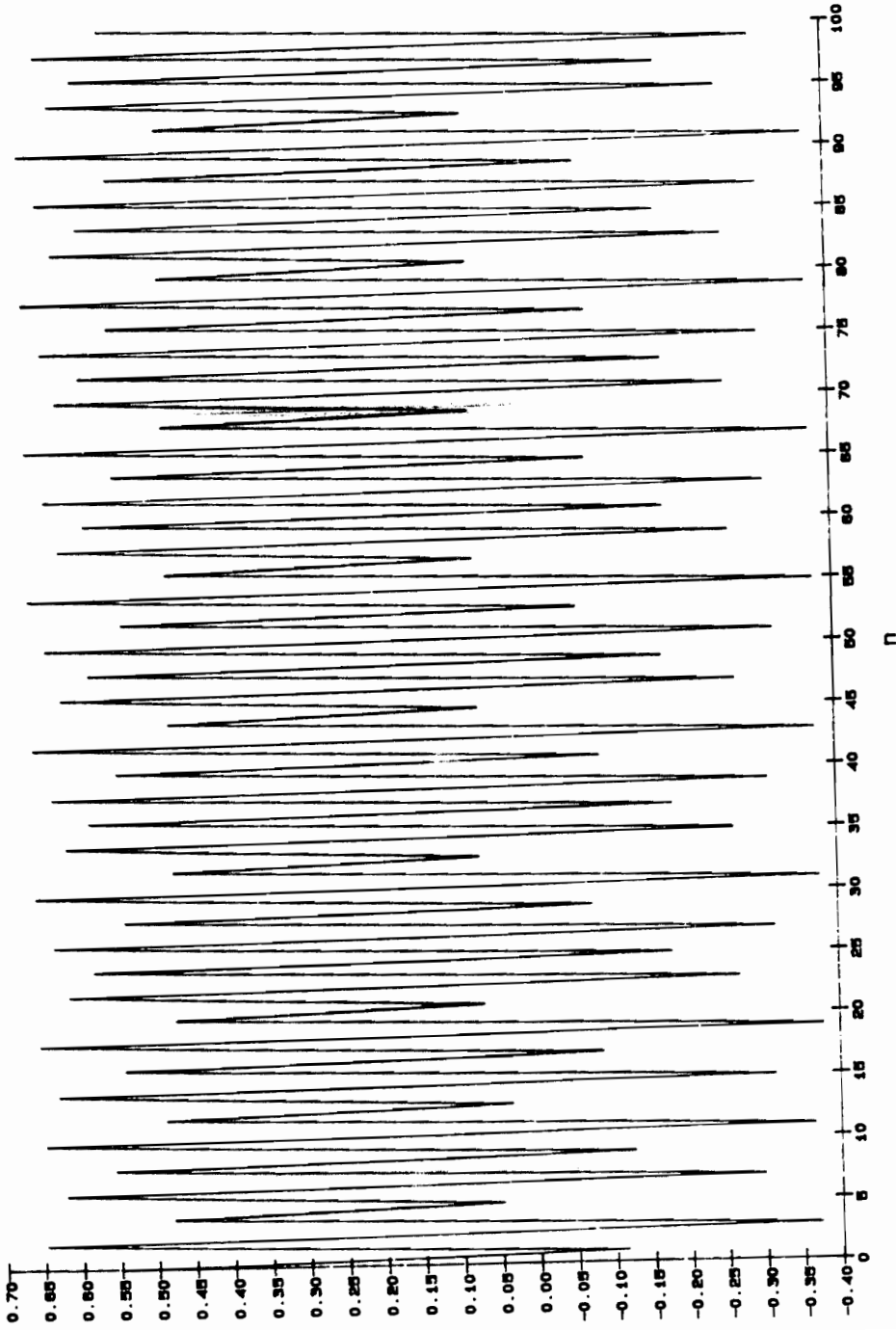


FIG. V.32 Almost periodic iterations—but chaotic indeed—for the map (V.6), with  $p=0.55$ ,  $q_1=0.1287$ , and coupling constant equal to 1.3.

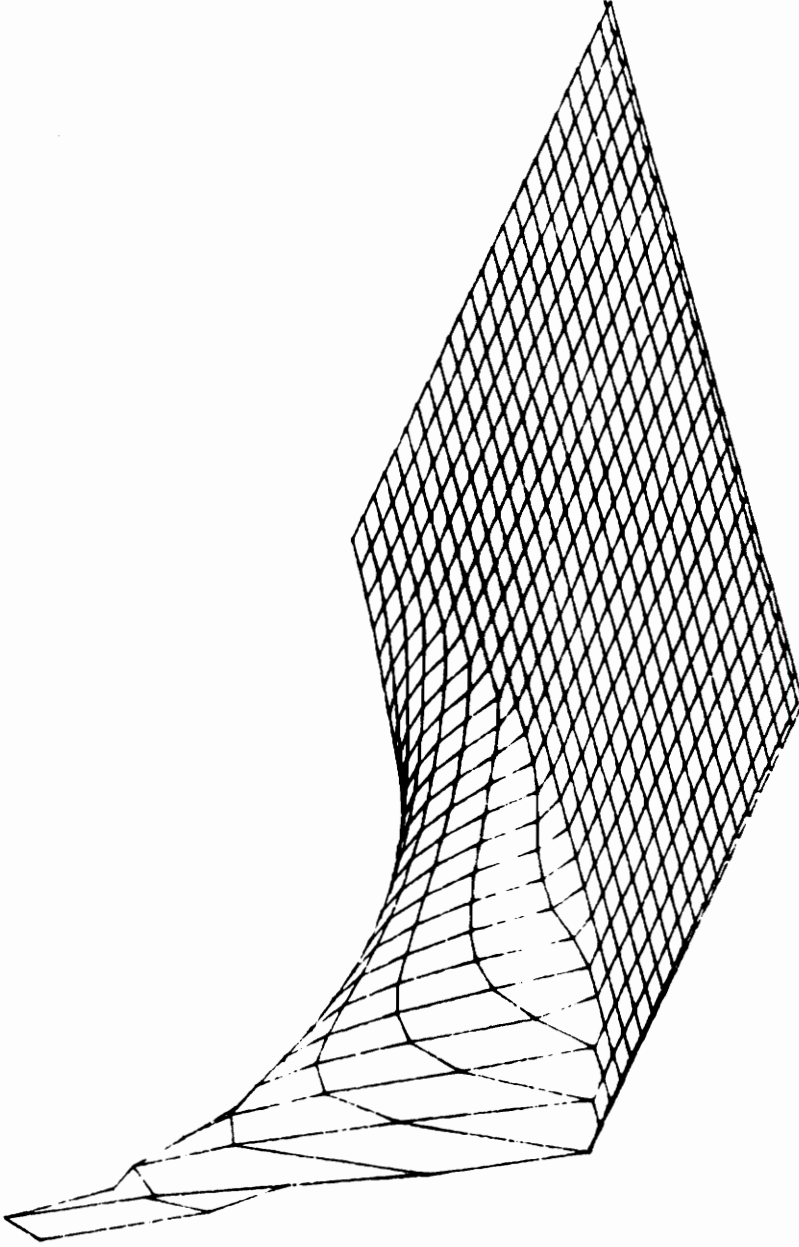


FIG V.33 The manifold of the fixed points of  $A + B = C + D$ .

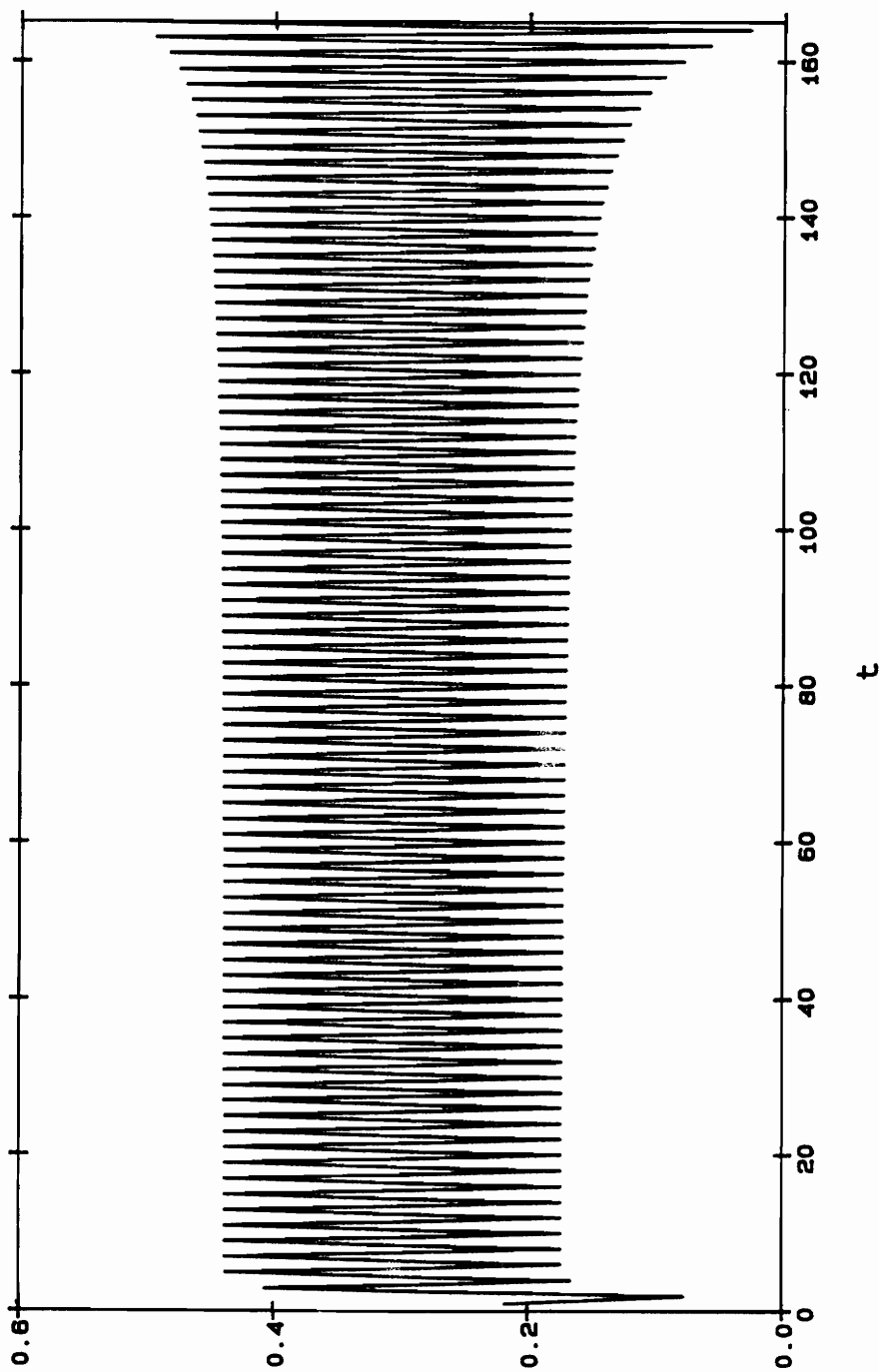


FIG. V.34 After many almost regular oscillations,  $p$  diverges, producing negative values as well. Here we have  $p(0)=0.001$  and  $q(0)=0.9$ . The coupling constants of the first and second reaction are respectively equal to 0.8714 and 0.813.

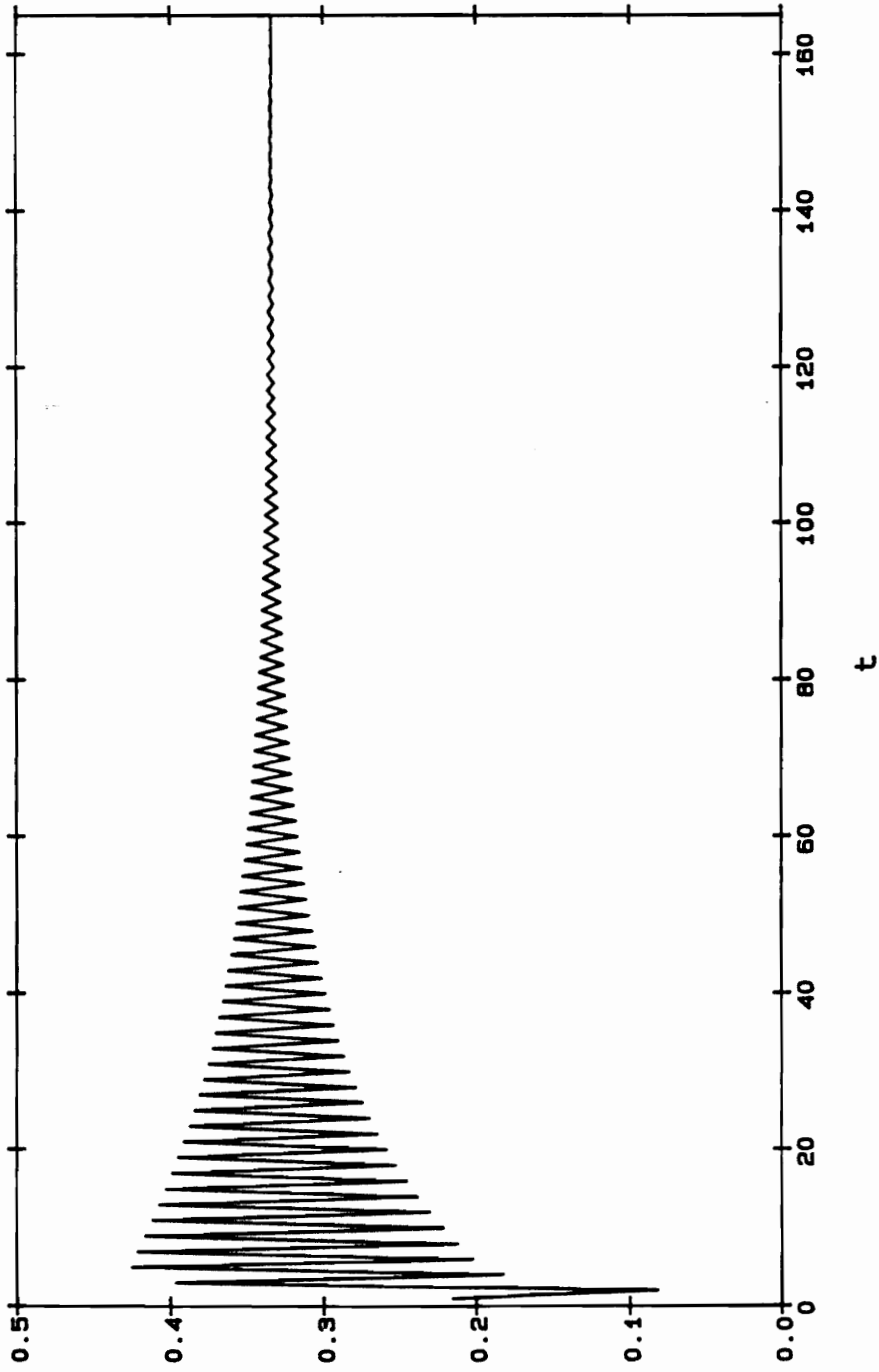


FIG. V.35 Same map and same initial conditions as in FIG. V.34. The first and the second coupling constants are respectively equal to 0.86 and 0.8.

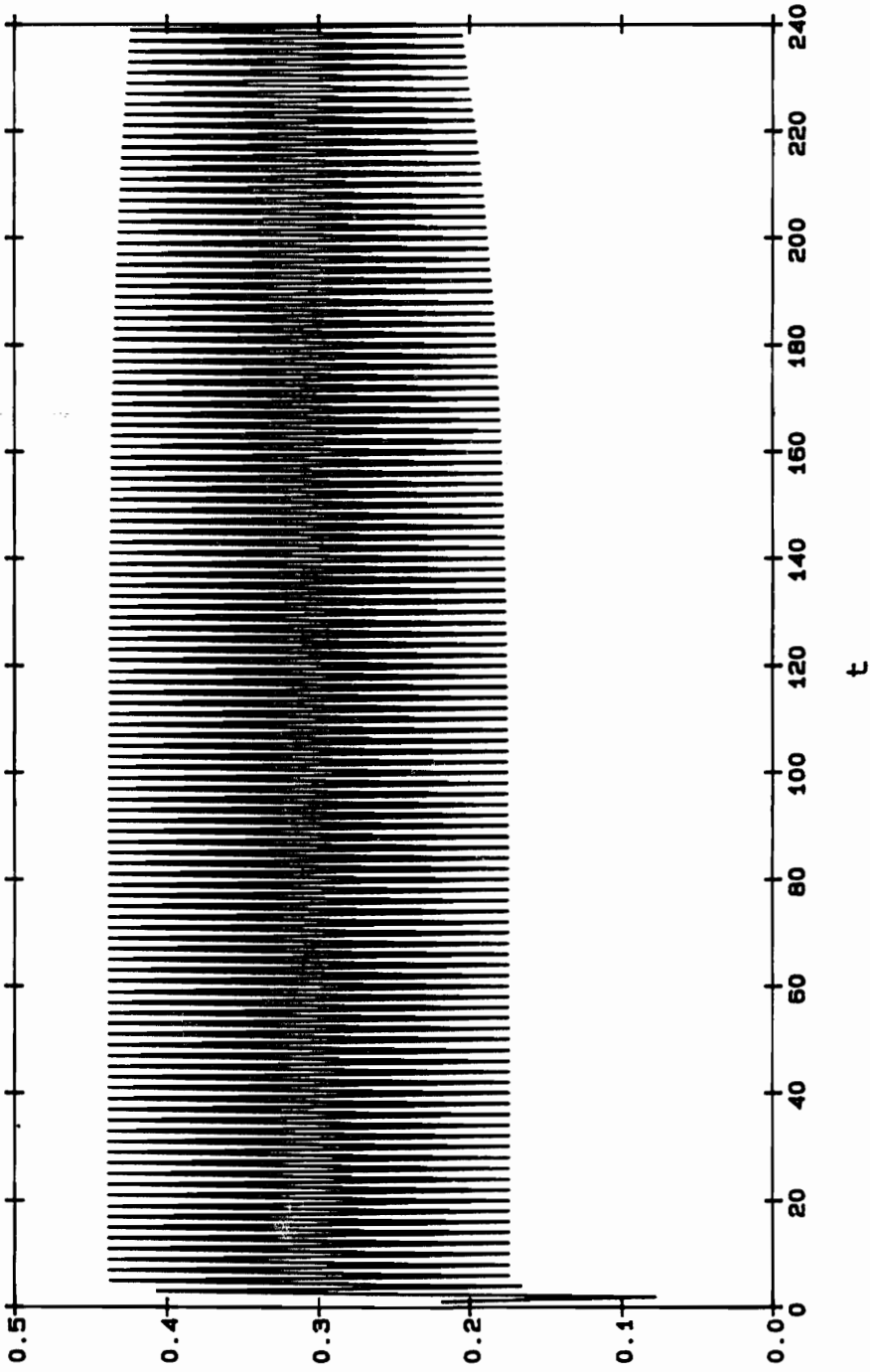


FIG. V.36 Same map and same initial conditions as in FIG. V.34. The first and the second coupling constants are respectively equal to 0.87133 and 0.813.



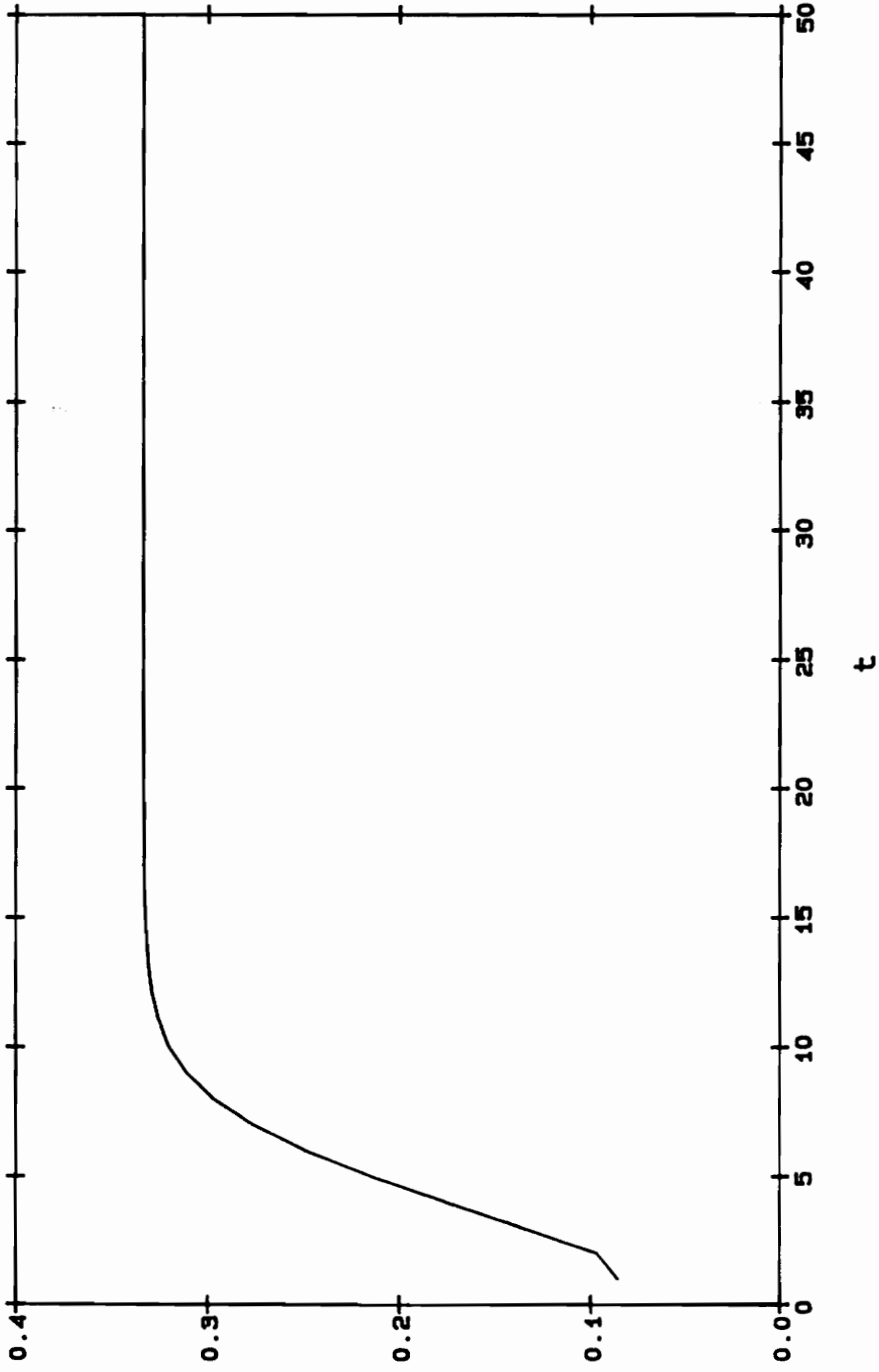
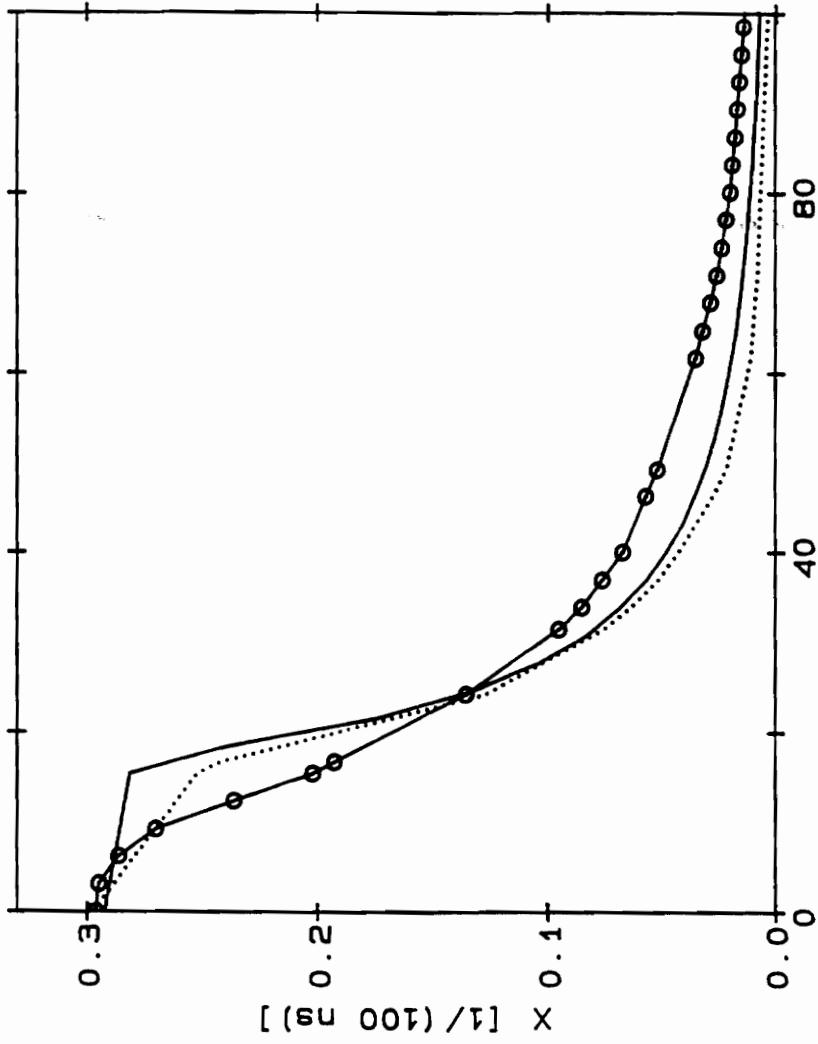


FIG. V.37 Same map and same initial conditions as in FIG. V.34. The first and the second coupling constants are equal to their bistochasticity limits, i.e.  $1/3$  and  $1/2$ .



**t ( 10 ns)**

FIG. VII.1 Comparison between our calculation (the solid line) and FIG.5 in [44] for the case where  $E_0=2$  eV,  $T=300$  K,  $d=0.23$  cm,  $p=0.188$  bar. Here, the solid line with circles gives the result of a Montecarlo simulation, while the dotted line represents what can be obtained by the method presented in [44].

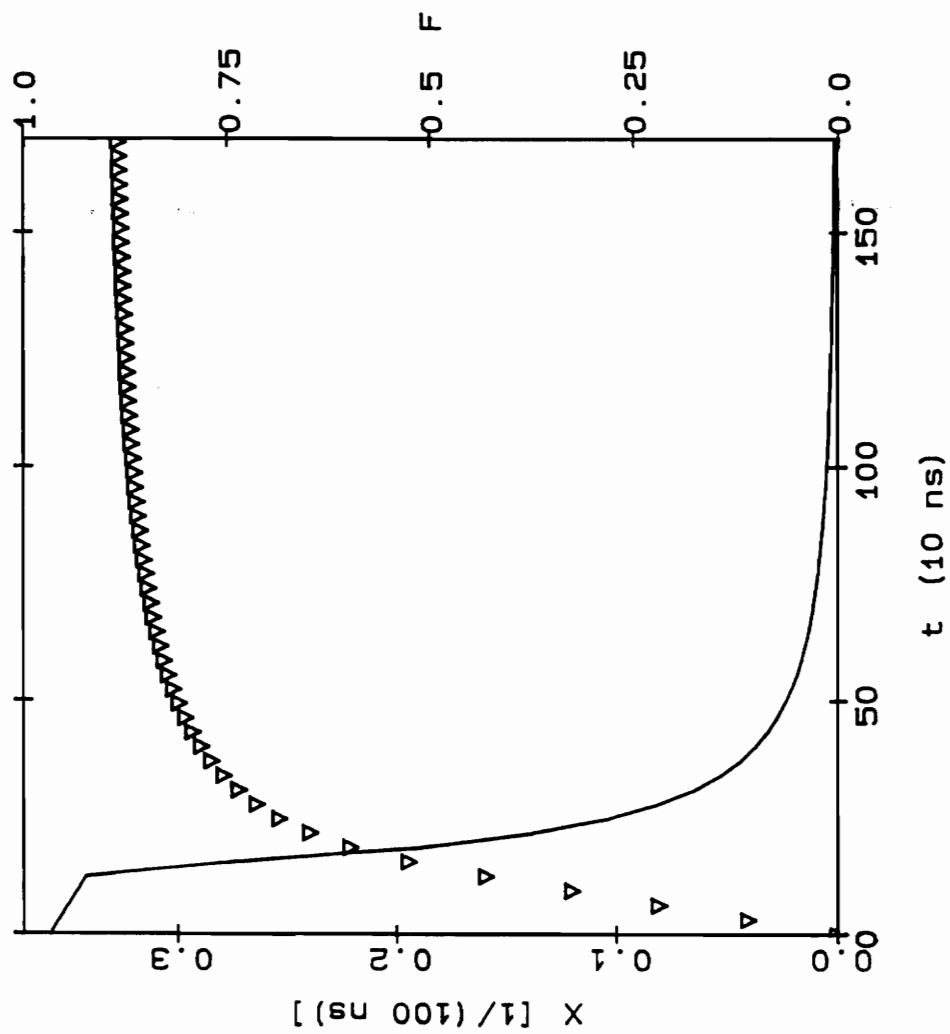


FIG. VII.2  $E_0=3$  eV,  $T=500$  K,  $d = 0.23$  cm,  $p=0.375$  bar. After 1.7 microseconds the flux has become negligible. The contribution of 0th and 1st order will exceed 85 percent.

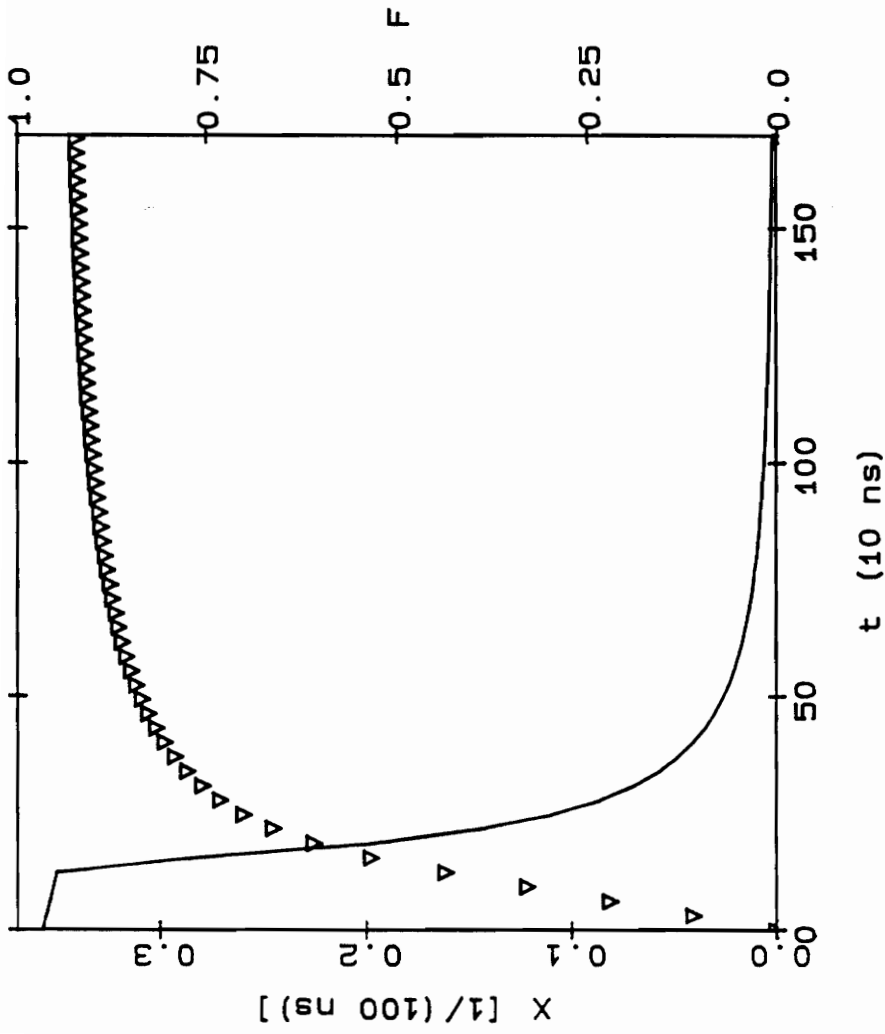


FIG. VII.3  $E_0 = 3$  eV,  $T = 1200$  K,  $d = 0.23$  cm,  $p = 0.375$  bar. The contribution of 0th and 1st order exceeds 90 percent.

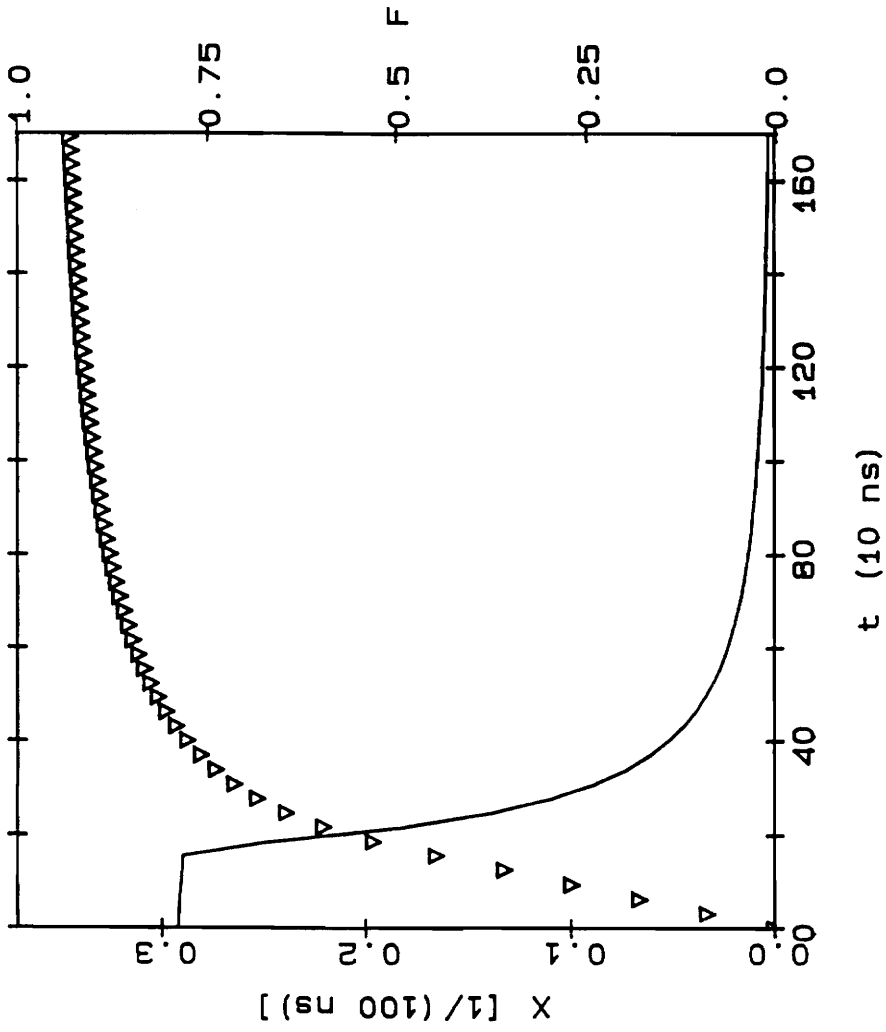


FIG. VII.4  $E_0 = 2$  eV,  $T = 1200$  K,  $d = 0.23$  cm,  $p = 0.188$  bar. The contribution of 0th and 1st order exceeds 90 percent.

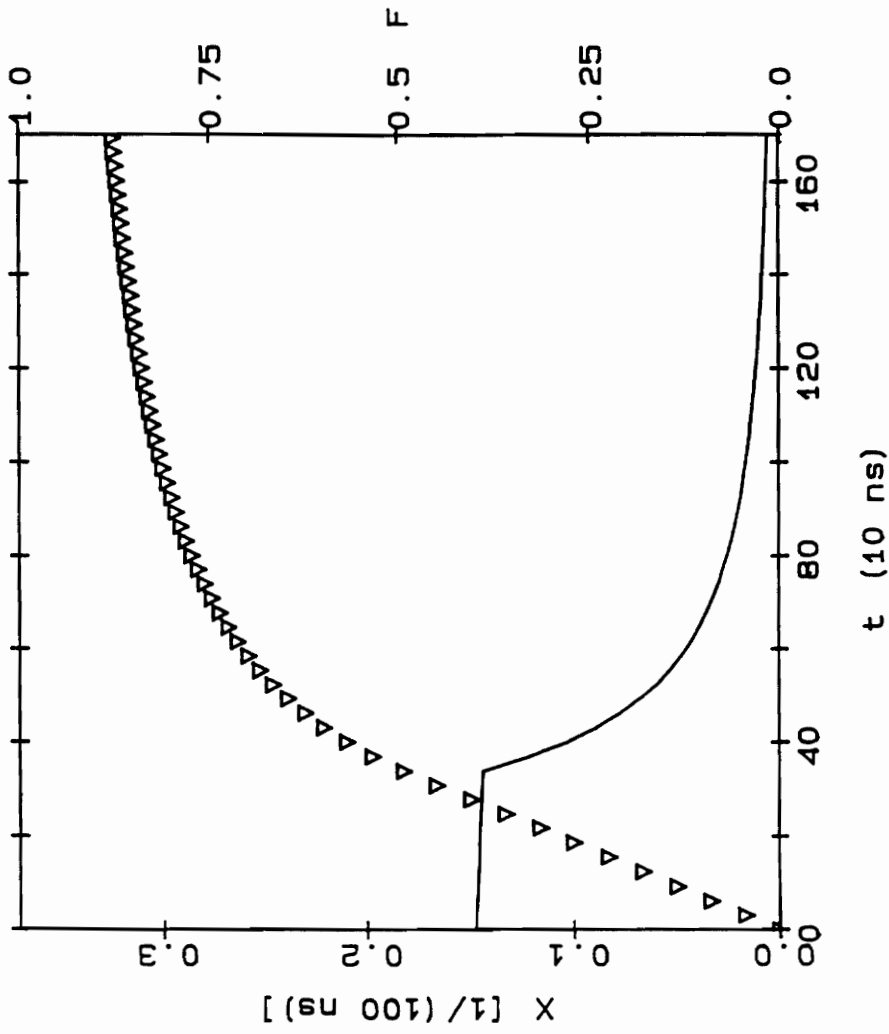


FIG. VII.5  $E_0 = 2$  eV,  $T = 1200$  K,  $d = 0.4572$  cm,  $p = 0.188$  bar. The contribution of 0th and 1st order is more than 85 percent.

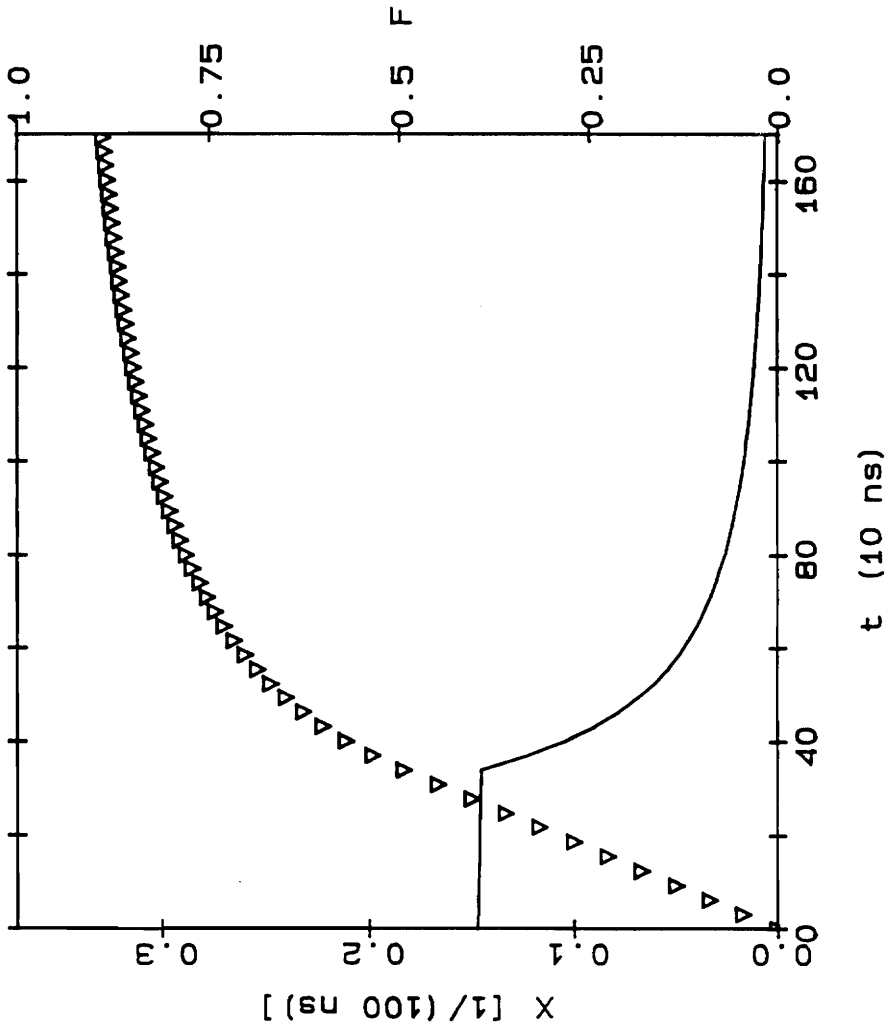


FIG. VII.6  $E_0 = 2$  eV,  $T=1200$  K,  $d = 0.4572$  cm,  $p = 0.094$  bar. The contribution of 0th and 1st order is about 90 percent.

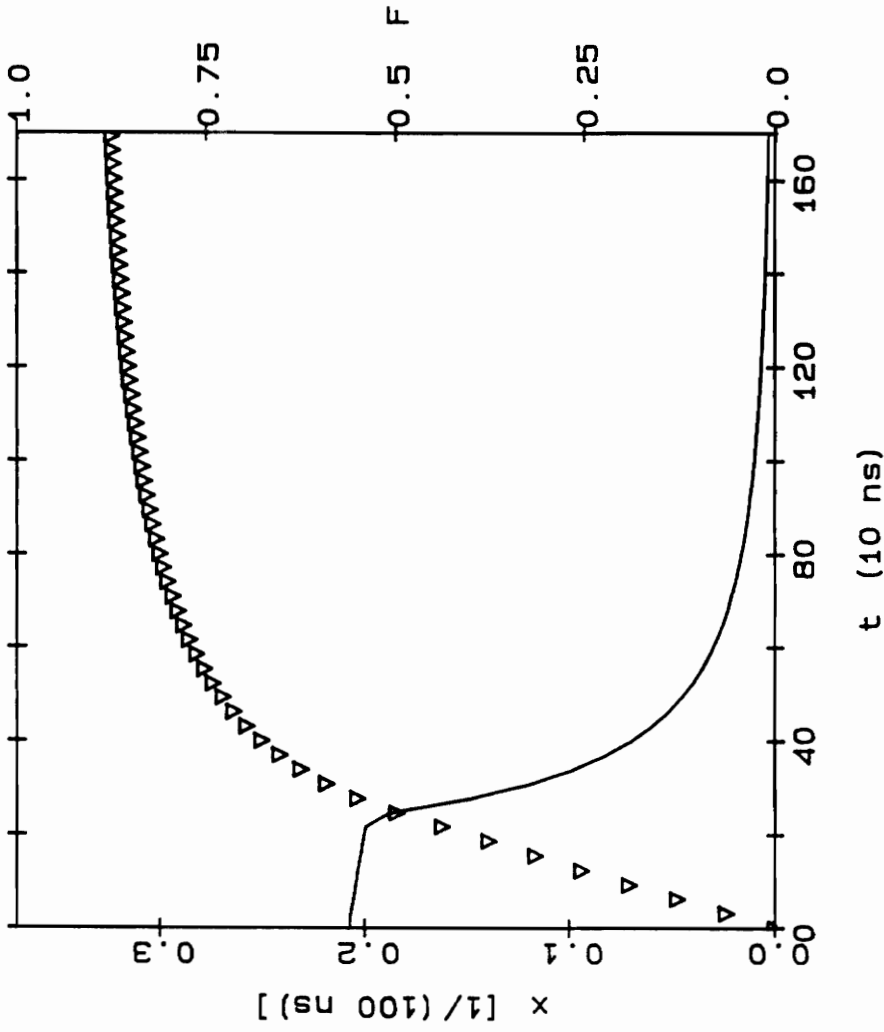


FIG. VII.7  $E_0 = 4$  eV,  $T = 300$  K,  $d = 0.4572$  cm,  $p = 0.094$  bar. The contribution of 0th and 1st order is about 90 percent.



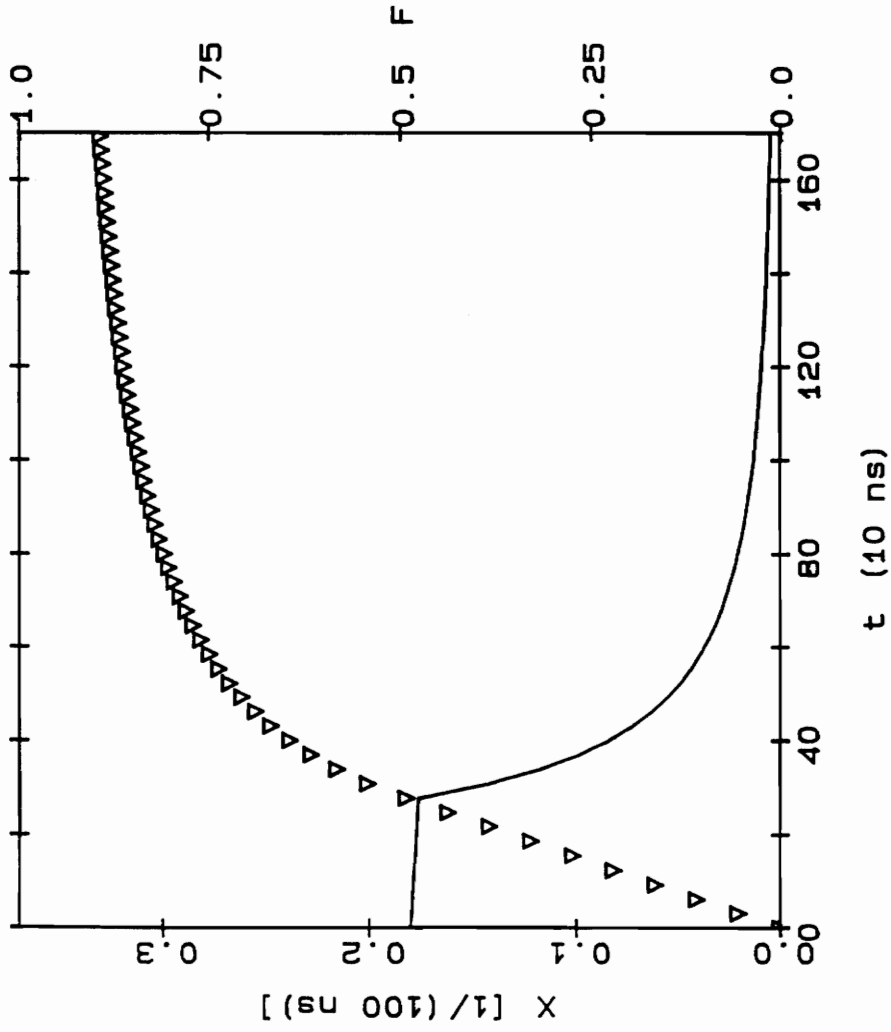


FIG. VII.8  $E_0 = 3 \text{ eV}$ ,  $T = 1200 \text{ K}$ ,  $d = 0.4572 \text{ cm}$ ,  $p = 0.188 \text{ bar}$ . The contribution of 0th and 1st order is about 90 percent.

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1. V.G. Molinari and L. Rondoni *Transport Phenomena in a Slab in the Presence of Temperature Gradients* Proceedings of the 15th International Symposium on Rarefied Gas Dynamics, June 16–20, 1986 Grado, Italy
2. L. Rondoni *Confronto dei Metodi Fisico-Matematici e Numerici Adottati nei Problemi di Transizione di Fase nei Metalli* Rapporto Interno relativo all’incarico di Servizio N° 15597, E.N.E.A., TIB/CALC/MATAPPL, Bologna, Italy (1987)
3. L. Rondoni and P.F. Zweifel *A Collided Flux Expansion Method for the Transport of Muonic Deuterium in Finite Media* Phys. Rev. A, to appear

4. L. Rondoni and R.F. Streater *Chemical Reactions as Dynamical Systems on the Interval*  
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A handwritten signature in cursive script that reads "Lamberto Rondoni". The signature is written in black ink on a white background.