On the Steady States and Dynamic Behavior of Two CSTR's in Series.

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By

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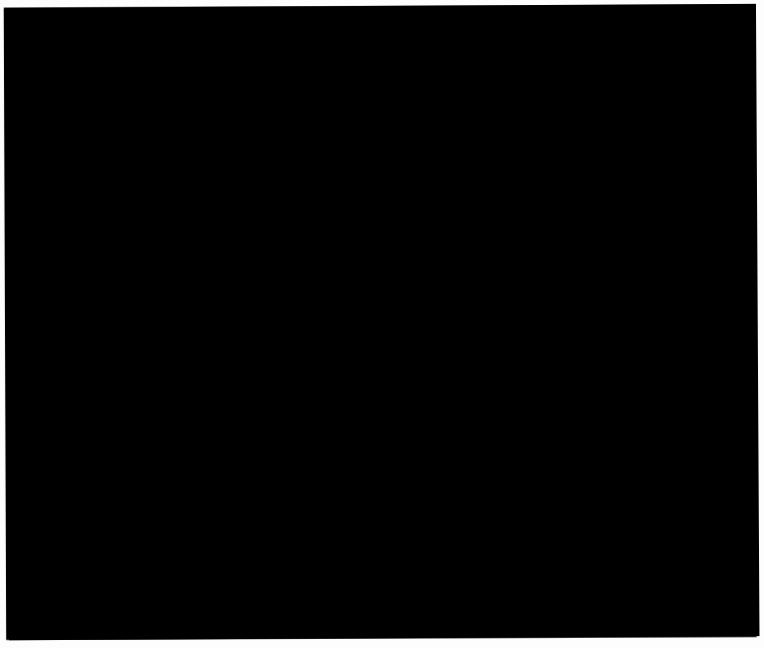

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To Annie, Natascha and Mehdi.

On the Steady States and Dynamic. Behavior of Two CSTR's in Series.

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Abstract

The mass and energy balances describing transcient behavior of two continuous flow stirred tank reactors in series are written in dimensionless form, for a first order reaction.

It is shown that the maximum number of steady states is nine. Parameter values are also given for which this maximum occurs. Some global statements about maximum multiplicity in the case of n - CSTR's in series are made.

In the search for a strange attractor, the dynamics are found to result in periodic orbits. A setting which could result in chaotic behavior, must consider finding a homoclinic orbit in the second reactor while maintaining the first one as close as possible to a hopf bifurcation point.

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Introduction

The continuous flow stirred tank reactor (CSTR) is perhaps the most widel studied system within chemical reactor theory. In many cases, it can be represented mathematically quite simply by a system of ordinary differential equation depending on the kind of reaction occurring in it. As contrasted with the tubul reactor (which is a distributed parameter system represented by partial differenti equations), this is a fortunate situation since much of the available mathematic theories and methods can handle , in many ways, ordinary differential equatior much easier than their partial counterparts. Furthermore, many models of distribute parameter systems may be broken into elementary pieces of lumped paramet systems. Such an approximation is widely spoken about in chemical engineerin where the empty tubular and the fixed bed reactors are modelled as an array o CSTR's. Other areas of science and engineering (nonlinear electric circuits, the mechanical analogues, modelling of biological cells.....) make use of these ide too.

Our object of study in this work is even simpler, namely two CSTR's i series in which a first order reaction is taking place and the possible gener statements that can be made about an array of n such CSTR's.

The problem is represented by four ordinary differential equations; these a derived in Chap.I. In Chap. II, we will be concerned with the question maximal multiplicity of steady states or equilibrium points. Here the proble provides an application for the theory of sequential bifurcations. In Chap. III, v investigate the dynamics of the problem, at least through numerical simulation searching for a strange attractor. We do not claim to have contained all the mar rich aspects of the problem, but we did get enough information to make son global statements. Our conclusions and recommendations are presented in the la part of this document.

Chapter I : The Mathematical Model of a Cascade of Two CSTR ' s .

The purpose of this chapter is to introduce the dynamic equations modelling a first order reaction in two continuous flow stirred tank reactors (CSTR's) in series, and to derive their steady state form. We also discuss the choice of a bifurcation parameter from a prospective which takes into account direct and possibly easy experimental verification of the results. Design and control considerations are the basis on which this choice is to be made .

1.)- Dynamic equations

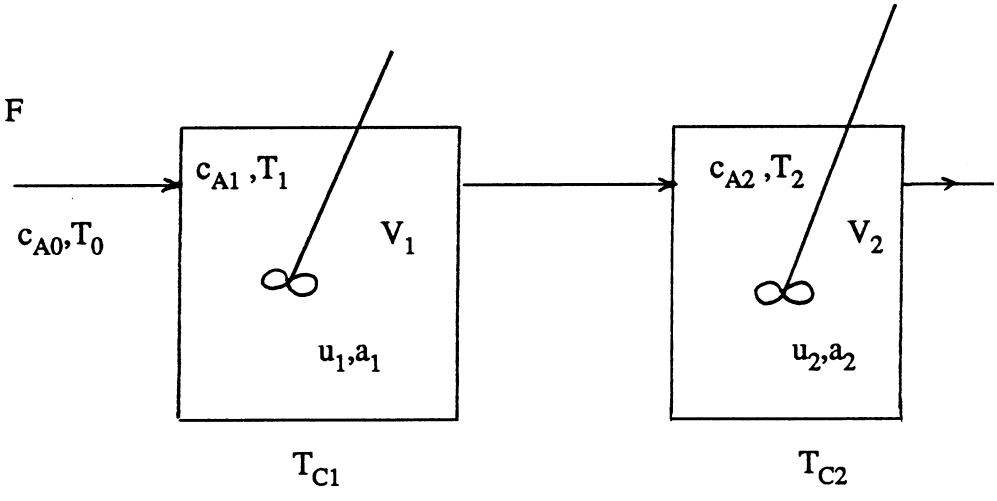


Fig.1.- Two CSTR's in series.

A schematic representation of the system is given in Fig.1. We assume that a first order reaction A —> B occurs in both reactors . The mass and energy balances for the two reactors obtained by considering the time interval t' to $t' + dt'$ are :

$$V_1 \frac{dc_{A1}}{dt'} = F(c_{A0} - c_{A1}) - V_1 k(T_1) c_{A1} \quad (1)$$

$$V_1 \rho C_p \frac{dT_1}{dt'} = F\rho C_p (T_0 - T_1) + V_1(-\Delta H) k(T_1) c_{A1} - u_1 a_1 (T_1 - T_{C1}) \quad (2)$$

$$V_2 \frac{dc_{A2}}{dt'} = F(c_{A1} - c_{A2}) - V_2 k(T_2) c_{A2} \quad (3)$$

$$V_2 \rho C_p \frac{dT_2}{dt'} = F\rho C_p (T_1 - T_2) + V_2 (-\Delta H) k(T_2) c_{A2} - u_2 a_2 (T_2 - T_{C2}) \quad (4)$$

where $k(T_i) = k_0 \, Exp\{ -E / RT_i \}$.

Our nondimensionalization follows that of Uppal, Ray and Poore [1], which introduces a reference time t_r and a dimensionless residence time τ ($\tau = V_1 / F t_r$). All the quantities in eqns. (1) through (4) are defined in the nomenclature section and serve to define the following dimensionless variables and parameters :

$$\theta_i = \frac{E}{RT_0} \frac{(T_i - T_0)}{T_0} \; ; \quad y_i = \frac{(c_{A0} - c_{Ai})}{c_{A0}} \; ; \quad \varepsilon = \frac{RT_0}{E}$$

$$B = \frac{(-\Delta H) c_{A0}}{\varepsilon \rho C_p T_0} \; ; \quad \beta_i = \frac{u_i a_i t_r}{V_i \rho C_p} \; ; \quad \alpha = \frac{V_2}{V_1}$$

$$\eta_i = \frac{E}{RT_0} \frac{(T_{ci} - T_0)}{T_0} \; ; \quad Da_0 = k_0 Exp(-1/\varepsilon) t_r \; ; \quad t = \frac{t'}{V_1 / F} .$$

In terms of these new quantities, eqns. (1) through (4) become :

$$\frac{dy_1}{dt} = -y_1 + Da_0\,\tau\,(1-y_1)\;E(\theta_1) \qquad (5)$$

$$\frac{d\theta_1}{dt} = -\theta_1 + Da_0\,\tau B\,(1-y_1)\;E(\theta_1) - \beta_1\,\tau\,(\theta_1 - \eta_1) \qquad (6)$$

$$\frac{dy_2}{dt} = \frac{y_1 - y_2}{\alpha} + Da_0\,\tau\,(1-y_2)\,E(\theta_2) \qquad (7)$$

$$\frac{d\theta_2}{dt} = \frac{\theta_1 - \theta_2}{\alpha} + Da_0\,\tau\,B\,(1-y_2)\,E(\theta_2) - \frac{\beta_2\,\tau}{\alpha}\,(\theta_2 - \eta_2) \qquad (8)$$

where

$$E(\theta_i) = \mathrm{Exp}\left(\frac{\theta_i}{1+\varepsilon\,\theta_i}\right)$$

Along with some initial conditions θ_{i0} and y_{i0}, eqns. (5) through (8) describe the time behavior of the system.

2.)- *Steady state equations* :

These represent the asymptotic behavior of the system as time becomes large. The solutions are stationary points and their stability analysis lays the ground for possible repeated behaviors in time (limit cycles being a good example), and for much of the delights and horrors that underlie nonlinear systems. They are derived by setting the derivatives to zero in eqns. (5) through (8), then multiplying (5) and (7) by B and substract them from (6) and (8) respectively to obtain :

$$y_1 = \frac{(1+\beta_1\tau)\theta_1 - \beta_1\tau\eta_1}{B} \qquad (9)$$

$$y_2 = \frac{(1+\beta_2\tau)\theta_2 - \beta_2\tau\eta_2 + B\,y_1 - \theta_1}{B} \qquad (10)$$

Using (9) and (10) in (6) and (8), we obtain the steady state equations :

$$-(1+\beta_1\tau)\theta_1 + Da_0\tau\{(B+\beta_1\tau\eta_1) - (1+\beta_1\tau)\theta_1\}E(\theta_1) + \beta_1\tau\eta_1 = 0 \qquad (11)$$

$$-(1+\beta_2\tau)\theta_2 + \theta_1 + \alpha Da_0\tau\{(B+\beta_2\tau\eta_2+\beta_1\tau\eta_1) - (1+\beta_2\tau)\theta_2 - \beta_1\tau\theta_1\}E(\theta_2) + \beta_2\tau\eta_2 = 0 \qquad (12)$$

3.)- Choice of a bifurcation parameter :

In eqns. (5) through (8), we have nine parameters from which to choose a bifurcation parameter. We will proceed by elimination on different grounds and isolate potential bifurcation parameters which are physically feasible. A look at the list of dimensionless parameters reveals that ε , B and Da_0 cannot be chosen, for they are characteristic of the kinetics of the reaction, and to claim that one may have control over them in a given experiment is a serious challenge. We have asked too much already by assuming that the kinetics of the reaction is first order. β_1 and β_2, average heat transfer coefficients, involve thermal and geometrical properties of the reactors. To select any of them as a bifurcation parameter would mean designing and constructing a set of reactors, made of different

materials, and of different sizes for a given set of experimental conditions. α is a statement of the relative sizes of the reactors and is also readily eliminated. The dimensionless residence time τ and the cooling temperatures η_1 and η_2 are the remaining ones. It is experimentally known that the control of the flow rate (or equivalently τ) is much easier to perform than the temperature control. From these considerations , the residence time will be adopted as a bifurcation parameter in this work, unless otherwise specified. The control of the flow rate may be accomplished by superposing a level controller at the output of the system, which would act on a feed pump according to a variable level set point.

We now express the steady state equations in terms of the bifurcation parameter. Algebraic manipulations of eqns. (11) and (12) yield the following :

$$\{ Da_0\beta_1(\eta_1-\theta_1)\, E(\theta_1)\}\ \tau^2 + \{ \beta_1 (\eta_1-\theta_1) + Da_0 (B-\theta_1)\, E(\theta_1) \}\ \tau - \theta_1 = 0 \qquad (13)$$

$$\{\alpha\, Da_0[\, \beta_1(\eta_1-\theta_1) + \beta_2(\eta_2-\theta_2)\,]\ E(\theta_2)\ \}\ \tau^2 + \{ \beta_2 (\eta_2-\theta_2) + \alpha\, Da_0 (B-\theta_2)\, E(\theta_2) \}\ \tau + (\theta_1-\theta_2) = 0 \qquad (14)$$

Note that (13) is independent of θ_2 . Equations (13) and (14) represent surfaces in a $(\theta_1, \theta_2, \tau)$ coordinate system, and their intersection for a given set of parameter values is the set of all equilibrium points of the system. The steady state analysis of these equations is the subject of the next chapter.

Chapter II : Maximum Multiplicity of Steady States.

Nonlinear models describing chemically reacting systems may exhibit a wide variety of exotic dynamical behaviors, and an analysis of the equilibria of these models is indeed a prerequisite for understanding these behaviors. The analysis includes the partition of the parameter space into regions where a given number of steady states occurs and the classification of these regions according to their bifurcation structure. The stability analysis then comes in to give hints about possible dynamical behaviors in each region.

A good place to start the analysis is to find the maximum possible number of steady states, and even this may be a formidable task. In this context , for the problem at hand and its variations, Varma [3] used graphical arguments, for the adiabatic and the isothermal occurrence of the reaction , to conclude that the maximum possible number of steady states for n-CSTR's in series is $2^{n+1} - 1$, of which at most n+1 are stable , the rest unstable. For two CSTR's , these considerations suggest that the maximum multiplicity of steady states is seven.Svoronos et al. [4] examined the problem under the " infinite activation energy approximation" , in the case of identical tanks ($\alpha = 0, \beta_1 = \beta_2, \varepsilon = 0$ in our notation). Their numerical results support Varma's conclusions. Kubicek et al [5] have worked on a more general configuration of two CSTR's with recirculation, different Damkohler numbers and different cooling fluid temperatures. Their plots show that the number of steady states may be as high as seven, thus supporting once more Varma's conclusions. It should be noted that the last two contributions are numerical in nature, and as such covered only part of the parameter space. Also the Damkohler number was the bifurcation parameter, which is not a convenient choice. Uppal, Ray and Poore [1] have shown for a single CSTR that the realistic choice of the residence time alters markedly the steady state behavior (bifurcation diagrams) from that found by choosing the Damkohler number. Their paper[1] is only a realistic encore of their previous one [2], in which they used the Damkohler number as the bifurcation parameter.

One must admit that the parameter space cannot be explored without any guidance in the analysis. It turns out that in the workshop of mathematical methods, the singularity theory proved to be very helpful, especially its version for the analysis of equilibria of dynamical systems. In its one state variable form, it is established as a valuable tool. Golubitsky and Keyfitz [6] have been able to characterize the organizing center in the case of a single CSTR (first order reaction), and thus prove that the numerical bifurcation diagrams of Uppal et al [1] are indeed complete. One feature is worth mentioning here, and that is the matching between the bifurcation diagrams generated numerically and those generated by qualitative analysis. Retzloff et al [7] have used this theory to prove the maximal multiplicity of steady states for two consecutive reactions occuring in a CSTR, and a discussion about the structure of the bifurcation diagrams for this case may be found in [8] and [9]. Other one state variable applications of the theory exist in other areas as well. The case of several state variables has been discussed by Golubitsky and Shaeffer[10], but only to show its limited aspects . This is not to say that ideas of this nature are nonexistant in the literature, they are indeed available ([11],[12]). However in the cycle of interaction between pure and applied mathematics, more experience is needed to find out how a complicated version of the theory would work. The work of Dangelmayr and Stewart ([13],[14]) is certainly a contribution in this direction. They devised a theory for sequential bifurcation problems, which is applied to the case of two CSTR's in series, based on the formulation of Svoronos et al. [4]. Mostly they confined themselves to a proof of the existence of certain types of sequential bifurcations. Their qualitative bifurcation diagrams in this case reveal that multiplicity of steady states may be as high as seven. They however stressed that due to the high complexity of the equations, their analysis is not complete.

In this chapter we make use of Dangelmayr and Stewart's theory of sequential bifurcations to show that for the problem of a first order reaction in two CSTR's, the maximum number of steady states is nine, and derive qualitatively different bifurcation diagrams to support this claim. We also discuss the maximal multiplicity of steady states in the case of n-CSTR's in series. In contrast with previous investigations, our formulation makes no assumptions other than that the reaction must be a first order one. Before addressing this, however, we present some background on singularity theory.

1.) - Description of singularity theory applied to bifurcation problems.

Bifurcation theory deals with the branching of solutions when one or more parameters are varied. Golubitsky and Shaeffer ([10],[12]) have developed a theory which considers the behavior of the solutions when a distinguished bifurcation parameter varies. In this section, we modestly describe some concepts of the theory, such as finite determinacy, codimension, normal form and universal unfolding. The reader is referred to the literature cited for a more detailed and concise description of the theory. We also say a word about the theory of sequential bifurcations developed by Dangelmayr and Stewart [13].

The local character of singularity theory stems from the fact that all of its concepts are to be understood in the language of germs of maps and manifolds. Definitions of these are ultimately based on "neighborhoods". The singularity of a germ of a map is a set of points where the differential or the Jacobian has less than the maximal possible rank. In the neighborhood of a singular point the implicit function theorem does not guarantee unique solutions. In this situation, the approach of the theory is to build a classification of germs with singularities through equivalence of singularities of germ maps. Two bifurcation problems are equivalent (see literature cited for definitions of equivalence relations [right, strong, contact, sequentially contact,..]) if they preserve the singularity and the qualitative configuration of the bifurcation diagram. To circumvent the difficulties presented to us by the original bifurcation problem, we would like to work in its equivalence class (in the neighborhood of a given singularity) and conveniently so, with its simplest representative (a polynomial is what is sought).

The concept of codimension involves the minimal number of additional dimensions that are necessary to create a stable germ from a given germ such that all other germs with higher dimensions factor through it. Finite codimension guarantees that the equivalence class contains the desired polynomial germ (the Taylor series expansion of the original bifurcation problem). The finite determinacy concept concerns the question of when a germ is determined by a finite piece of its Taylor series expansion. Thus, next to a singularity, finite codimension and finite determinacy allow for local analysis of the original bifurcation problem through one described by a polynomial. Furthermore coordinate transformations may be found to reduce this polynomial as much as possible to a very simple form called the normal form.

When the normal form has been determined, the next step is to determine the universal unfolding using a procedure in the same spirit as the one used to determine the normal form, for k-parameter families of germ maps based at the normal form. Here the codimension specifies exactly the minimum number of parameters necessary to obtain the universal unfolding. This description of the perturbations of the normal form is achieved through enumerating all the qualitatively different bifurcation diagrams found in the connected components of the transition set, which is the union of all the sets of codimension one, where the diagram's qualitative structure changes.

Sequential bifurcation theory of singularities is an extension of the concepts of one state variable singularity theory to problems of the form :

$$A(u, \lambda) = 0$$

$$B(x, u, \lambda) = 0$$

where λ is the distinguished bifurcation parameter and the sequentiality of the problem is embodied in the fact that A is independent of x.

Dangelmayr and Stewart [13] have classified these problems and listed six hierarchies of normal forms together with their unfoldings. Of particular interest to us in this work is the bifurcation problem $(2)_{mn}$ given by :

$$A(u, \lambda) = u^m + \varepsilon_1 \lambda$$

$$B(x, u, \lambda) = x^n + \varepsilon_2 u x \qquad (\varepsilon_i = \pm 1) \qquad (15)$$

These are just sequences of standard one dimensional bifurcation problems. The case $m = n = 3$ intuitively coincides with our claim that , since three steady states are possible in one single CSTR with a unique input, each of these will provide three steady states in the second tank in series with the first, thus totaling nine steady states for the exit variable. The next section discusses this claim.

2.) - Results from sequential bifurcation theory of singularities :

a) - Normal form and universal unfolding :

To establish that the bifurcation problem (11) and (12) may have nine solutions for a given choice of parameters, we need to show that it is sequentially equivalent to the

normal form $(2)_{33}$, and that the system is its own universal unfolding. To show sequential equivalence, a system of equations involving the derivatives must be solved. In the original variables, differentiation of (11) and (12) becomes quickly cumbersome and the algebra becomes impossible to handle. This difficulty can be avoided by introducing a change of variables (due to Dr. Chan) :

$$x_i = \text{Exp}\left\{ \theta_i / (1 + \varepsilon\, \theta_i) \right\}$$

whereupon the steady state equations (11) and (12) become :

$$F_1(x_1, \tau) = \frac{(1+\beta_1 \tau)\,\text{Ln}\, x_1}{(1-\varepsilon\, \text{Ln}\, x_1)} - \frac{B\, Da_0\, \tau\, x_1}{(1+Da_0\, \tau\, x_1)} - \beta_1 \tau \eta_1 = 0 \qquad (16)$$

$$F_2(x_1, x_2, \tau) = \frac{(1+\beta_2 \tau)\,\text{Ln}\, x_2}{(1-\varepsilon\, \text{Ln}\, x_2)} - \frac{\alpha\, B\, Da_0\, \tau\, x_2}{(1+Da_0\, \tau\, x_1)\,(1+\alpha\, Da_0\, \tau\, x_2)} - \frac{\text{Ln}\, x_1}{(1-\varepsilon\, \text{Ln}\, x_1)} - \beta_2 \tau \eta_2 = 0 \qquad (17)$$

The algebraic criteria that F_1 and F_2 must satisfy in order to be sequentially equivalent to $(2)_{33}$ are given in [13]. These are (Subscripts stand for partial differentiation) :

$$F_1 = F_{1_{x_1}} = F_{1_{x_1 x_1}} = 0 \qquad F_{1_{x_1 x_1 x_1}} \cdot F_{1_{\lambda}} \neq 0 \qquad (18)$$

$$F_2 = F_{2_{x_2}} = F_{2_{x_2 x_2}} = 0 \qquad F_{2_{x_2 x_2 x_2}} \cdot F_{2_{x_1 x_2}} \neq 0 \qquad (19)$$

$$F_{2_{x_1}} = 0 \qquad (20)$$

at $(x_{1c}, x_{2c}, \lambda_c)$, which are the coordinates of the origin in the neighborhood of which the equivalence holds.

The solution to the system (18) through (20), applied to the sequential problem (16) and (17), is given in Appendix I and yields the following :

$$B = \frac{4(1+\beta_1\tau+\varepsilon\beta_1\tau\eta_1)^2}{(1+\beta_1\tau)-4\varepsilon(1+\beta_1\tau+\varepsilon\beta_1\tau\eta_1)} \qquad (21)$$

$$x_1 = \mathrm{Exp}\left\{2 + \frac{\beta_1\tau\eta_1}{(1+\beta_1\tau+\varepsilon\beta_1\tau\eta_1)}\right\} \qquad (22)$$

$$Da_0 = \frac{1}{\tau x_1}\left\{1 - 4\varepsilon\frac{(1+\beta_1\tau+\varepsilon\beta_1\tau\eta_1)}{(1+\beta_1\tau)}\right\} \qquad (23)$$

$$\beta_2 = \frac{4\varepsilon^2\beta_1 B}{(1+Da_0\tau x_1)(\beta_1\tau-1)^2} - \frac{1}{\tau} \qquad (24)$$

η_2 is calculated from : (k and h are also given in Appendix I)

$$(1+\varepsilon\eta_2)\beta_2\tau = k\beta_2\tau + h \qquad (25)$$

x_2 may be computed from :

$$\mathrm{Ln}\, x_2 = 2 + \frac{\beta_2\tau\eta_2(1-\varepsilon\,\mathrm{Ln}\, x_1)+\mathrm{Ln}\, x_1}{1+\beta_2\tau(1+\varepsilon\eta_2)(1-\varepsilon\,\mathrm{Ln}\, x_1)} \qquad (26)$$

and α may be obtained from :

$$\alpha \, Da_0 \, \tau \, x_2 = \frac{1}{\beta_1 \tau} \qquad (27)$$

The resulting equalities define a four parameter family of singular points.

It is now easy to see why previous results do not exhibit a multiplicity of steady states of nine. If we set $\beta_1 = \beta_2 = \beta$ as in [4], the system (18) through (20) is not solvable since it can be shown to yield $\beta = 4\,(1+\beta)$. Also if we set $\eta_1 = \eta_2 = 0$, the value of ε is confined to a small interval not containing the value of 10^{-3} used in [5].

In order to verify that nine roots can indeed be obtained, we have to show that the system of equations (16) and (17) is its own universal unfolding. For this fact to be established, the following two determinants (due to Dr. Retzloff) must be nonzero :

$$\begin{vmatrix} 0 & 0 & F_{1\,x_1 x_1 x_{1|c}} \\ F_{1\,\lambda|_c} & F_{1\,\lambda x_{1|c}} & F_{1\,\lambda x_1 x_{1|c}} \\ F_{1\,\delta|_c} & F_{1\,\delta x_{1|c}} & F_{1\,\delta x_1 x_{1|c}} \end{vmatrix}$$

$$\begin{vmatrix} 0 & F_{2\,x_1 x_{2lc}} & 0 & F_{2\,x_2 x_2 x_{2lc}} \\ F_{2\,\alpha_{lc}} & F_{2\,\alpha x_{1lc}} & F_{2\,\alpha x_{2lc}} & F_{2\,\alpha x_2 x_{2lc}} \\ F_{2\beta_{lc}} & F_{2\beta x_{1lc}} & F_{2\,\beta x_{2lc}} & F_{2\,\beta x_2 x_{2lc}} \\ F_{2\,\gamma_{lc}} & F_{2\gamma\, x_{1lc}} & F_{2\gamma\, x_{2lc}} & F_{2\,\gamma\, x_2 x_{2lc}} \end{vmatrix}$$

where $(\alpha, \beta, \gamma, \delta)$ are the unfolding parameters.

b) - Bifurcation diagrams :

The universal unfolding of $(2)_{33}$ is [13] :

$$\begin{aligned} A(u, \lambda) &= u^3 - \lambda + \delta u \\ B(x, u, \lambda) &= x^3 - u x + \gamma x^2 + \beta x + \alpha \end{aligned} \qquad (28)$$

where $\underset{\sim}{\xi} = (\alpha, \beta, \gamma, \delta)$ is an element of the unfolding space.

In order to generate all the qualitatively different bifurcation diagrams for this problem, we need to determine the transition set Σ. The topological type of a diagram is constant on every connected component of IR^4 / Σ. The components of the transition set for sequential bifurcations are given below and the degeneracies corresponding to them are shown in Fig.2.

Bifurcation or isola point in A coupled with regular point in B (Fig.2 (a)) :

$$\{ \underset{\sim}{\xi} \; C \; IR^4 \; / \quad A = A_\lambda = 0, \quad B_x \neq 0 \quad \text{at} \; (u, x, \lambda, \underset{\sim}{\xi}) \}$$

This set is empty since A_λ is never zero.

Hysteresis in A coupled with regular point in B (Fig.2 (b)) :

$\{ \xi \in IR^4 / \quad A = A_u = A_{uu} = 0, \quad B_x \neq 0 \quad \text{at} (u, x, \lambda, \xi) \}$

This set leads to $u = 0$, and no other relation between the parameters can be derived.

Double limit point in A coupled with regular point in B (Fig.2 (c)) :

$\{ \xi \in IR^4 / \quad A = A_u = 0, \quad B_x \neq 0 \quad \text{at} (u_i, x_i, \lambda, \xi) \text{ with } u_1 \neq u_2 \}$

This set is empty as well since no relation between the parameters can be found.

The Ordinary Bifurcation and Isola Centre (Fig.2 (d)) :

$$B = \{ \xi \in IR^4 / A = B = B_x = A_u B_\lambda - A_\lambda B_u = 0 \quad \text{at} (u, x, \lambda, \xi) \}$$

$$\begin{aligned} & u^3 - \lambda + \delta u = 0 \\ & x^3 - u x + \gamma x^2 + \beta x + \alpha = 0 \\ & 3 x^2 - u + 2 \gamma x + \beta = 0 \\ & x = 0 \end{aligned} \quad \Longleftrightarrow \quad \begin{aligned} & x = 0 \\ & \beta = u \\ & \alpha = 0 \\ & \lambda = \beta^3 + \delta \beta \end{aligned}$$

The set B is given by :

$$\alpha = 0$$

The Ordinary Hysterisis (Fig.2 (e)) :

$$H = \{ \xi \in IR^4 / A = B = B_x = B_{xx} = 0 \quad \text{at} (u, x, \lambda, \xi) \}$$

$$\begin{aligned} & u^3 - \lambda + \delta u = 0 \\ & x^3 - u x + \gamma x^2 + \beta x + \alpha = 0 \\ & 3 x^2 - u + 2 \gamma x + \beta = 0 \\ & 6x + 2 \gamma = 0 \end{aligned} \quad \Longleftrightarrow \quad \begin{aligned} & \gamma = -3 x \\ & \gamma^2 = 3 \beta - 3 u \\ & -\alpha = x^3 - u x + \gamma x^2 + \beta x \\ & u^3 - \lambda + \delta u = 0 \end{aligned}$$

This set is given by :

$$\alpha = \frac{\gamma^3}{27}$$

The Ordinary Double Limit (Fig.2 (f)) :

$$D_0 = \{ \xi \ C \ IR^4 \ / \ \Xi (x_1 , x_2 , u, \lambda) \ C \ IR^4 \ (x_1 \neq x_2) \\ A = B = B_x = 0 \ \text{ at } (u , x_i, \lambda , \xi) ; i = 1,2 \}$$

$$u^3 - \lambda + \delta u = 0$$
$$x_i^3 - u x_i + \gamma x_i^2 + \beta x_i + \alpha = 0$$
$$3 x_i^2 - u + 2 \gamma x_i + \beta = 0$$

This set is shown to be empty (Appendix II).

The Two - Sheet Double Limit (Fig.2 (g)) :

$$D_1 = \{ \xi \ C \ IR^4 \ / \ \Xi (x_1 , x_2 , u_1 , u_2, \lambda) \ C \ IR^5 \ (u_1 \neq u_2) \\ A = B = B_x = 0 \ \text{ at } (u_i , x_i, \lambda , \xi) ; i = 1,2 \}$$

The set D_1 is fully derived in Appendix II , and is given by the union of the following two branches :

First branch :

$$\beta = \gamma^2 / 12 .$$
$$\alpha = - (48 \delta + \gamma^4) / 216 \gamma .$$

Second branch :

$$(23328 \gamma^3) \alpha^3 + \{ 7776 \gamma^2 (2 \delta + \beta \gamma^2 - 6 \beta^2) + 324 \gamma^2 (\gamma^2 - 12 \beta)^2 + \\ 27 (\gamma^2 - 12 \beta)^3 \} \alpha^2 + \{ 864 \gamma (2 \delta + \beta \gamma^2 - 6\beta^2)^2 + \\ 36 \gamma (6 \delta + 2 \beta \gamma^2 - 12 \beta^2) (\gamma^2 - 12 \beta)^2 + (4 \gamma^3 - 18 \beta \gamma) (\gamma^2 - 12 \beta)^3 \} \alpha + \\ \{ 32 (2 \delta + \beta \gamma^2 - 6\beta^2)^3 + 4 (2 \delta + \beta \gamma^2 - 6\beta^2) (4 \delta + \beta \gamma^2 - 6\beta^2) (\gamma^2 - 12 \beta)^2 \\ - \beta^2 (\gamma^2 - 4 \beta) (\gamma^2 - 12 \beta)^3 + \delta (\gamma^2 - 12 \beta)^4 \} = 0$$

$$-3\ (2\delta+\beta\gamma^2-6\beta^2+9\alpha\gamma)^2-\delta\ (\gamma^2-12\beta)^2\ >\ 0$$

This branch does not exist for values of δ greater than zero.

The Edge Limit Singularity $(1)_{22}$ (Fig.2 (h)) :

$$E\ =\{\xi\ C\ IR^4\ /\ A=B=A_u=B_x=0\quad at\ (u,x,\lambda,\xi)\}$$

$$u^3-\lambda+\delta u\ =0$$
$$x^3-ux\ +\gamma x^2+\beta x+\alpha=0$$
$$3x^2-u\ +2\gamma x+\beta\ =0$$
$$3u^2+\delta=0$$

This set is also fully derived in Appendix II, and is composed of :

$$u\ =\pm\sqrt{-\delta/3}$$

$$\alpha=\{9\gamma(\beta-u)-2\gamma^3\pm2[\gamma^2-3(\beta-u)]^{3/2}\}/\ 27$$

We present the bifurcation diagrams on IR^4/Σ for parameter values at which all the sets exist simultaneously . The set Σ is shown in Fig.3 and the bifurcation diagrams are shown in Fig.4. These diagrams have been generated by choosing values of the parameters in the numbered regions of Fig.3 and using the equations of the universal unfolding :

$$u=x^2+\gamma x+\beta+\frac{\alpha}{x}$$

$$\lambda=u^3+\delta u \qquad (29)$$

Notice that (29) is not defined at $x = 0$, and that the behavior of the diagram on the left and the right of 0 is determined by the sign of α.

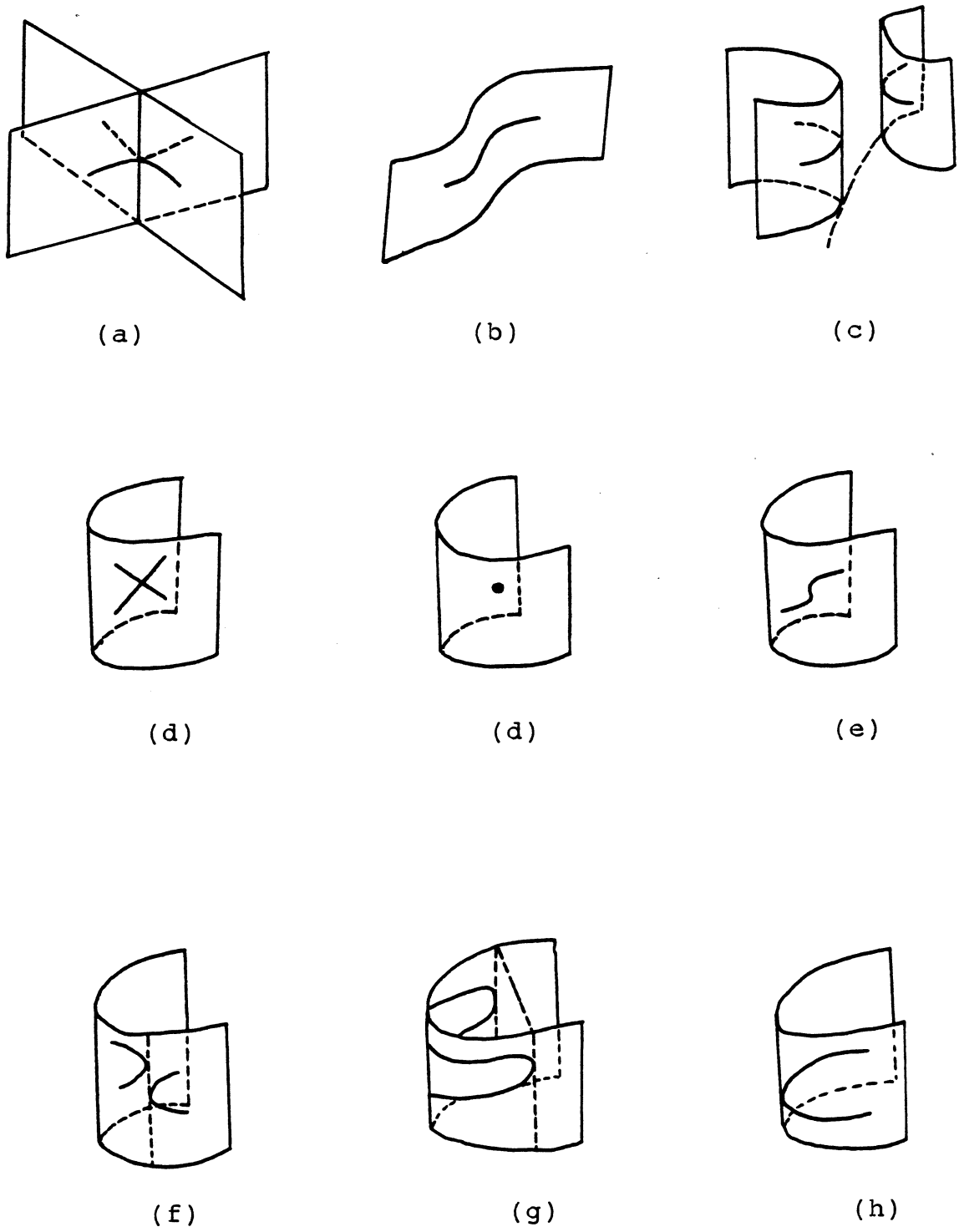


Fig.2.- Illustration of the degeneracies of the transition set.

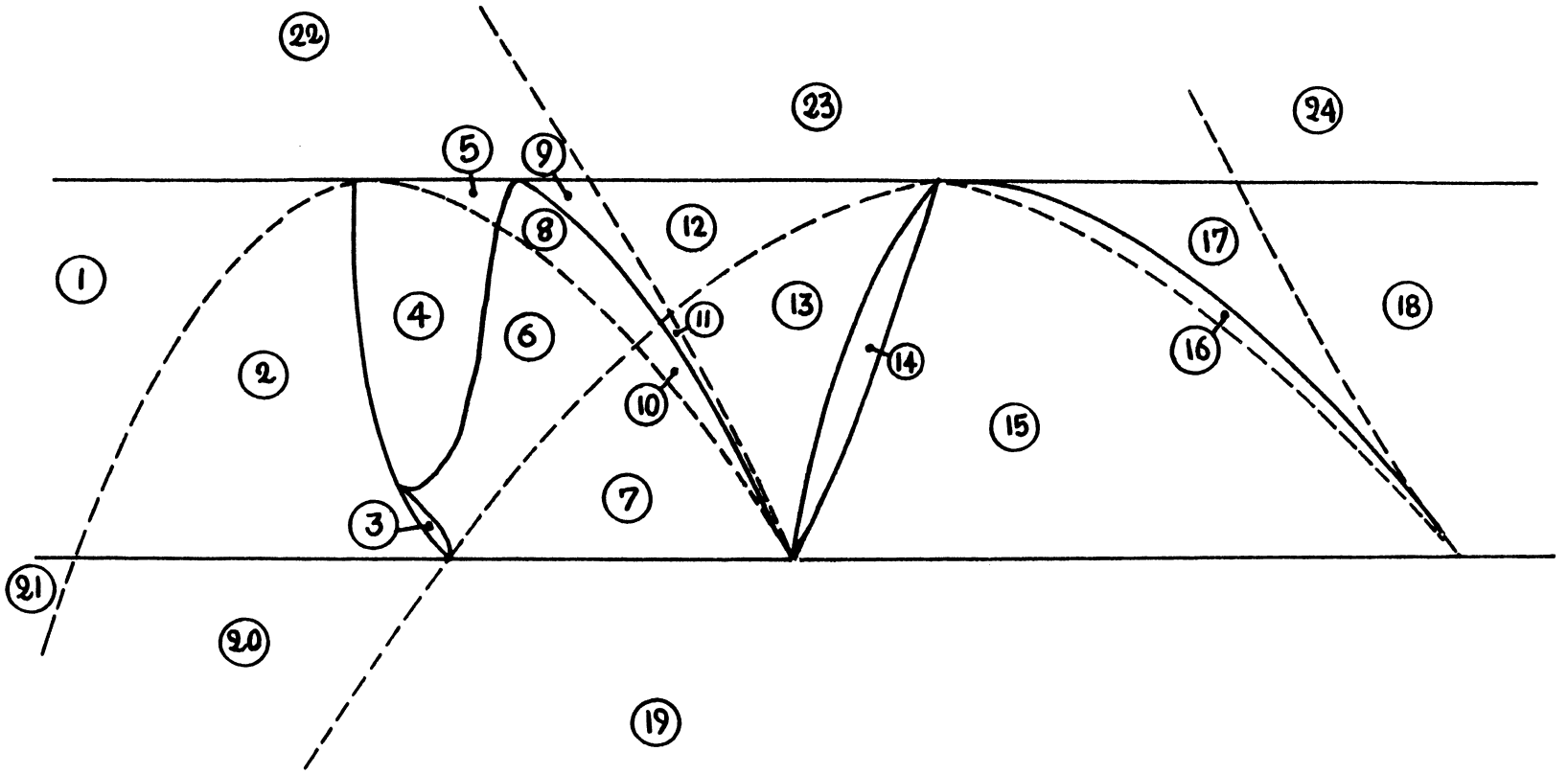


Fig.3.- The transition set for $\delta = -3$ and $\gamma = -2$.

------ D_1

_____ E

coordinates: vertical α, horizontal β.

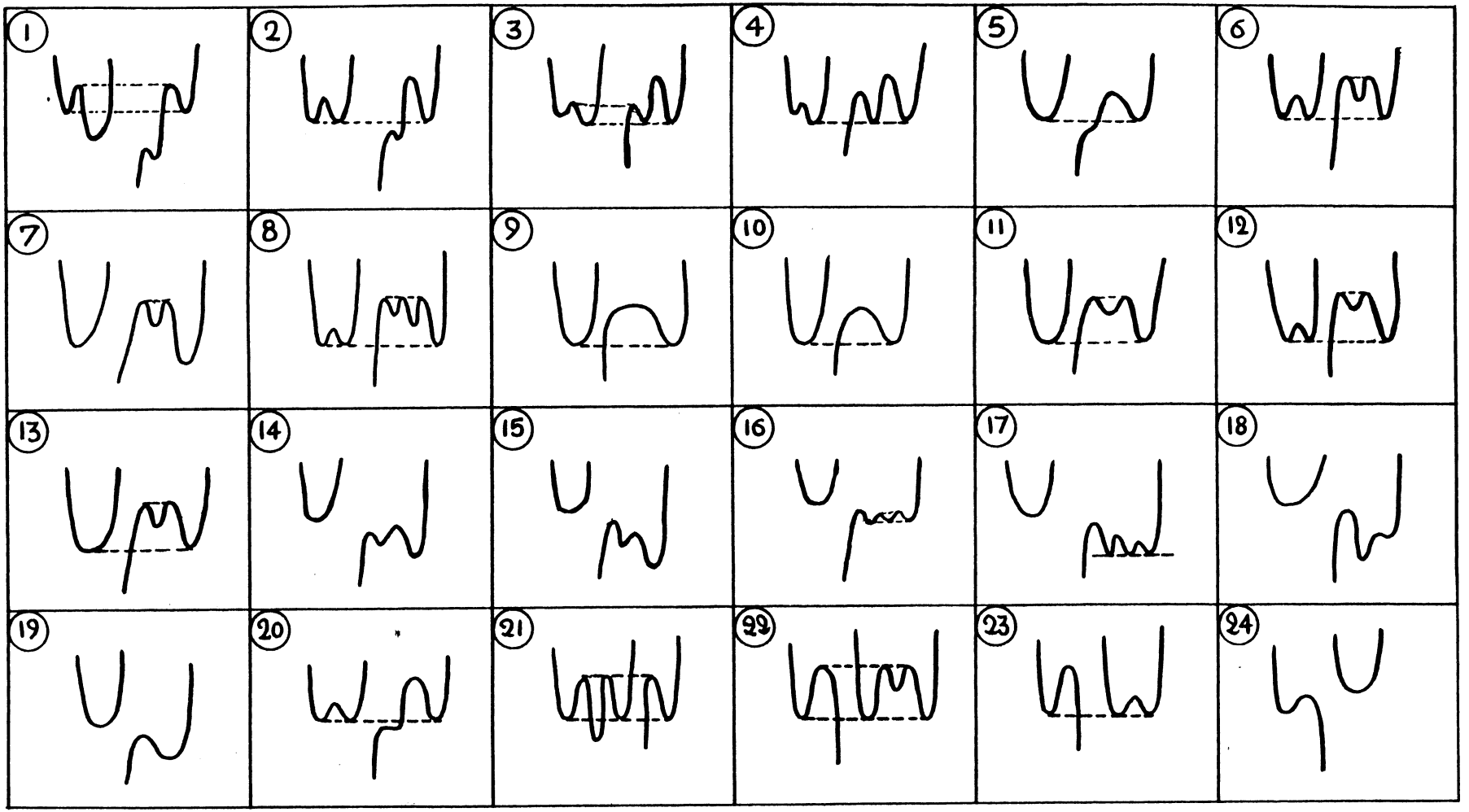


Fig.4.- Bifurcation diagrams corresponding to numbered regions of Fig.3.
coordinates: vertical λ, horizontal x.

3.) Numerical results from the model :

For computational purposes, one can view the solution of the system (11) and (12) as the intersection of two surfaces f_1 and f_2 with the plane $Da_0\,\tau$ in the three dimensional space of coordinates $(\tau, \theta_1, \theta_2)$. f_1 and f_2 are given by :

$$f_1(\tau, \theta_1) = \frac{(1+\beta_1\,\tau)\,\theta_1 - \beta_1\,\tau\,\eta_1}{(B+\beta_1\,\tau\,\eta_1) - (1+\beta_1\,\tau)\,\theta_1} \qquad G(\theta_1) = Da_0\,\tau \tag{30}$$

$$f_2(\tau, \theta_1, \theta_2) = \frac{(1+\beta_2\,\tau)\,\theta_2 - \theta_1 - \beta_2\,\tau\,\eta_2}{\alpha\{(B+\beta_1\tau\,\eta_1+\beta_2\tau\,\eta_2) - \beta_1\tau\,\theta_1 - (1+\beta_2\tau)\theta_2\}} \qquad G(\theta_2) = Da_0\,\tau \tag{31}$$

where $G(\theta_i) = \mathrm{Exp}\left\{-\frac{\theta_i}{1+\varepsilon\,\theta_i}\right\}$

It is convenient for what is coming next to write the following :

$k_1 = (1+\beta_1\,\tau)$; $k_{11} = \beta_1\,\tau\,\eta_1$

$m_1 = (B+\beta_1\,\tau\,\eta_1)$.

$k_2 = (1+\beta_2\,\tau)$; $k_{22} = \beta_2\,\tau\,\eta_2$; $k_4 = \beta_1\,\tau$

$m_2 = (B+\beta_1\,\tau\,\eta_1+\beta_2\,\tau\,\eta_2)$.

Analysis of f_1 :

Since f_1 is independent of θ_2 , it will keep the same shape in the θ_2 direction as it has in the (τ, θ_1) plane.

We are interested only in values of τ that are positive and therefore θ_1 will be constrained to the interval $[k_{11}/k_1 , m_1/k_1 [$. This restriction is equivalent to saying that the conversion is between 0 and 1. m_1/k_1 is an asymptotic plane for f_1.
In this interval , f_1 has a maximum and a minimum according to whether the following quadratic :

$$[\varepsilon^2(m_1k_1 - k_{11}k_1) + k_1^2]\,\theta_1^2 + [2\varepsilon(m_1k_1 - k_{11}k_1) - (m_1k_1 + k_{11}k_1)]\;\theta_1 +$$

$$+ [(m_1k_1 - k_{11}k_1) + m_1k_{11}] = 0$$

has distinct roots or not. A sketch of the surface is depicted in Fig.5-a. for a constant τ.

Analysis of f_2 :

For the same reasons as for f_1 , θ_2 will be constrained to the interval $[(\theta_1 + k_{22})/k_2 \;,\; (m_2 - k_4\theta_1)/k_2\,[$ for a given τ . $(m_2 - k_4\theta_1)/k_2$ is an asymptotic plane for f_2 .

f_2 crosses the (θ_1, θ_2) plane at $(\theta_1 + k_{22})/k_2$ which might be called the zero line. The zero line meets the asymptotic plane at $\theta_1 = (m_2 - k_{22})/(1 + k_4)$. For given values of τ and θ_1, F_2 will have a maximum and a minimum as long as roots for the following quadratic exist :

$$[\varepsilon^2(h_1k_2 - h_2k_2) + k_2^2]\,\theta_2^2 + [2\varepsilon(h_1k_2 - h_2k_2) - (h_1k_2 + h_2k_2)]\;\theta_2 +$$

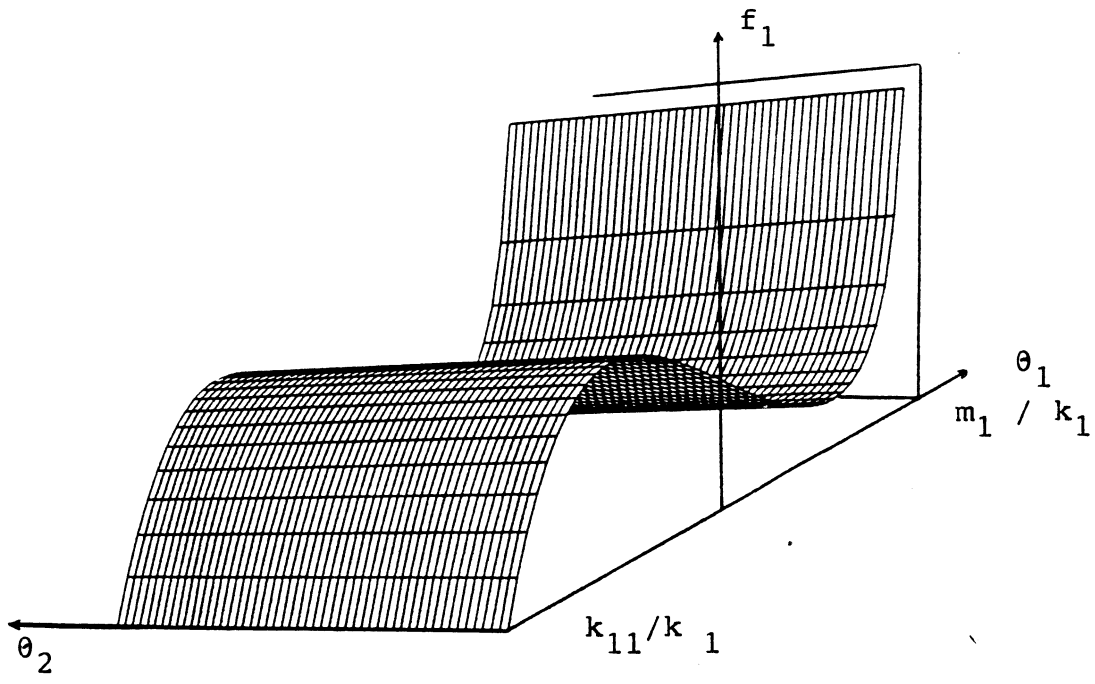
$$+ [(h_1k_2 - h_2k_2) + h_1h_2] = 0$$

where $h_1 = m_2 - k_4\theta_1$ and $h_2 = \theta_1 + k_{22}$

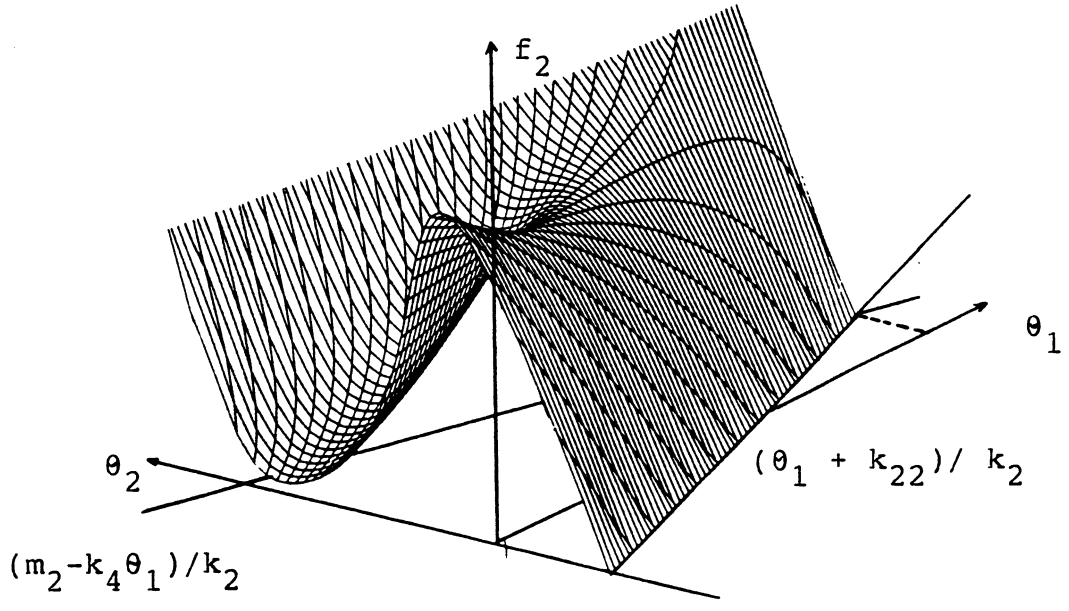
There exist two values of θ_1, for which the maximum and minimum collapse into inflection points in the θ_1 - direction. Fig.5-b depicts that part of f_2 of interest to us. The computer program CSTRS (Appendix III) had been written on the basis of the above analysis. It starts by finding the roots of eqn. (30) , using the bisection method and for each of the roots computes the roots of eqn. (31) in the θ_2 -direction, using the same procedure.

IMSL routines could not bear on this problem for the following reasons :

- All routines using derivatives in the computational scheme are not suitable because of the exponential nature of the equations and the presence of asymptotes.
- Most of the multiroot finders available require prior knowledge of the number of roots present.



(a)



(b)

Fig. 5.- Sketches of f_1 and f_2 .

CSTRS does not require this prior knowledge and does not make use of derivatives. It does however present a problem in post data processing, and especially in plotting it. Our approach was to use a pointwise plotting procedure of SAS using signs.

Concerning the accuracy, data values were put back in the steady state equations to see how close to zero they are. As Appendix IV shows, it depends on the point itself and how close to the asymptote it is.

Eqns. (21) through (27) provide the coordinates of a singular point for an arbitrary choice of the parameters ε, β_1, η_1 and τ. One starts perturbing the parameter values obtained in different directions for the purpose of finding the maximum number of steady states. For $\varepsilon = 0$, $\beta_1 = 1.2$ and $\eta_1 = -3.0$ Fig.6 shows the number of solutions of θ_2 as the residence time is varied. Around $\tau = 1.5$, nine solutions exist and an enlargement of that particular region is provided in Fig.7. For the following values of the parameters:

$\varepsilon = 0.0$ $\qquad$ $\beta_1 = 1.8 / 1.5$

$\beta_2 = 0.001 / 1.5$ $\qquad$ $\eta_1 = -3.0$

$Da_0 = 0.414615$ $\qquad$ $B = 13$

$\alpha = 0.06017$ $\qquad$ $\eta_2 = -6.0$

and $\tau = 1.5$, the steady state temperatures are:

θ_1	θ_2
-1.1897188	- 1.053915
-	2.692481
-	9.708056
1.2526125	2.938399
-	3.042330
-	3.880740
1.2607165	2.872114
-	3.228100
-	3.577394

Even though the bifurcation parameter's neighborhood is very small, the steady state values are very distinct.

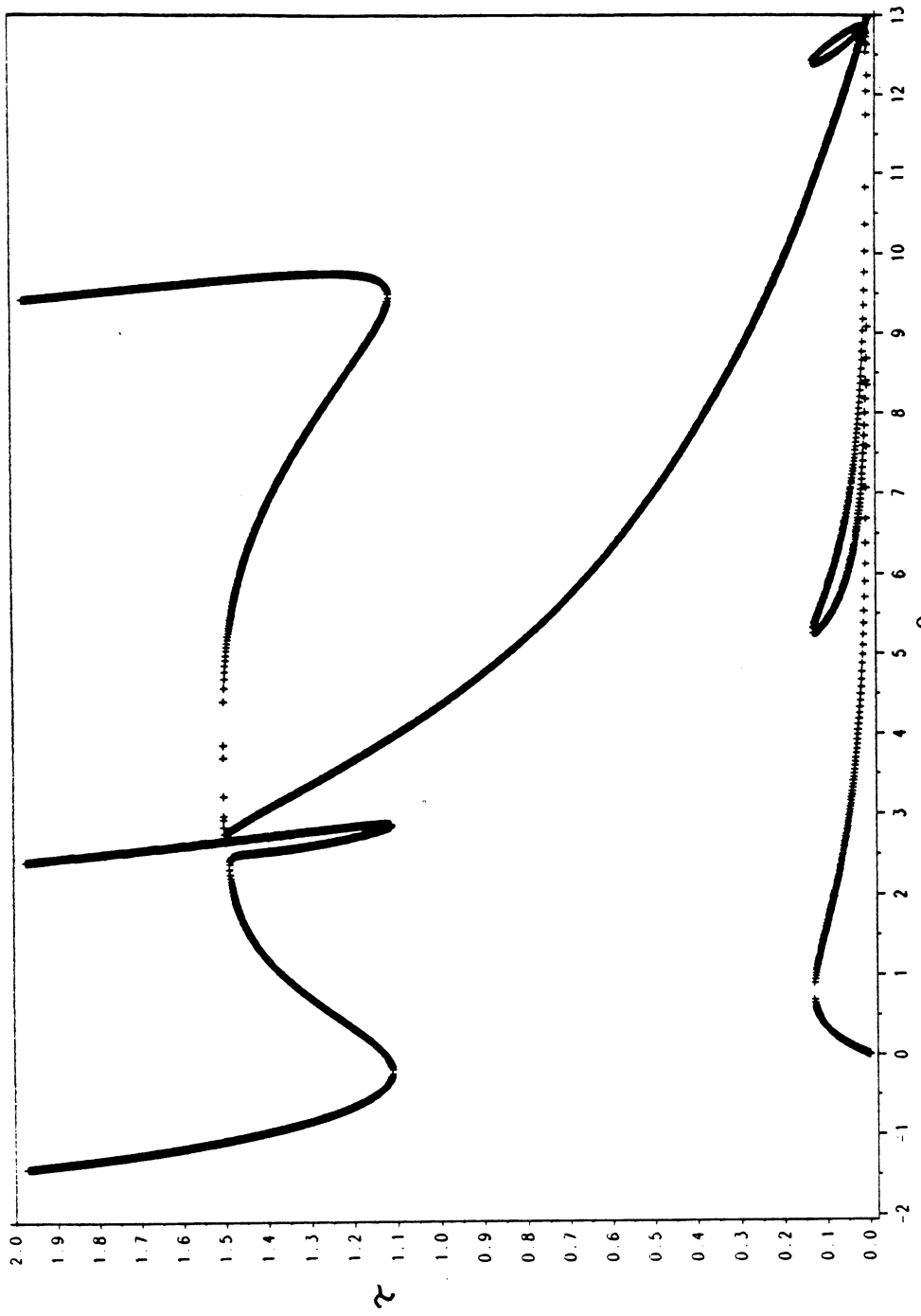


Fig.6 .- Exit temperature versus residence time.

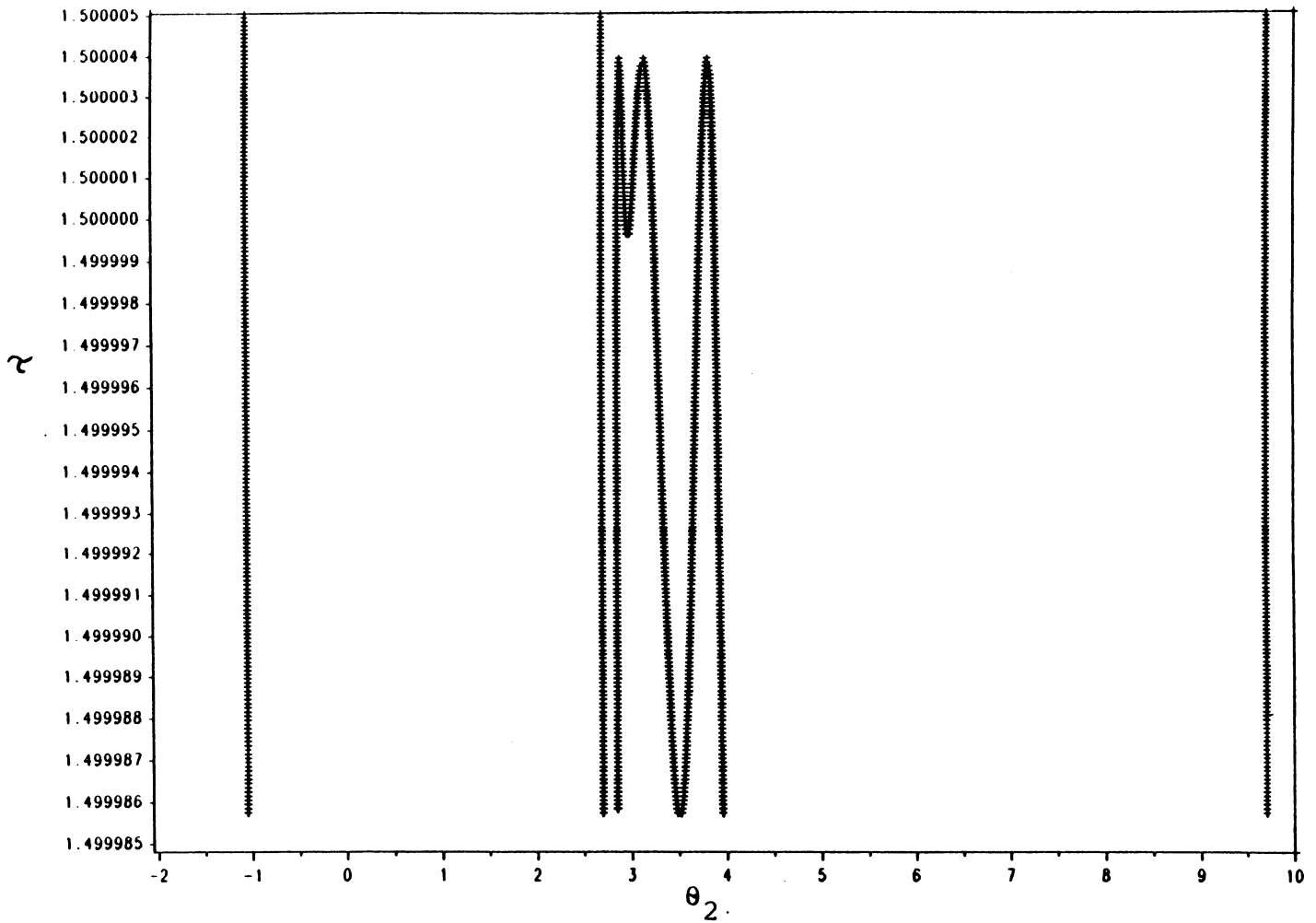


Fig. 7.- Enlargement of Fig.8.around $\tau = 1.5$.

4.) - Concluding remarks :

The maximum multiplicity of steady states for a single first order reaction occurring in two CSTR's in series has been approached using the theory of sequential bifurcations. It is proven that the bifurcation problem is sequentially equivalent to the normal form $(2)_{33}$, and that the unfolding space of $(2)_{33}$ contains regions in which the number of solutions is as high as nine. Furthermore , for a choice of ε , β_1 , η_1 and τ, a high degeneracy point may be computed (satisfying the nondegeneracy conditions) and perturbations around it will certainly yield nine numerical solutions. Previous investigations could not result in this conclusion due to the various assumptions employed and to the fact that the region in which nine solutions occur is very small.

The stability question has not been mathematically treated. However it is physically perceivable, that for the cascade to be stable, its components must all be stable. A straightforward calculation of the eigenvalues of the Jacobian matrix (Chap.III) indeed shows that it is exactly the product of the characteristic equations of the components of the cascade.

For the case of n - CSTR's in series, one may conjecture that reiteration of the same methods used here, along with an induction reasoning, would lead to the following :

The maximum possible number of steady states is 3^n , *of which at most only* 2^n *are stable , the rest unstable.*

The question of the triple crossing raised in [14] which results from the intersection of three branches of the bifurcation diagram at exactly one point, is expected to occur in a larger region of the parameter space , especially in the residence time formulation of the equations. It is indeed a result of the projection in a (τ , θ_2) diagram, and is not related to the choice of the activation energy whatsoever.

Finally we have only treated the question of maximum multiplicity. It seems that a full steady state analysis is necessary both topologically and numerically from the model. Uppal et al. [1] have shown that there are about five possible steady state behaviors in a single CSTR. In two in series one should expect about 25 at least. It is recommended for further analysis that the topological partition (given by the transition set) be found numerically in the model itself , after an appropriate

identification of the universal unfolding parameters. This will provide a check on the classification and will allow an evaluation of the sequential bifurcations theory of singularities.

Chapter III : On the Dynamics

The dynamics of a single reactor in which a first order reaction is taking place have been analyzed in [1]. As the reactor residence time is varied, some 17 different types of dynamic behavior were found to occur. Regions of the parameter space in which these behaviors occur were also specified.

In the two CSTR's in series arrangement, the first reactor may be considered as a perturbing device to the second. This perturbation, however, is to be distinguished from those artificial ones, where one deliberately chooses a sine or cosine variation in time of any of the operating variables. The forcing in question here is a result of a natural bifurcation to a periodic orbit in the first reactor when a bifurcation parameter is varied, and therefore the periodicity will manifest itself only in the conversion and the temperature.

Logically , one may think of expecting $(17)^2$ different types of dynamic behaviors for two CSTR' s in series. These would result from sequentially arranging the 17 known behaviors in the unperturbed part of the second reactor and the perturbing one. However, one must bear in mind that we have the same reaction taking place in both reactors and therefore kinetic parameters such as B , Da_0 and ε are chosen only once. These considerations will alter considerably the total number of different dynamic behaviors. The rest of the parameters α, η_1, η_2 , β_1 and β_2 may be chosen independently and it is in these quantities indeed that regions with different dynamic behaviors must be determined. Notice that in [1], the regions were classified in a (B , Da_0) plane , all other parameters fixed. Using those results in the case of two CSTR 's would mean a study of identical sequential oscillators ($\alpha = 1$). The parameters of the first and the second reactors are chosen from the same region where a particular dynamic behavior occurs.

The differential equations describing the dynamics are given in Chap. I (eqns. (5) through (8)). One method of investigating the dynamics of the two CSTR's in series is by numerical simulation, and here the literature gives conflicting results. These conflicts arise mostly from promotion of the numerical codes, dealing with the determination of the points where a Hopf bifurcation takes place. Kubicek [15], designed an algorithm for the purpose of computing complex bifurcation points in ordinary differential equations and his test example was the problem of two CSTR's in series with recycle. The author specified regions in a two dimensional

parametric plane where stable periodic solutions exist. Hassard and El Henawy [16] and Hassard [17], in advertising for the code BIFOR2, used the same example for the numerical evaluation of Hopf bifurcation formula. In some instances their results contradict those of [15].

Other classes of papers which might be considered interesting , deal with the periodically perturbed Hopf bifurcation and with the periodically forced single CSTR. The first category deals mostly with degenerate bifurcations whereby more than two eigenvalues cross the imaginary axis and with secondary bifurcations in other systems such as the Van Der Pol oscillator. The equations modeling the systems studied in this category are very different from the ones we have. In the second category, which is much closer to our problem, Mankin and Hudson [18] used a sine perturbation of the cooling fluid tempeature in a single CSTR (eqns. (5) and (6) with $\eta_1 = A \sin(\varpi t) + \eta_c$ in our notation.) . In the neighborhood of η_c , the unperturbed CSTR bifurcates to a stable limit cycle. The authors have shown that with an increase in the amplitude A of the forcing , quasi-periodic behavior occurs, followed by a sequence of period doubling bifurcation to chaos. They also indicated that oscillatory states can arise , where both states are periodic or one state periodic and the other chaotic. In their concluding remarks, the authors noted that the problem was a limiting case of coupled reactors where each of the reactors would serve as a forcing function for the other , and that while the cooling fluid temperature was chosen to vary in time, the feed concentration or temperature could have been chosen as well.

Caneba and Crossey [19] have chosen both the feed flow rate and the cooling fluid temperature to be periodic in time. By varying the amplitude of the cooling fluid forcing temperature, they observed period doubling behavior leading to a strange attractor. The unperturbed part of the system was maintained as close as possible to the phase plot of a homoclinic orbit. Their analysis was based on the Melnikov theory, which had been applied extensively in Hamiltonian systems. The theory in essence says that chaos will occur in periodically perturbed planar systems, provided the unperturbed system has a homoclinic orbit and the Melnikov function exhibits simple zeros when evaluated along the homoclinic orbit.

The dynamics of two CSTR' s in series are certainly very rich in periodic and oscillatory behavior. However our concern for the most part is with the occurrence of a strange attractor. In the next section we will show that the characteristic

equation is the product of the characteristic equations of each reactor and that this result may be generalized to n - CSTR' s in series. Subsequently , we will set the reactors in a situation which we think , based on the above considerations, will lead to a strange attractor. Our comments and recommendations on this search are made at appropriate locations.

1.) - The characteristic equation of the cascade :

In the neighborhood of a hyperbolic or nondegenerate steady state, the asymptotic behavior of the solutions, and hence the stability of the steady state itself is determined by the linearization. If J is the Jacobian matrix of eqns. (5) through (8) , the characteristic equation of the system is given by :

$$\mathrm{Det}\,(J - \lambda I) = 0 \qquad (32)$$

where Det refers to the determinant operation and I is the identity matrix.

A straightforward differentiation shows that :

$$J - \lambda I = \begin{pmatrix} a_{11} - \lambda & a_{12} & 0 & 0 \\ a_{21} & a_{22} - \lambda & 0 & 0 \\ a_{31} & 0 & a_{33} - \lambda & a_{34} \\ 0 & a_{42} & a_{43} & a_{44} - \lambda \end{pmatrix}$$

where
$$a_{11} = -(1 + Da_0 \tau\, E(\theta_1))$$
$$a_{12} = Da_0 \tau\, (1 - y_1)\, E'(\theta_1)$$
$$a_{21} = -B\, Da_0 \tau\, E(\theta_1)$$
$$a_{22} = -(1 + \beta_1 \tau) + B\, Da_0 \tau\, (1 - y_1)\, E'(\theta_1)$$
$$a_{31} = a_{42} = 1/\alpha$$
$$a_{33} = -((1/\alpha) + Da_0 \tau\, E(\theta_2))$$
$$a_{34} = Da_0 \tau\, (1 - y_2)\, E'(\theta_2)$$
$$a_{43} = -B\, Da_0 \tau\, E(\theta_2)$$
$$a_{44} = -((1 + \beta_2 \tau)/\alpha) + B\, Da_0 \tau\, (1 - y_2)\, E'(\theta_2)$$

and $E'(\theta_i) = E(\theta_i) / (1 + \varepsilon \theta_i)^2$

θ_i and y_i being evaluated at the steady state values.

If one sets tr_i and Det_i as being the trace and the determinant of the 2 x 2 Jacobian matrix associated with tank i , a straightforward evaluation of the determinant of eqn. (30) leads to the following :

$$Det(J - \lambda I) = (\lambda^2 - tr_1 \lambda + Det_1) (\lambda^2 - tr_2 \lambda + Det_2)$$

where $tr_1 = a_{11} + a_{22}$

$tr_2 = a_{33} + a_{44}$

$Det_1 = a_{11} a_{22} - a_{21} a_{12}$

$Det_2 = a_{33} a_{44} - a_{34} a_{43}$

For the case of n - CSTR' s , the n^{th} reactor will only depend on the $(n - 1)^{th}$ one. The general result is a band Jacobian matrix, the characteristic equation of which may be written as :

$$Det(J - \lambda I) = \prod_{i=1}^{n} (\lambda^2 - tr_i \lambda + Det_i)$$

where the symbol $\prod$ stands for product . The stability of the cascade is therefore determined by the stability of its components. This suggests that stable steady states will be hard to find as the number of CSTR's becomes larger.

2.) - Case study : search for a strange attractor .

As stated in the introduction to this chapter , our main concern is with the occurrence of a strange attractor in phase space . The suggestions of Mankin and Hudson [18] and the analysis of Caneba and Crossey [19] almost guarantee the existence , at least through numerical simulations, of chaotic behavior in the problem of two CSTR's in series. The fundamental guide for the search is the Melnikov theory :

Given a set of nonautonomous ordinary differential equations :

$$\frac{dX}{dt} = f(X) + g(X, t)$$

where $g(X, t)$ is periodic. Chaos can occur in the above set of equations if its unperturbed part,

$$\frac{dX}{dt} = f(X)$$

possesses a homoclinic orbit to a hyperbolic saddle point. Chaos is the result of a homoclinic bifurcation in which the stable and unstable manifolds intersect transversely. A homoclinic orbit, at least as a proposed behavior in the case of one CSTR, is a transition point between two kinds of dynamic behaviors, and as such occurs at given values of the parameters including the bifurcation one. Fig.8 illustrates this particular point. Because it happens exactly at one point, the numerical determination of a homoclinic orbit becomes fairly difficult. However as reported in [19], chaos may still occur with large periodic perturbations even if parameter values of the unperturbed system are somehow only in the vicinity of those of a homoclinic orbit. In the light of Melnikov theory eqns. (7) and (8) may be written as :

$$\frac{d}{dt}\begin{pmatrix} y_2 \\ \theta_2 \end{pmatrix} = \begin{pmatrix} \dfrac{-y_2}{\alpha} + Da_0\,\tau\,(1-y_2)\,E(\theta_2) \\ \dfrac{-\theta_2}{\alpha} + Da_0\tau\,B\,(1-y_2)E(\theta_2) - \dfrac{\beta_2\,\tau}{\alpha}(\theta_2-\eta_2) \end{pmatrix} + \frac{1}{\alpha}\begin{pmatrix} y_1 \\ \theta_1 \end{pmatrix}$$

The unperturbed part of this system when $\alpha = 1$ merely represents the equations of a single CSTR (i.e. when the second term on the right hand side is neglected). The appearance of a homoclinic orbit has been reported for this case by Uppal et al [1], along with regions of the parameter space where this behavior

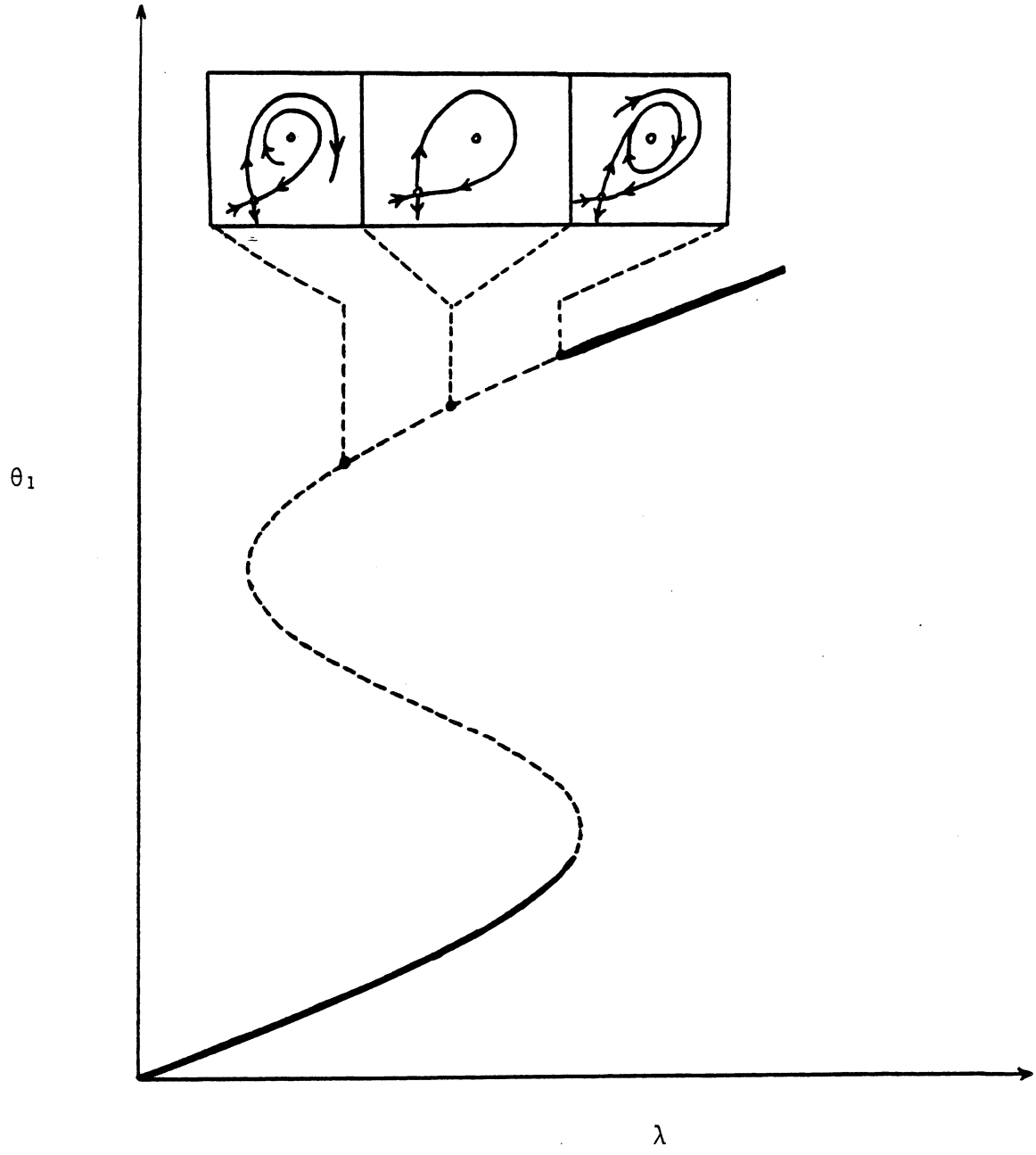


Fig.8. Illustration of a homoclinic orbit.

occurs. In our setting however, we will take parameter values reported in [19] for the unperturbed part of the second reactor, namely:

$\tau = 1.0$	$\beta_2 = 2.9821$	$\eta_2 = 0.0$
$\varepsilon = 1/30$	$B = 30$	$Da_0 = 0.04254$

With these values of the parameters, integration forward in time along the unstable manifold of the saddle and backwards in time along the stable one show that the phase portrait of the system, is very close to that of a homoclinic orbit. The integration along the unstable manifold in the direction specified by the eigenvector is shown in Fig.9, and the full orbit has been reported in [19].

The forcing term $g(X, t)$ comes from the first reactor, and one necessary condition for the occurrence of a strange attractor is that it be periodic. Therefore, the first reactor must operate under limit cycle conditions. Here care must be taken not to choose a bifurcation parameter that will push the unperturbed part of the second reactor far away from the homoclinic orbit. Thus in this case, the residence time τ is readily eliminated, and from the discussion of Chap.I, sect.3, our bifurcation parameter will be η_1. The other parameters are chosen as

$\tau = 1.0$, $\beta_1 = 2.9821$, $Da_0 = 0.04254$,
$\varepsilon = 1/30$, and $B = 30.0$

Fig.10 shows the steady state structure and the dynamic behavior of the first reactor as η_1 is varied. Starting at a Hopf point, as η_1 is decreased, the amplitude of the oscillations of the limit cycle increases all the way to $\eta_1 = 0.0$, then the limit cycle disappears. Indirectly, by using η_1 as a bifurcation parameter, we are in fact acting on the amplitude of the oscillations of the limit cycle, just as suggested in [18], except that in our case the amplitude will never exceed a value determined by the process itself.

The results of the search for a strange attractor are indeed disappointing. Figs.11 and 12 show the phase portrait respectively for $\eta_1 = 0.0$ and $\eta_1 = 0.02$ and Figs.13 and 14 show the exit temperature of the second reactor as a function of time for both situations. This suggests that in this setting, all that is possible is a periodic limit cycle and no strange attractor occurs.

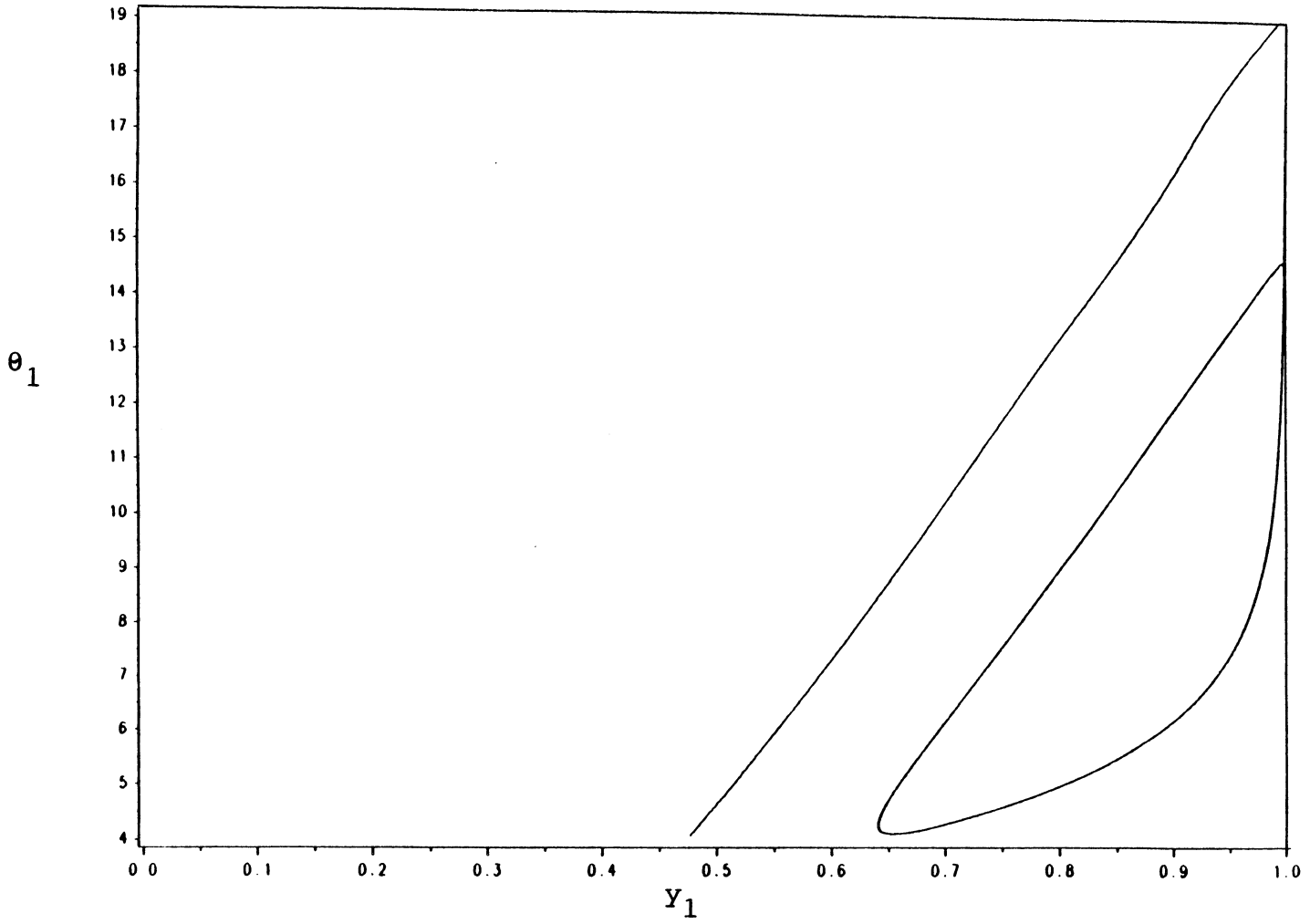


Fig. 9.- Phase plot close to a homoclinic orbit.

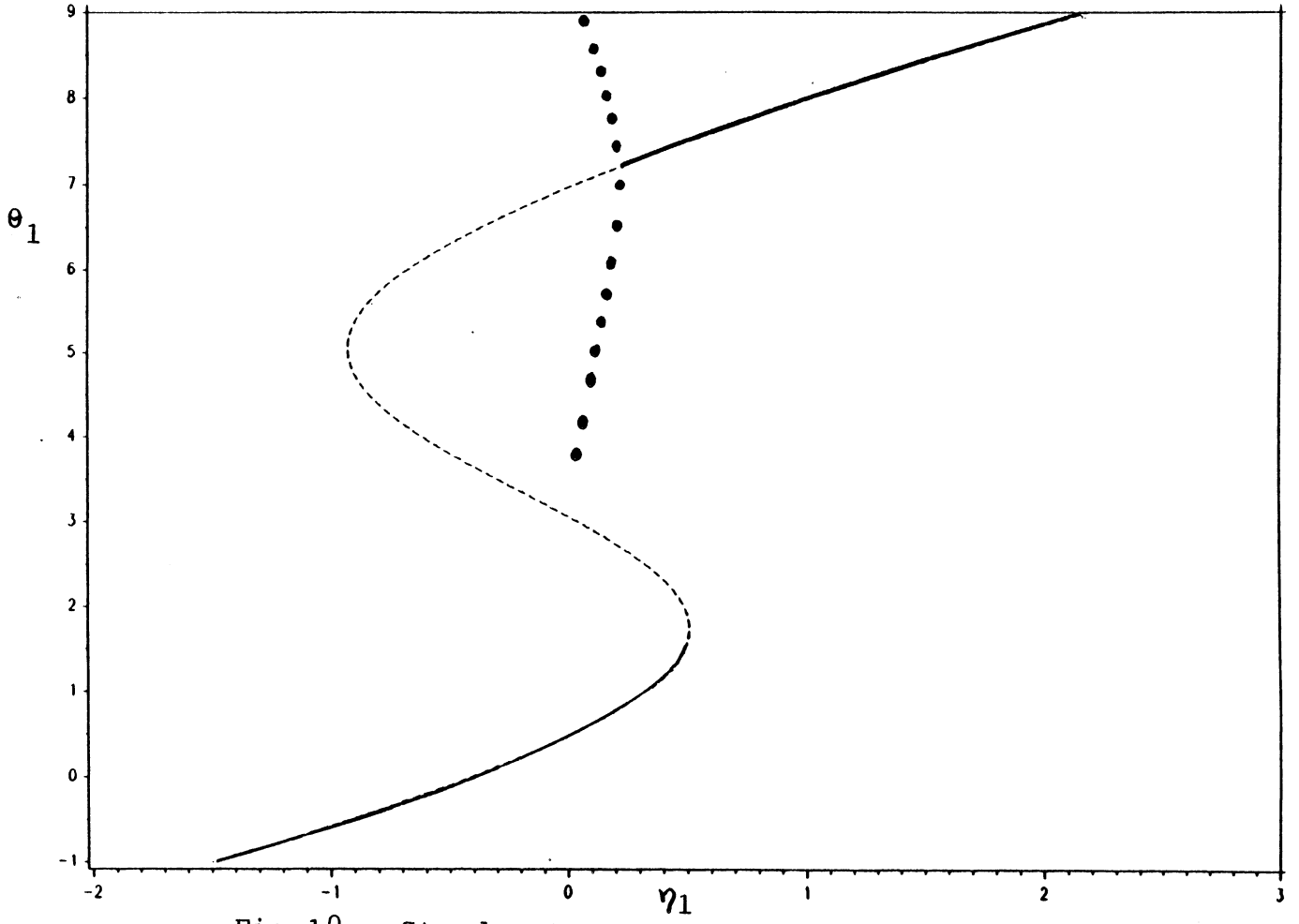


Fig.10.- Steady states and dynamic behavior of one CSTR as η_1 is varied.

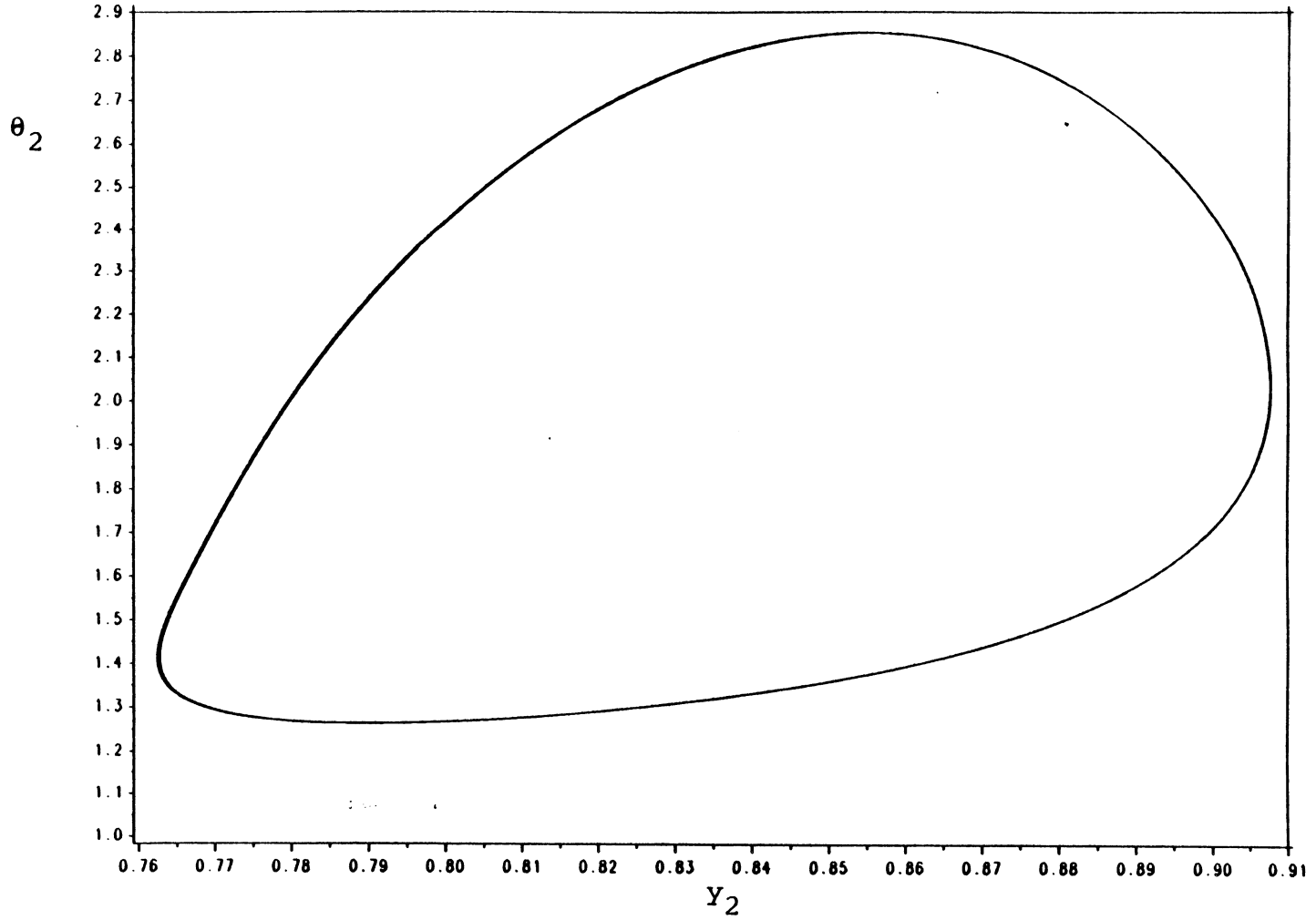


Fig.11.- Phase portrait in reactor 2 for $\eta_1 = 0.0$.

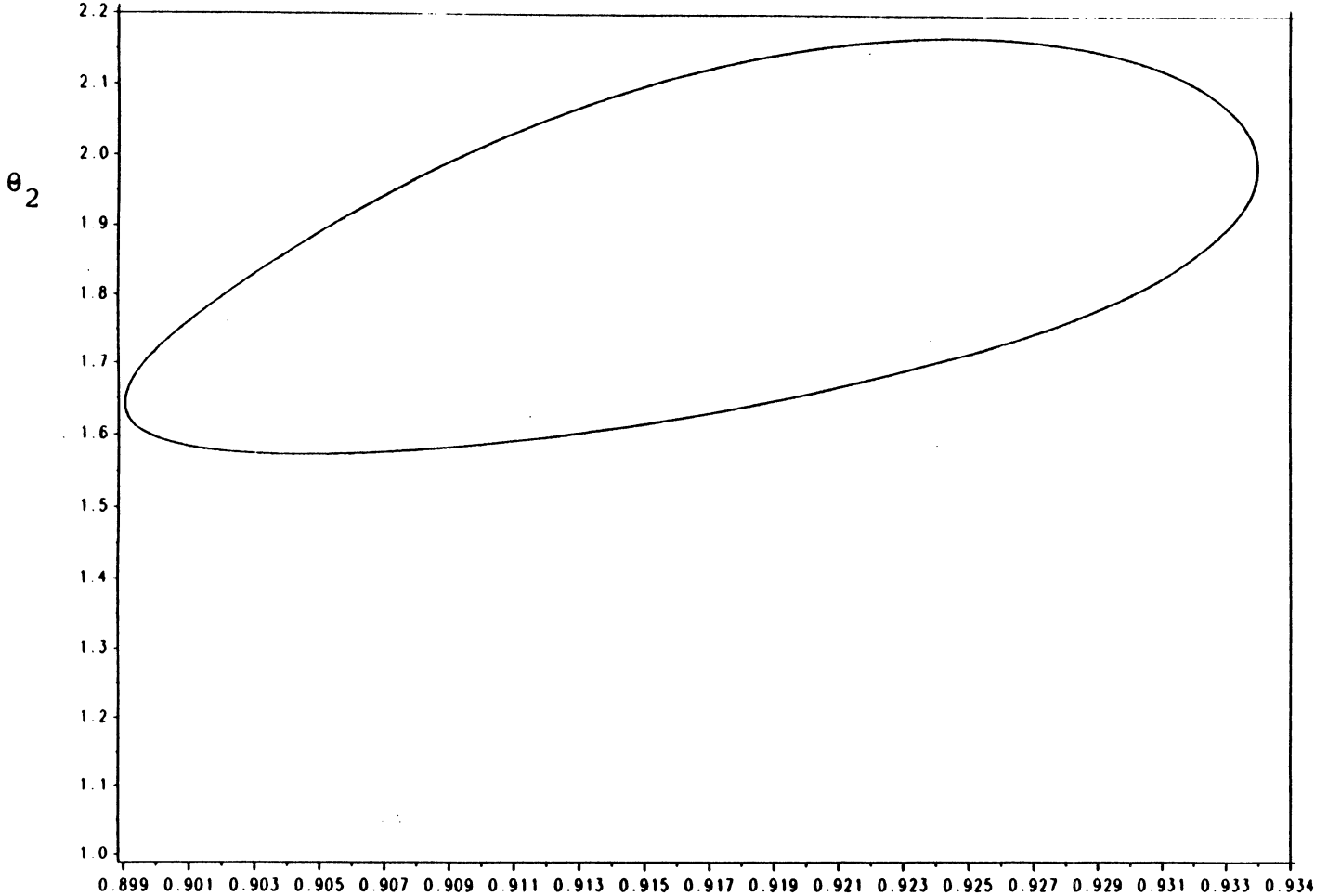


Fig.12.- Phase portrait in reactor 2 for $\eta_1 = 0.02$.

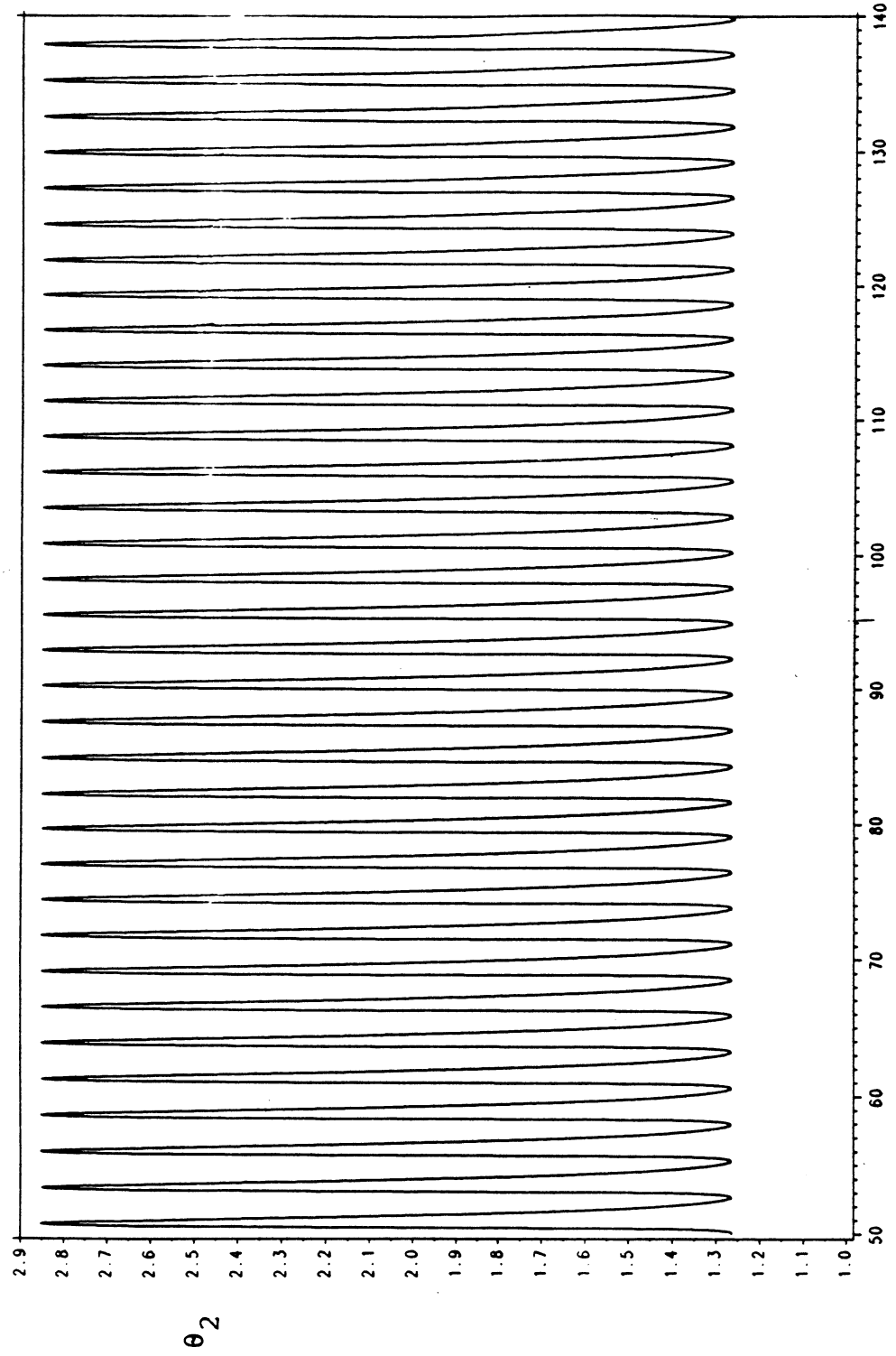


Fig.13.- Temperature in reactor 2 versus time for $\eta_1 = 0.0$.

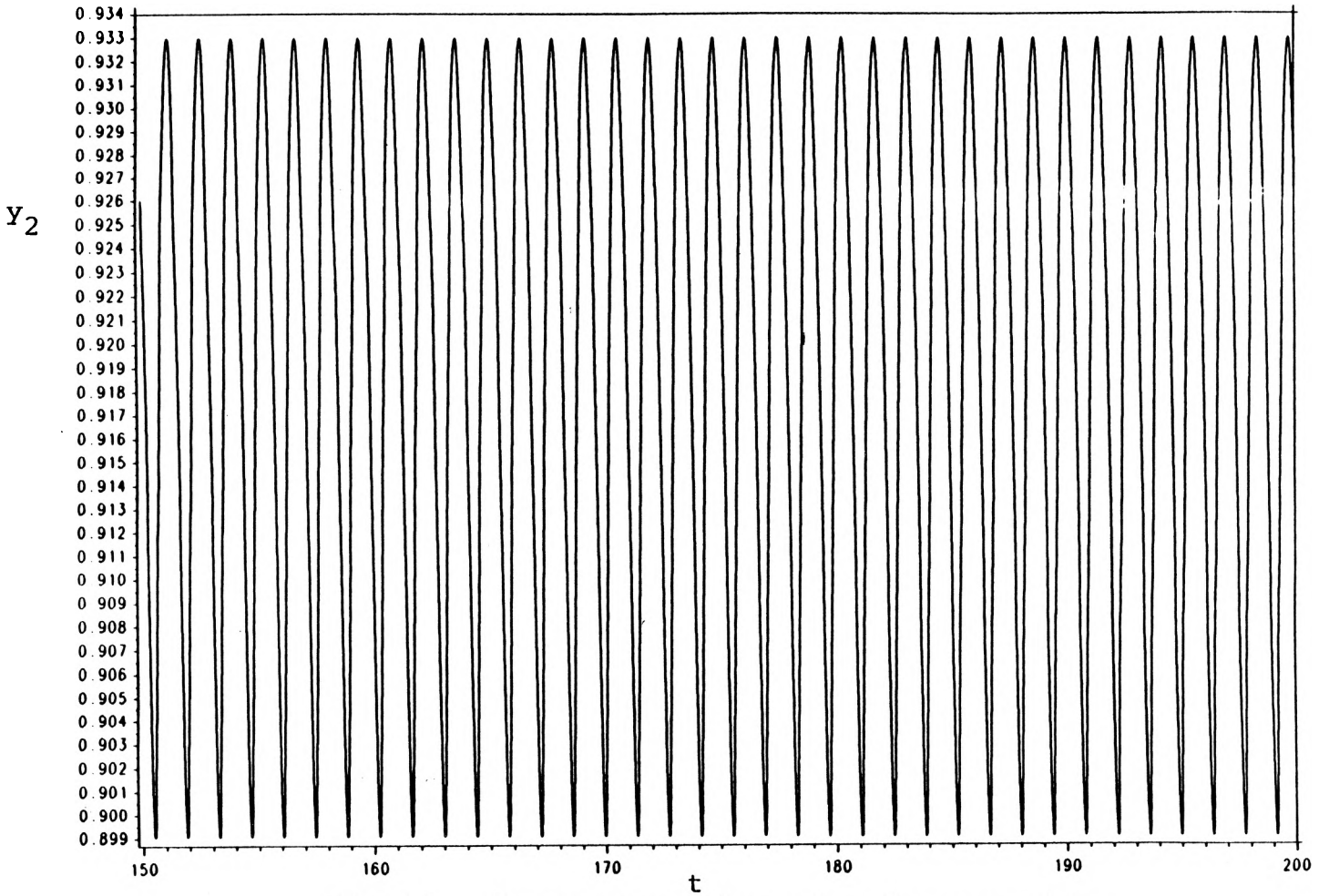


Fig.14.- Conversion in reactor 2 versus time for $\eta_1 = 0.02$.

3.) - Concluding remarks :

Two comments bear on the failure of our search for chaos. First, Melnikov theory requires the Melnikov function to exhibit simple zeros independent of the magnitude of the forcing term. This may be a delicate matter in the problem we have studied. Unfortunately, we cannot evaluate the Melnikov integral accurately, because we do not have an analytic expression for the homoclinic orbit in the second reactor. It is of course possible that the Melnikov function does not exhibit zeros for this problem. The second comment is that the results of Mankin and Hudson [18] exhibiting chaos were obtained by crossing two periodic behaviors. Chaos occurred for a specific choice of frequency of the oscillations. While they had a hold on the amplitude and the frequency of the oscillations, in our case we are constrained, since oscillations in the first reactor are natural as η_1 is varied, and any desired higher amplitudes or frequencies cannot be obtained at will.

Finally chaotic dynamics were reported in many different systems under different conditions, and it is our belief that the simpler the system is the easier our understanding of the chaotic dynamics will be. The simplest system that we have found so far is the single CSTR with periodic variation in time for the cooling fluid temperature [18] just mentioned above. This instance corresponds , in a three dimensional space , to a crossing of a limit cycle in the unperturbed system and a periodic sinusoidal function whose amplitude is taken as a bifurcation parameter.

An analysis of the impact of the frequency of the oscillations used in that study on the existence of a strange attractor , should help provide an answer to the failure of our search.

Chapter IV : Conclusions and Recommendations.

We have looked into the problem of two CSTR's in series, in which a first order reaction is taking place. Besides the industrial value of the information one may acquire from the problem, the system is a mathematical object, and as such its analysis is both interesting and important in its own right. Guided by the sequential bifurcation theory of singularities, we have been able to prove that the maximum number of steady states is nine. This has been achieved by deriving more than one bifurcation diagram in the unfolding space of $(2)_{33}$, which show nine crossings as the bifurcation parameter was varied. Furthermore, numerical examples were obtained which support the analysis. It remains to be derived from the model itself, the geometry found in the unfolding space, after an appropriate identification of the unfolding parameters is made. One must admit that the parameter space is multidimensional, and that the task of subdividing it into regions where a given number of equilibria occurs is a real challenge.

Inspired by the Melnikov theory, which can ascertain chaotic behavior through periodic perturbation of a homoclinic orbit, we searched for a strange attractor. This search did not succeed, and this might be due to the fact that the amplitude of the indirect periodic perturbations was not appropriate to provide such a phenomena. Our recommendation therefore, is to study the frequencies and amplitudes generated when a single CSTR bifurcates to a limit cycle as a parameter is varied. The study of Mankin and Hudson will certainly help in obtaining a strange attractor. This will indeed provide a basis for applying the Melnikov theory to this particular problem.

Finally, we have made some statements about an array of n - CSTR's, and have indicated how such statements may be approached in order to provide the missing proofs. We close this chapter by simply stating that the dynamics of this problem are very rich , and provide a nice setting for the study of sequential oscillators, which has a wide range of applications.

Nomenclature.

F	Volumetric flow rate (m^3 / hr.).
c_{Ai}	Concentration of reactant A in reactor i (kg / m^3).
T_i	Temperature in reactor i (^0K).
V_i	Volume of reactor i (m^3).
a_i	Heat exchange surface area (m^2).
u_i	Heat transfer coefficient ($W / m^2\,^0K$).
C_p	Heat capacity of the mixture ($J / ^0K$).
$(-\Delta H)$	Enthalpy of the reaction ($J / ^0K$).
$k(T_i)$	Reaction rate coefficient (s^{-1}).
ρ	Density of the mixture (kg / m^3).

Dimensionless Quantities :

θ_i	Temperature in reactor i.
η_i	Cooling fluid temperature in reactor i.
B	Adiabatic temperature rise.
Da_0	Damkohler number.
ε	$R T_0 / E$, inverse of the activation energy.
β_i	Heat transfer coefficients.
α	V_2 / V_1.
τ	Dimensionless residence time.

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Appendices.

Appendix I : Solution to the system formed by the derivatives conditions .

The steady state equations are :

$$F_1(x_1, \tau) = \frac{(1+\beta_1 \tau)\,\mathrm{Ln}\, x_1}{(1-\varepsilon\,\mathrm{Ln}\, x_1)} - \frac{B\,Da_0\,\tau\,x_1}{(1+Da_0\,\tau\,x_1)} - \beta_1\,\tau\,\eta_1 = 0 \qquad (I\text{–}1)$$

$$F_2(x_1, x_2, \tau) = \frac{(1+\beta_2 \tau)\,\mathrm{Ln}\, x_2}{(1-\varepsilon\,\mathrm{Ln}\, x_2)} - \frac{\alpha\,B\,Da_0\,\tau\,x_2}{(1+Da_0\,\tau\,x_1)\,(1+\alpha\,Da_0\,\tau\,x_2)} -$$

$$- \frac{\mathrm{Ln}\, x_1}{(1-\varepsilon\,\mathrm{Ln}\, x_1)} - \beta_2\,\tau\,\eta_2 = 0 \qquad (I\text{–}2)$$

A straightforward differentiation of F_1 yields the following :

$$\mathrm{Ln}\, x_1 = \frac{B+\beta_1\,\tau\,\eta_1}{(1+\beta_1\,\tau+\varepsilon\,\beta_1\,\tau\,\eta_1+\varepsilon\,B)} - 2 \qquad (I-3)$$

$$Da_0\,\tau\,x_1 = \frac{B(1+\beta_1\,\tau)}{2\,(1+\beta_1\,\tau+\varepsilon\,\beta_1\,\tau\,\eta_1+\varepsilon\,B)^2} - \frac{(1+\beta_1\,\tau+\varepsilon\,\beta_1\,\tau\,\eta_1)}{(1+\beta_1\,\tau+\varepsilon\,\beta_1\,\tau\,\eta_1+\varepsilon\,B)} \qquad (I-4)$$

$$B = \frac{4\,(1+\beta_1\tau+\varepsilon\beta_1\tau\eta_1)^2}{(1+\beta_1\tau)-4\varepsilon\,(1+\beta_1\tau+\varepsilon\beta_1\tau\eta_1)} \qquad (I-5)$$

Using (I-5) in (I-3) and (I-4) we get

$$\mathrm{Ln}\,x_1 = 2+\frac{\beta_1\tau\eta_1}{(1+\beta_1\tau+\varepsilon\beta_1\tau\eta_1)} \qquad (I-6)$$

$$Da_0\,\tau\,x_1 = 1-4\varepsilon\,\frac{(1+\beta_1\tau+\varepsilon\beta_1\tau\eta_1)}{(1+\beta_1\tau)} \qquad (I-7)$$

For conditions (19), analogous results may be obtained by identifying $\mathrm{Ln}\,x_1$, $Da_0\,\tau\,x_1$, $1+\beta_1\tau$, $\beta_1\tau\eta_1$ and B respectively with $\mathrm{Ln}\,x_2$, $\alpha\,Da_0\,\tau\,x_2$,

$(1+\beta_2\tau)$, $\beta_2\tau\eta_2+\dfrac{\mathrm{Ln}\,x_1}{(1-\varepsilon\,\mathrm{Ln}\,x_1)}$ and $\dfrac{B}{(1+Da_0\,\tau\,x_1)}$:

$$B = \frac{4\,(1+Da_0\,\tau\,x_1)}{(1-\varepsilon\,\mathrm{Ln}\,x_1)}\;\frac{\{\,1+\beta_2\tau(1+\varepsilon\eta_2)(1-\varepsilon\,\mathrm{Ln}\,x_1)\,\}^2}{\{\,1+\beta_2\tau-4\varepsilon\beta_2\tau(1+\varepsilon\eta_2)\,\}\;(1-\varepsilon\,\mathrm{Ln}\,x_1)-4\varepsilon} \qquad (I-8)$$

$$\alpha\,Da_0\,\tau\,x_2 = 1-4\varepsilon\,\frac{\beta_2\tau\,(1+\varepsilon\eta_2)(1-\varepsilon\,\mathrm{Ln}\,x_1)+1}{(1+\beta_2\tau)\;(1-\varepsilon\,\mathrm{Ln}\,x_1)} \qquad (I-9)$$

$$\text{Ln } x_2 = 2 + \frac{\beta_2 \tau \eta_2 \ (1 - \varepsilon \text{ Ln } x_1) + \text{Ln } x_1}{1 + \beta_2 \tau \ (1 + \varepsilon \eta_2) \ (1 - \varepsilon \text{ Ln } x_1)} \qquad (I-10)$$

Condition (20) yields the following:

$$\alpha \, Da_0 \, \tau \, x_2 = \frac{1}{\beta_1 \tau} \qquad (I-11)$$

Rearrangement of (I - 5) through (I - 7) gives the following :

$$B = \frac{4 \ (1 + \beta_1 \tau + \varepsilon \beta_1 \tau \eta_1)^2}{(1 + \beta_1 \tau) - 4 \varepsilon \ (1 + \beta_1 \tau + \varepsilon \beta_1 \tau \eta_1)} \qquad (I-5)$$

$$x_1 = \text{Exp} \left\{ 2 + \frac{\beta_1 \tau \eta_1}{(1 + \beta_1 \tau + \varepsilon \beta_1 \tau \eta_1)} \right\} \qquad (I-12)$$

$$Da_0 = \frac{1}{\tau x_1} \left\{ 1 - 4 \varepsilon \frac{(1 + \beta_1 \tau + \varepsilon \beta_1 \tau \eta_1)}{(1 + \beta_1 \tau)} \right\} \qquad (I-13)$$

For nonzero ε, (I - 9) and (I-11) may be combined to give :

$$(1 + \varepsilon \eta_2) \ \beta_2 \tau = k \beta_2 \tau + h \qquad (I-14)$$

where $k = \dfrac{\beta_1 \tau - 1}{4 \varepsilon \beta_1 \tau}$ and $h = \dfrac{\beta_1 \tau - 1}{4 \varepsilon \beta_1 \tau} - \dfrac{1}{(1 - \varepsilon \text{ Ln } x_1)}$

(I-14) may then be used with (I-8) to get β_2 :

$$\beta_2 = \frac{4\,\varepsilon^2 \beta_1 B}{(1+ Da_0 \tau\, x_1)\,(\beta_1 \tau - 1)^2} - \frac{1}{\tau} \qquad \text{(I-15)}$$

η_2 is now evaluated using (I-14) and x_2 by (I-10).

Appendix II : Derivation of the sets D_0, D_1 and E

Among the defining conditions of these sets we have ($B = B_x = 0$) :

$$\begin{aligned} x^3 - u\,x + \gamma x^2 + \beta x + \alpha &= 0 \\ 3x^2 - u + 2\gamma x + \beta &= 0 \end{aligned} \qquad \text{(II-1)}$$

This system is equivalent to :

$$\begin{aligned} \gamma x^2 + 2(\beta - u)\,x + 3\alpha &= 0 \\ 3x^2 + 2\gamma x + (\beta - u) &= 0 \end{aligned} \qquad \text{(II-2)}$$

Using Cramer's rule we get the following :

$$u \neq \frac{2\gamma^2 - 6\beta}{6} \qquad \text{(II-3)}$$

$$x = \frac{9\alpha - (\beta - u)\,\gamma}{2\gamma^2 - 6(\beta - u)} \qquad \text{(II-4)}$$

$$y = \frac{2(\beta - u)^2 - 6\alpha\gamma}{2\gamma^2 - 6(\beta - u)} \qquad \text{(II-5)}$$

$$y = x^2 \qquad \text{(II-6)}$$

(II-6) translates into :

$$4\,u^3 + u^2(\gamma^2 - 12\beta) + u(-2\beta\gamma^2 + 12\beta^2 - 18\alpha\gamma) + (\beta^2\gamma^2 - 4\alpha\gamma^3 - 4\beta^3 + 18\alpha\beta\gamma - 27\alpha^2) = 0 \qquad \text{(II-7)}$$

Solutions u of this polynomial satisfying (II-3) will yield solutions x by (II-4).

The set D_0 :
==========

This set requires two solutions x to the system $B = B_x = 0$. This is possible only if (II-3) is violated, thus leading to $\gamma^2 = 3(\beta - u)$. Then $x = -\gamma / 3$ is the only solution, and this implies that the set is empty.

The set D_1 :
==========

This set is defined by $A = B = B_x = 0$ for $u_1 \neq u_2$

$$A = 0 \quad ======> \quad u_1^2 + u_2^2 + u_1 u_2 = -\delta \qquad \text{(II-8)}$$

It can be shown that (II-8) and (II-7) are equivalent to :

$$4\,u^3 + u^2(\gamma^2 - 12\beta) + u(-2\beta\gamma^2 + 12\beta^2 - 18\alpha\gamma) + (\beta^2\gamma^2 - 4\alpha\gamma^3 - 4\beta^3 + 18\alpha\beta\gamma - 27\alpha^2) = 0 \qquad \text{(II-7)}$$

$$(\gamma^2 - 12\beta)^2 u^2 - (\gamma^2 - 12\beta)(4\delta + 2\beta\gamma^2 - 12\beta^2 + 18\alpha\gamma)\,u + (4\delta + 2\beta\gamma^2 - 12\beta^2 + 18\alpha\gamma)^2 + \delta(\gamma^2 - 12\beta)^2 = 0 \qquad \text{(II-9)}$$

This system may be reduced to a system of two quadratics in u by eliminating the cubic term from (II-7). By considering solutions u and u^2 as before, it is easy to show that for multiple roots u to exist the determinant of the system as well as

the numerators resulting from using Cramer's rule must vanish. These considerations give the analytical expression of the set D_1 :

(i) $(\gamma^2 - 12\beta) = 0$ and (II-9)

$$\Longrightarrow \qquad \beta = \gamma^2 / 12$$
$$\alpha = -(48\delta + \gamma^4) / 216\gamma$$

(ii) $(23328\gamma^3)\alpha^3 + \{7776\gamma^2(2\delta + \beta\gamma^2 - 6\beta^2) + 324\gamma^2(\gamma^2 - 12\beta)^2 + 27(\gamma^2 - 12\beta)^3\}\alpha^2 + \{864\gamma(2\delta + \beta\gamma^2 - 6\beta^2)^2 + 36\gamma(6\delta + 2\beta\gamma^2 - 12\beta^2)(\gamma^2 - 12\beta)^2 + (4\gamma^3 - 18\beta\gamma)(\gamma^2 - 12\beta)^3\}\alpha + \{32(2\delta + \beta\gamma^2 - 6\beta^2)^3 + 4(2\delta + \beta\gamma^2 - 6\beta^2)(4\delta + \beta\gamma^2 - 6\beta^2)(\gamma^2 - 12\beta)^2 - \beta^2(\gamma^2 - 4\beta)(\gamma^2 - 12\beta)^3 + \delta(\gamma^2 - 12\beta)^4\} = 0$

and the condition :

$-3(2\delta + \beta\gamma^2 - 6\beta^2 + 9\alpha\gamma)^2 - \delta(\gamma^2 - 12\beta)^2 > 0$

The set E :

Here $A_u = 0 \Longrightarrow u_i = \pm\theta$ and $\theta = \sqrt{-\delta/3}$ $(\delta < 0)$

We already have two solutions u, so use these values in (II-7) to obtain the expression of the set :

$$\alpha = \{9\gamma(\beta - u_i) - 2\gamma^3 + 2[\gamma^2 - 3(\beta - u_i)]^{3/2}\} / 27$$

Appendix III : Computer program CSTRS

This program computes the steady states of two CSTR's in series, as the residence time is varied, for a set of problem parameters.

```
      DOUBLE PRECISION DEL1,T1MIN,T1MAX,T1,V1,S1,DV,TAU,A,T1M,T1L,T1U,A
     $1,B1,C1,T1C,DA1MAX,DA1MIN,T1MINO,T1MAXO,T1MI,T1MA,RT1,RT2,RT3,RT4
      DOUBLE PRECISION DEL2,T2MIN,T2MAX,T2,V2,S2,ES,XRT,Y,XTAU,DU,TAV,A2
     $,B2,C2,T2C,DA2MAX,DA2MIN,T2MINO,T2MAXO,T2MI,T2MA,T2L,T2M,T2U,RT11,
     $V4,RT5,V11,V22,VT1
      COMMON ALPHA,H1,H2,TC1,TC2,B,E,DA0
C
C
      TAU=   Starting value of the residence time.
C     ALPHA= Ratio of the  volumes of the reactors.
C     H1=    Heat exchange coefficient of reactor 1.
C     H2=    Heat exchange coefficient of reactor 2.
C     TC1=   Cooling fluid temperature in reactor 1.
C     TC2=   Cooling fluid temperature in reactor 2.
C     B=     Adiabatic temperature  rise.
C     E=     Inverse  of  activation  energy.
C     DA0=   Damkohler number.
      GO TO 4567
```

Loop Over Tau : calculate possible steady states in reactor 1, using FINRT1 (find roots in reactor 1), then call CSTR2 to calculate possible steady states in reactor 2.

```
 4567 HELLO=0.0
C
C
      V1=(1.0+H1*TAU)
      S1=B+(H1*TAU*TC1)
      V11=H1*TAU*TC1
C
C
      B1=((2*E*(S1-V11))-(S1+V11))*V1
      A1=V1*(E**2)*(S1-V11)+(V1**2)
      C1=V1*(S1-V11)+(S1*V11)
      DEL1=(B1**2)-(4.0*A1*C1)
C
C
      IF(DEL1.LT.0.0) GO TO 111
      GO TO 222
C
C
  222 T1MI=(-B1+DSQRT(DEL1))/(2.0*A1)
```

```
      T1MA=(-B1-DSQRT(DEL1))/(2.0*A1)
      IF(T1MI.GT.T1MA) GO TO 223
      GO TO 224
  223 T1MIN=T1MI
      T1MAX=T1MA
      GO TO 225
  224 T1MIN=T1MA
      T1MAX=T1MI
      GO TO 225
C
C
  225 DA1MAX=((V1*T1MAX-V11)/(S1-V1*T1MAX))*DEXP(-T1MAX/(1.0+E*T1MAX))
      DA1MIN=((V1*T1MIN-V11)/(S1-V1*T1MIN))*DEXP(-T1MIN/(1.0+E*T1MIN))
C
C
      Y=T1MIN
      YF=S1/V1
C
C
      CALL FINRT1(Y,S1,V1,V11,YF,1000.0,DA1MAX,TAU,RT1)
      T1MAXO=RT1
      Y=V11/V1
      YF=T1MAX
      CALL FINRT1(Y,S1,V1,V11,YF,1000.0,DA1MIN,TAU,RT2)
      T1MINO=RT2
C
C
      IF(DU-DA1MAX) 227,228,229
  227 IF(DU-DA1MIN) 230,231,232
  228 CALL CSTR2(T1MAX,TAU,DU)
      CALL CSTR2(T1MAXO,TAU,DU)
      GO TO 239
C
C
  229 Y=T1MAXO
      YF=S1/V1
      CALL FINRT1(Y,S1,V1,V11,YF,1000.0,DU,TAU,RT3)
      CALL CSTR2(RT3,TAU,DU)
      GO TO 239
C
C
  231 CALL CSTR2(T1MIN,TAU,DU)
      CALL CSTR2(T1MINO,TAU,DU)
      GO TO 239
C
C
  230 Y=V11/V1
      YF=T1MINO
      CALL FINRT1(Y,S1,V1,V11,YF,1000.0,DU,TAU,RT4)
      XT1=RT4
      CALL CSTR2(XT1,TAU,DU)
      GO TO 239
C
C
  232 Y=T1MINO
```

```
      YF=T1MAX
      CALL FINRT1(Y,S1,V1,V11,YF,1000.0,DU,TAU,T1L)
      XT1=T1L
      CALL CSTR2(XT1,TAU,DU)
      Y=T1MAX
      YF=T1MIN
      CALL FINRT1(Y,S1,V1,V11,YF,1000.0,DU,TAU,T1M)
C
      XT1=T1M
      CALL CSTR2(XT1,TAU,DU)
      Y=T1MIN
      YF=T1MAXO
      CALL FINRT1(Y,S1,V1,V11,YF,1000.0,DU,TAU,T1U)
C
      XT1=T1U
      CALL CSTR2(XT1,TAU,DU)
      GO TO 239
C
  111 Y=V11/V1
      YF=S1/V1
      CALL FINRT1(Y,S1,V1,V11,YF,1000.0,DU,TAU,RT5)
      XT1=RT5
      CALL CSTR2(XT1,TAU,DU)
      GO TO 239
C
  239 HELLO=0.0
      IF(TAU.GT.1.4987) STOP
      TAU=TAU+0.000001
      GO TO 4567
C     STOP
      END
C
C
C
      SUBROUTINE FINRT1(Y,SI,VI,V1I,YF,FMAX,DX,TO,RT)
      DOUBLE PRECISION Y,Y1,YAVG,FAVG,FMAX,HY,YI,YF,DX,RT,TO,FY,FY1,VI,S
     $I,EI,V1I
      COMMON ALPHA,H1,H2,TC1,TC2,B,E,DA0
C
      HY=(YF-Y)/1000
C
    3 FY=-((VI*Y-V1I)*DEXP(-Y/(1.0+E*Y)))+DX*(SI-VI*Y)
      GO TO 4
    4 Y1=Y+HY
      FY1=-((VI*Y1-V1I)*DEXP(-Y1/(1.0+E*Y1)))+DX*(SI-VI*Y1)
      IF(FY*FY1) 8,5,7
    5 RT=Y1
      Y=Y1+HY
      GO TO 3
    7 IF(Y1.GE.YF) GO TO 16
      Y=Y1
      FY=FY1
      GO TO 4
    8 DO 11 I=1,200
      YAVG=(Y+Y1)/2.0
```

$Y = \theta_1$

$E = \epsilon$

```
      FAVG=-((VI*YAVG-V1I)*DEXP(-YAVG/(1.0+E*YAVG)))+DX*(SI-VI*YAVG)
      IF(DABS(FAVG).GT.FMAX) GO TO 14
      IF(FY*FAVG) 10,12,9
    9 Y=YAVG
      FY=FAVG
      GO TO 11
   10 Y1=YAVG
      FY1=FAVG
   11 CONTINUE
   12 RT=YAVG
C     WRITE(6,6) TO,YAVG
   13 FY=FY1
      Y=Y1
      GO TO 4
   14 HELLO=0.0
      GO TO 13
   16 HELLO=0.0
      RETURN
      END
C
C
C
      SUBROUTINE CSTR2(XT1,XTAU,XDU)
C
      DOUBLE PRECISION DEL2,T2MIN,T2MAX,T2,V2,S2,ES,XRT,Y,XTAU,DV,VT1,A2
     $,B2,C2,T2C,DA2MAX,DA2MIN,T2MINO,T2MAXO,T2MI,T2MA,T2L,T2M,T2U,RT11
      DOUBLE PRECISION Y1,YAVG,FAVG,FMAX,HY,YF,RT,DX,FY,FY1,RT22,RT33,RT
     $44,RT55,V22,V4,XT1,XDU,D2MIN,D2MAXO,D2MAX,D2MINO,DT22,DT33,DT44,DT
     $55
      COMMON ALPHA,H1,H2,TC1,TC2,B,E,DA0

      XDU=DA0*XTAU
      V2=(1.0+H2*XTAU)
      V22=(H2*XTAU*TC2)
      V4=H1*XTAU
      S2=B+(H1*XTAU*TC1)+(H2*XTAU*TC2)
C
C
      BT=S2-(V4*XT1)
      AL=(XT1+V22)
      A2=(E**2)*(BT-AL)*V2+(V2**2)
      B2=2*E*(BT-AL)*V2-(BT+AL)*V2
      C2=(BT-AL)*V2+AL*BT
C
C
      DEL2=(B2**2)-4*A2*C2
      IF(DEL2.LT.0.0) GO TO 1111
      GO TO 1222
C
C
C
 1222 T2MI=(-B2+DSQRT(DEL2))/(2.0*A2)
      T2MA=(-B2-DSQRT(DEL2))/(2.0*A2)
      IF(T2MI.GT.T2MA) GO TO 1223
      GO TO 1224
```

```
C
C
 1223 T2MIN=T2MI
      T2MAX=T2MA
      GO TO 1225
 1224 T2MIN=T2MA
      T2MAX=T2MI
      GO TO 1225
C
C
C
 1225 DA2MAX=((V2*T2MAX-XT1-V22)/(S2-V4*XT1-V2*T2MAX))*DEXP(-T2MAX
     $+E*T2MAX))/ALPHA
      DA2MIN=((V2*T2MIN-XT1-V22)/(S2-V4*XT1-V2*T2MIN))*DEXP(-T2MIN
     $+E*T2MIN))/ALPHA
C
C
      Y=T2MIN
      YF=(S2-V4*XT1)/V2
C
      CALL FINRT2(Y,S2,V2,V22,V4,YF,1000.0,DA2MAX,XT1,XTAU,RT11)
      T2MAXO=RT11
      Y=(XT1+V22)/V2
      YF=T2MAX
      CALL FINRT2(Y,S2,V2,V22,V4,YF,1000.0,DA2MIN,XT1,XTAU,RT22)
      T2MINO=RT22
C
      IF(XDU-DA2MAX) 1227,1228,1229
 1227 IF(XDU-DA2MIN) 1230,1231,1232
 1228 VT1=((1+H1*XTAU)*XT1-H1*XTAU*TC1)/B
      D2MAX=((1+H2*XTAU)*T2MAX+(B*VT1-XT1)-(H2*XTAU*TC2))/B
C     WRITE(9,1233) XTAU,VT1,D2MAX
      WRITE(9,1233) XTAU,XT1,T2MAX
      D2MAXO=((1+H2*XTAU)*T2MAXO+(B*VT1-XT1)-(H2*XTAU*TC2))/B
C     WRITE(9,1233) XTAU,VT1,D2MAXO
      WRITE(9,1233) XTAU,XT1,T2MAXO
 1233 FORMAT(3(1X,D15.8))
      GO TO 1239
C
 1229 Y=T2MAXO
      YF=(S2-V4*XT1)/V2
      CALL FINRT2(Y,S2,V2,V22,V4,YF,1000.0,XDU,XT1,XTAU,RT33)
      VT1=((1+H1*XTAU)*XT1-H1*XTAU*TC1)/B
      DT33=((1+H2*XTAU)*RT33+(B*VT1-XT1)-(H2*XTAU*TC2))/B
C     WRITE(9,1233) XTAU,VT1,DT33
      WRITE(9,1233) XTAU,XT1,RT33
      GO TO 1239
C
 1231 VT1=((1+H1*XTAU)*XT1-H1*XTAU*TC1)/B
      D2MIN=((1+H2*XTAU)*T2MIN+(B*VT1-XT1)-(H2*XTAU*TC2))/B
C     WRITE(9,1233) XTAU,VT1,D2MIN
      WRITE(9,1233) XTAU,XT1,T2MIN
      D2MINO=((1+H2*XTAU)*T2MINO+(B*VT1-XT1)-(H2*XTAU*TC2))/B
C     WRITE(9,1233) XTAU,VT1,D2MINO
      WRITE(9,1233) XTAU,XT1,T2MINO
```

```
      GO TO 1239
C
 1230 Y=(XT1+V22)/V2
      YF=T2MINO
      CALL FINRT2(Y,S2,V2,V22,V4,YF,1000.0,XDU,XT1,XTAU,RT44)
      VT1=((1+H1*XTAU)*XT1-H1*XTAU*TC1)/B
      DT44=((1+H2*XTAU)*RT44+(B*VT1-XT1)-(H2*XTAU*TC2))/B
C     WRITE(9,1233) XTAU,VT1,DT44
      WRITE(9,1233) XTAU,XT1,RT44
      GO TO 1239
C
 1232 Y=T2MINO
      YF=T2MAX
      CALL FINRT2(Y,S2,V2,V22,V4,YF,1000.0,XDU,XT1,XTAU,T2L)
      VT1=((1+H1*XTAU)*XT1-H1*XTAU*TC1)/B
      D2L=((1+H2*XTAU)*T2L+(B*VT1-XT1)-(H2*XTAU*TC2))/B
C     WRITE(9,1233) XTAU,VT1,D2L
      WRITE(9,1233) XTAU,XT1,T2L
      Y=T2MAX
      YF=T2MIN
      CALL FINRT2(Y,S2,V2,V22,V4,YF,1000.0,XDU,XT1,XTAU,T2M)
      D2M=((1+H2*XTAU)*T2M+(B*VT1-XT1)-(H2*XTAU*TC2))/B
C     WRITE(9,1233) XTAU,VT1,D2M
      WRITE(9,1233) XTAU,XT1,T2M
      Y=T2MIN
      YF=T2MAXO
      CALL FINRT2(Y,S2,V2,V22,V4,YF,1000.0,XDU,XT1,XTAU,T2U)
      D2U=((1+H2*XTAU)*T2U+(B*VT1-XT1)-(H2*XTAU*TC2))/B
C     WRITE(9,1233) XTAU,VT1,D2U
      WRITE(9,1233) XTAU,XT1,T2U
      GO TO 1239
C
 1111 Y=(XT1+V22)/V2
      YF=(S2-V4*XT1)/V2
      CALL FINRT2(Y,S2,V2,V22,V4,YF,1000.0,XDU,XT1,XTAU,RT55)
      VT1=((1+H1*XTAU)*XT1-H1*XTAU*TC1)/B
      DT55=((1+H2*XTAU)*RT55+(B*VT1-XT1)-(H2*XTAU*TC2))/B
C     WRITE(9,1233) XTAU,VT1,DT55
      WRITE(9,1233) XTAU,XT1,RT55
      GO TO 1239
C
 1239 HELLO=0.0
      RETURN
      END
C
C
C
C
C
      SUBROUTINE FINRT2(Y,SI,VI,VJ,VK,YF,FMAX,DX,XT,TO,RT)
      DOUBLE PRECISION Y,Y1,YAVG,FAVG,FMAX,HY,YI,YF,DX,RT,TO,FY,FY1,VI,S
     $I,EI,VJ,VK
      COMMON ALPHA,H1,H2,TC1,TC2,B,E,DAO
C
      HY=(YF-Y)/1000
```

```
C
  23   FY=-((VI*Y-XT-VJ)*DEXP(-Y/(1+E*Y))/ALPHA)+DX*(SI-VK*XT-VI*Y)
       GO TO 24
  24   Y1=Y+HY
       FY1=-((VI*Y1-XT-VJ)*DEXP(-Y1/(1+E*Y1))/ALPHA)+DX*(SI-VK*XT-VI*Y1)
       IF(FY*FY1) 28,25,27
  25   RT=Y1
       Y=Y1+HY
       GO TO 23
  27   IF(Y1.GE.YF) GO TO 216
       Y=Y1
       FY=FY1
       GO TO 24
  28   DO 211 I=1,200
       YAVG=(Y+Y1)/2.0
       FYAVG=-((VI*YAVG-XT-VJ)*DEXP(-YAVG/(1+E*YAVG))/ALPHA)+DX*(SI-VK*XT
      $-VI*YAVG)
       IF(DABS(FAVG).GT.FMAX) GO TO 214
       IF(FY*FAVG) 210,212,29
  29   Y=YAVG
       FY=FAVG
       GO TO 211
 210   Y1=YAVG
       FY1=FAVG
 211   CONTINUE
 212   RT=YAVG
 213   FY=FY1
       Y=Y1
       GO TO 24
 214   HELLO=0.0
       GO TO 213
 216   HELLO=0.0
       RETURN
       END
```

Appendix IV:

OUTPUT OF CSTRS PUT BACK IN THE STEADY STATE EQUATIONS

TAU	F1	F2
0.1480000D+01	-.9562849D-06	0.5763512D-03
0.1490000D+01	0.5056571D-05	-.8052017D-02
0.1490000D+01	0.5056571D-05	0.6683370D-02
0.1490000D+01	0.5056571D-05	-.1455262D-04
0.1490000D+01	-.1864171D-07	0.9724245D-04
0.1490000D+01	-.3533905D-06	0.4187899D-03
0.1500000D+01	0.2224817D-05	0.8264799D-02
0.1500000D+01	0.2224817D-05	-.1044544D-01
0.1500000D+01	0.2224817D-05	-.3152869D-04
0.1500000D+01	-.7884791D-06	-.1399432D-05
0.1500000D+01	-.7884791D-06	-.2387395D-05
0.1500000D+01	-.7884791D-06	0.5538736D-05
0.1500000D+01	-.7942121D-06	-.3424336D-05
0.1500000D+01	-.7942121D-06	-.6177017D-05
0.1500000D+01	-.7942121D-06	-.2861007D-05
0.1510000D+01	0.2967979D-05	-.2236512D-01
0.1510000D+01	0.2967979D-05	-.5028279D-02
0.1510000D+01	0.2967979D-05	-.4803599D-04
0.1520000D+01	0.5341844D-05	-.7110123D-02
0.1520000D+01	0.5341844D-05	0.2909898D-03
0.1520000D+01	0.5341844D-05	-.6462850D-04
0.1530000D+01	0.5513893D-05	0.7847625D-02
0.1530000D+01	0.5513893D-05	0.5516573D-02
0.1530000D+01	0.5513893D-05	-.8011425D-04
0.1540000D+01	0.2841092D-05	0.2251179D-01
0.1540000D+01	0.2841092D-05	0.1064943D-01
0.1540000D+01	0.2841092D-05	-.9510324D-04
0.1550000D+01	0.2738081D-05	-.1158423D-01
0.1550000D+01	0.2738081D-05	-.8087066D-02
0.1550000D+01	0.2738081D-05	-.1102663D-03
0.1560000D+01	0.2557895D-05	0.2083657D-02
0.1560000D+01	0.2557895D-05	-.3345499D-02
0.1560000D+01	0.2557895D-05	-.1243381D-03
0.1570000D+01	0.3569556D-05	0.1548157D-01
0.1570000D+01	0.3569556D-05	0.1310444D-02
0.1570000D+01	0.3569556D-05	-.1371576D-03
0.1580000D+01	0.3136051D-05	-.2124663D-01
0.1580000D+01	0.3136051D-05	0.5877808D-02
0.1580000D+01	0.3136051D-05	-.1509680D-03
0.1590000D+01	0.5110693D-05	-.8806382D-02
0.1590000D+01	0.5110693D-05	0.1036346D-01
0.1590000D+01	0.5110693D-05	-.1637773D-03
0.1600000D+01	0.6614980D-05	0.3382897D-02
0.1600000D+01	0.6614980D-05	-.9877322D-02
0.1600000D+01	0.6614980D-05	-.1762302D-03
0.1610000D+01	0.1195405D-05	0.1531763D-01
0.1610000D+01	0.1195405D-05	-.5759638D-02

Vita

Ben Youssef Bisbis was born [redacted] in Khemisset , Morocco. After attending secondary school in Kenitra, he joined the Department of Chemical Engineering of the Mohammadia School of Engineering. Upon graduation in 1979, he accepted a teaching position in the Department of Chemistry at the University Cadi Ayyad, Marrakech. In 1982, he was awarded a fullbright scholarship to undertake a graduate program in Chemical Engineering at the University of Missouri , Columbia. He married Anne C. Wagner there and had two children Natascha and Mehdi. Presently Mr. Bisbis is a member of the faculty of the Department of Chemistry , Marrakech, Morocco.

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