MAXIMAL MULTIPLICITY AND BIFURCATION IN A CSTR WITH TWO CONSECUTIVE FIRST ORDER REACTIONS

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ABSTRACT

The steady state equation of a continuous stirred tank reactor is considered in the frame work of singularity theory. The maximal multiplicity of seven is obtained. The importance of the bifurcation parameter is studied and a new normal form equivalent to the original function is obtained. This normal form corresponds to the most degenerate singularity and its universal unfolding can predict all the bifurcation diagrams existing for this problem.

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I. INTRODUCTION

In recent years there has been considerable effort in determining the maximum number of solutions that can arise from the equations describing the steady state behavior of a continuous flow stirred tank reactor (CSTR). The case of a single first-order reaction is well understood, and the maximum number of roots has been shown to be three. For n consecutive reactions, the maximum multiplicity has for a long time been conjectured to be 2n+1. Recently, however, Chicone and Retzloff (1982) rigorously established a global upper bound for maximal multiplicity of $2^{n+1}-1$. The prediction is partially confirmed in a paper submitted two years ago that recently appeared in print (Retzloff et al., 1987) in which they proved via singularity theory that for two consecutive reactions ($A \rightarrow B \rightarrow C$, $n = 2$), seven solutions can be obtained. This conclusion follows from the fact that a seventh order contact is shown to exist and the function involved is proven to be its own universal unfolding (star singularity). At about the same time, Farr and Aris (1986) obtained numerical examples which indeed demonstrate seven roots. However, these results originate from the unfolding of a sixth order contact (wigwam singularity). Since the number of solutions is always odd, the existence of six solutions guarantees seven.

Both investigations mentioned above differ from earlier efforts in that the two popular simplifications, namely infinitely large and/or equal activation energies, are no longer employed. This follows the observation by ourselves and others (Retzloff and Chicone, 1981; Chicone and Retzloff, 1982; and Balakotaiah and Luss, 1984) that when these simplifications are imposed the global maximum multiplicity can only be five. For simplicity of the algebraic manipulations, Farr and Aris (1986) assumed however that species B is not present in the feed. As a result, although a seventh order contact can still be obtained, it is located at the boundary of the physical region and the unfolding in general fails to yield seven physical roots.

The star singularity derived in Retzloff et al. (1987) exists in the feasible region and as an organizing center must subsume the results of any other lower singularity including those obtained by Farr and Aris (1986). In this work we employ the same procedure from singularity theory (Brocker and Lander, 1975; Golubitsky and Schaeffer, 1979, 1985) to obtain seven steady states for two consecutive reactions in a CSTR. The numerical examples from Farr and Aris (1986) are shown to be a specific case of our general result. It must be pointed out that first, the procedure used is a local one in that the seven roots are only guaranteed to obtain in a parameter neighborhood of the seventh order contact. This observation must be true even when the most degenerate singularity is unique in the entire parameter space. Second, there is no requirement of physical (feasible) roots, which means that when unphysical roots exist the procedure may yet fail to give the expected number of feasible steady states. An example of this situation is the single exothermic zeroth order reaction analyzed by Balakotaiah and Luss (1984). Third, there are no restrictions on the parameter values themselves other than that they must be real numbers. Therefore, if any additional conditions on the parameters are imposed (e.g. the reaction rates are to be positive), they must be taken into consideration as well.

The special version of singularity theory developed by Golubitsky and Schaeffer (1985) identifies a distinguished parameter (bifurcation parameter), and all the bifurcation diagrams that may exist can be predicted by considering the neighborhood next to the most degenerate singularity. The general ideas of this procedure are applied in Chapter III where the most degenerate singularity is identified and the bifurcation of its normal form is compared to that of the original function. The flow rate will be chosen as the bifurcation parameter here, as it is an operating variable easy to control and measure, thus making the predictions of the theory amenable to experimental verification. As we will see, this choice of the bifurcation parameter makes the model slightly more complicated since the number of dimensionless groups will increase by two. This difficulty can be overcome by use of the chain rule which allows us to use the analysis of Chapter II and its results in identifying a new normal form and its universal unfolding.

II. STAR SINGULARITY AND MAXIMAL MULTIPLICITY

2.1 MATHEMATICAL MODEL

We consider the problem of two consecutive first order reactions ($A \rightarrow B \rightarrow C$) in a single CSTR. The mass and energy balances are

$$\frac{VdC_A}{dt} = FC_{Af} - FC_A - C_a V\ k_{0A} \exp(-\frac{E_A}{RT}) \tag{1}$$

$$\frac{VdC_B}{dt} = FC_{Bf} - FC_B - C_B V\ k_{0B} \exp(-\frac{E_B}{RT}) + C_A V k_{0A} \exp(-\frac{E_A}{RT}) \tag{2}$$

$$V\rho C_p \frac{dT}{dt} = F\rho C_p T_f - F\rho C_p T + (-\Delta H_A) C_A V k_{0A} \exp(-\frac{E_A}{RT}) + (-\Delta H_B) C_B V k_{0B} \exp(-\frac{E_B}{RT}) - hA(T - T_C) \tag{3}$$

For steady problems $\{d/dt = 0\}$, a single algebraic equation in T can be obtained from (1) - (3). In dimensionless form, the function that results for enumeration of the critical points is:

$$\begin{aligned} f(x, \varepsilon, Da_1, Da_2, B_1, B_2, B_3, k) &= Da_1 B_1 x \\ &+ Da_2 B_3 x^k + Da_1 Da_2 (B_1 + B_2 + B_3) x^{1+k} - \ln x \\ &- Da_1 (1 + \varepsilon B_1) x \ln x - Da_2 (1 + \varepsilon B_3) x^k \ln x \\ &- Da_1 Da_2 [1 + \varepsilon (B_1 + B_2 + B_3)] x^{1+k} \ln x \end{aligned} \tag{4}$$

where $x = \exp[\frac{E_A}{RT_m}(1 - \frac{1}{T})]$, $\varepsilon = \frac{RT_m}{E_A}$, $Da_1 = k_{0A} \frac{V}{F} \exp(\frac{E_A}{RT_m})$,

$$Da_2 = k_{0B}\,\frac{V}{F}\,\exp\left(\frac{E_B}{RT_m}\right),\quad B_1 = \frac{E_A}{RT_m}\,\frac{(-\Delta H_A)C_{Af}F}{F\rho C_p T_f + hAT_c}$$

$$B_2 = \frac{E_A}{RT_m}\,\frac{(-\Delta H_B)C_{Af}F}{F\rho C_p T_f + hAT_c},\quad B_3 = \frac{E_A}{RT_m}\,\frac{(-\Delta H_B)C_{Bf}F}{F\rho C_p T_f + hAT_c}$$

$$k = \frac{E_B}{E_A};\ \text{with } T_m = \frac{F\rho C_p T_f + hAT_C}{F\rho C_p + hA}\ .$$

From physical considerations, we require that $0<\varepsilon,k,Da_1,$ $Da_2<\infty$. Furthermore,

$$0 < x < \exp(1/\varepsilon), \tag{5}$$

where the upper bound follows from the physical constraint that $T>0$.

Any results obtained for (4) when $0<k<1$ can be mapped to $1<k<\infty$. To prove this, assume that $0<k<1$. The diffeomorphic transformation

$$\begin{aligned} &\frac{1}{k} = k',\ B_1 k = B_3',\ B_2 k = B_2',\ B_3 k = B_1', \\ &Da_1 = Da_2',\ Da_2 = Da_1',\ \frac{\varepsilon}{k} = \varepsilon',\ x^k = x' \end{aligned} \tag{6}$$

when applied to (4) then gives the same equation written in primedvariables, but now $1 < k' < \infty$. Therefore, for brevity, we only need to consider $0 < k < 1$.

The maximum number of roots for (4) has been rigorously established by Chicone and Retzloff (1982) to be seven. They used a dimensionless equation different from (4) but which is equivalent to it via a diffeomorphic variable transformation (Retzloff et al., 1987). Their analyses did not assume that the activation energies are equal ($k = 1$) or large ($\varepsilon = 0$), or that the reactions are exothermic (B_1, B_2, $B_3 > 0$). On the other hand, the possibility of unfeasible solutions (either unphysical roots or unphysical parameter values) was not examined. In this work, numerical examples of seven feasible solutions are obtained by analyzing (4) in the framework of singularity theory, which is the subject of the next two sections.

2.2 MAXIMAL MULTIPLICITY

We now apply the singularity theory to obtain the maximal multiplicity of steady states in eqn. (4) of the last section. The reader may refer to Golubitsky and Schaeffer (1985) where a rigorous treatment of this method is given. Brief summaries are also found in the work of Balakotaiah and Luss (1982, 1983, 1984). Here it suffices to recall the following: given any function $f(x;\lambda)$, if a solution can be found for some (x_0,λ_0) to the equations $f = \partial f/\partial x = \ldots = \partial^{m-1}f/\partial x^{m-1} = 0$, then an m-th order contact exists at (x_0, λ_0). In addition, if $f(x;\lambda)$ is contact equivalent to the appropriate normal form, then in some neighborhood of x_0,λ_0, $f(x,\lambda)$ will have m solutions. Examples of these solutions are obtained in a systematic fashion by constructing the loci of successively lower singularities $\{ f = \partial f/\partial x = \ldots = \partial^{m-2p} f/\partial x^{m-2p} = 0 \}$ for a specific set of the first (2p-2) parameters, starting with $p = 1$, until $p = (m-1)/2$ if m is odd or $p = m/2$ if m is even.

To derive the maximum number of solutions obtainable from singularity theory for any given function, it is therefore necessary to determine first its most degenerate singularity, i.e. the largest possible value of m. Clearly, $m = 7$ should be expected for the present problem. Since the term Da_1B_1x in (4) will be annihilated by differentiating twice, only five unknowns, namely $Da_2B_3x^k$, $Da_1Da_2(B_1 + B_2 + B_3)x^{1+k}$, $Da_1(1 + \varepsilon B_1)x$, $Da_2(1 + \varepsilon B_3)x^k$, $Da_1Da_2[1 + \varepsilon(B_1 + B_2 + B_3)]x^{1+k}$ remain in the equations.

$$x^2\ \partial^2 f/\partial x^2 = x^3\ \partial^3 f/\partial x^3 = \ldots = x^6\ \partial^6 f/\partial x^6 = 0 \qquad (7)$$

Note that the qth derivative is multiplied by x^q so that the order in x remains unchanged for each term. These equations can now be solved as a 5x5 matrix problem via Kramer's rule (or more conveniently, a judicious use of Gaussian elimination) with the unknowns expressed in terms of lnx and k. Substituting into the remaining equations

$$f = x\ \partial f/\partial x = 0 \qquad (8)$$

then gives Da_1B_1x, and lnx itself, in terms of k. By a tedious manual calculation as reported by Retzloff et at. (1987), the solution is

$$\ln x = \frac{2}{k(k+1)} (k^2 + 3k + 1) \tag{9}$$

$$Da_1 B_1 x = \frac{4}{(k - 1)^3} (k^2 - 2)(k + 1) \tag{10}$$

$$Da_2 B_3 x^k = \frac{4}{k(k - 1)^3} (2k^2 - 1)(k + 1) \tag{11}$$

$$Da_1 Da_2 (B_1 + B_2 + B_3) x^{1+k} = \frac{4}{k(k + 1)} (k^2 + 3k + 1) \tag{12}$$

$$Da_1 (1 + \varepsilon B_1) x = \left\{ \frac{k + 1}{k - 1} \right\}^2 \tag{13}$$

$$Da_2 (1 + \varepsilon B_3) x^k = \left\{ \frac{k + 1}{k - 1} \right\}^2 \tag{14}$$

$$Da_1 Da_2 [1 + \varepsilon (B_1 + B_2 + B_3)] x^{1+k} = 1 \tag{15}$$

The mapping from $0<k<1$ to $1<k<\infty$ described earlier is valid in these equations. If $k = \{1, 0, -1\}$, the solution (9) - (15) is degenerate. For each choice of $k = \{1, 0, -1\}$, $(x, \varepsilon, Da_1, Da_2, B_1, B_2, B_3)$ can be uniquely determined as follows: Multiplying (12) by ε and subtracting from (15), we obtain

$$Da_1 Da_2 x^{1+k} = 1 - \frac{4\varepsilon}{k(k + 1)} (k^2 + 3k + 1) \tag{16}$$

Similarly, from (10) and (13), (11) and (14), we obtain $Da_1 x$ and $Da_2 x^k$. These expressions are combined to give

$$2\varepsilon^2 (k^2 - 2)(k + 1)^3 (2k^2 - 1) - 4\varepsilon k (k - 1)^2 \\ (k^2 + 3k + 1)(k^2 + 1) + k^2 (k - 1)^2 (k + 1)(k^2 + 1) = 0 \tag{17}$$

whereupon (16) can now be rewritten as

$$Da_1Da_2x^{1+k} = -2\varepsilon^2\frac{(k^2 - 2)(k + 1)^2(2k^2 - 1)}{k^2(k - 1)^2(k^2 + 1)} \tag{18}$$

If the seventh order contact is to lie within physically realizable parameter space, it is necessary by (18) that $1/2 < k^2 < 1$ or $1 < k^2 < 2$. This latter result had been previously observed by Retzloff and Chicone (1981). For these values of k, the signs of the coefficients in (17) (a quadratic in ε) are such that only one root can be positive, so that ε is uniquely determined. Returning to (9)-(15), it is easily seen that all the remaining parameters can now be calculated.

In order to rigorously prove that seven solutions must exist, it is also necessary to show that the function f is its own universal unfolding. This is a straightforward but tedious procedure which involves verifying that a certain determinant is nonzero at the parameter values given by (9) - (15). The determinant contains the derivatives of a specified bifurcation parameter and five other unfolding parameters. Essentially then, only six parameters are necessary to obtain the universal unfolding (codimension five). As there are seven parameters in (4), one can be chosen a priori. From the earlier discussion, it is evident that the best approach is to specify k. It was reported earlier (Retzloff et al., 1987) that the determinant as calculated in this manner is indeed nonzero for $1/2 < k^2 < 1$ and $1 < k^2 < 2$.

Farr and Aris (1986) also attempted to derive the star singularity using a similar procedure. They assumed, however, that species B is not present in the feed ($B_3 = 0$). It then follows that the parameters are

$$k^2 = 1/2,\ \varepsilon = 1/12,\ Da_1 = 0,$$
$$Da_2 = ((\ 1 + \sqrt{2}\ )/(\ 1 - \sqrt{2}\ ))^2 \exp(-6/\sqrt{2}) \tag{19}$$
$$B_1 \rightarrow \infty \quad \text{and } B_2 \rightarrow \infty,$$

or, in terms of the variables defined in their paper, $\alpha \rightarrow 0$, $\sigma \rightarrow \infty$, $B \rightarrow \infty$. The fact that some variables are undefined was believed by these authors to be responsible for the numerical difficulties that they encountered. If this is true, then it appears that the difficulties can be avoided by rescaling

$$\bar{\sigma} = \sigma\alpha,\ \bar{B} = B\alpha \tag{20}$$

as new variables are finite when $\alpha \rightarrow 0$. Our choice of $Da_2 (= \bar{\sigma})$ rather than $Da_2/Da_1\ (= \sigma)$ essentially takes this into consideration. In the subsequent section, we shall verify that this is indeed the 'correct' choice for this problem.

In the most general situation, a non-degenerate seventh order contact therefore exists for $1/2 < k^2 < 1$ or $1 < k^2 < 2$. For any choice of k within these limits, the procedure to obtain parameter regions with specific number of roots is a straightforward one which involves calculating successively the lower singularities (Golubitsky and Schaeffer, 1979, 1985; Balakotaiah and

Luss, 1984). Here, the loci of the wigwam points

$$f = \partial f/\partial x = \ldots = \partial^5 f/\partial x^5 = 0 \tag{21}$$

must first be obtained. The objective of the calculation is to then project the solution of (21) onto the plane of any two unfolding parameters to form a cusp. Seven solutions can be obtained within the cusp in the neighborhood of its apex for certain parameter values. Here, we have chosen to consider the (ε, B_3) plane, as various assumptions on their values (e.g. $\varepsilon = 0$) have previously been made. By a straightforward calculation, we obtain (Chan et al., 1987)

$$Da_1B_1x = \frac{k+1}{(k-1)^3}\left[(k^2-1)(\ln x)^2 - \frac{4}{k}(2k^2-1)\ln x + \frac{4}{k^2}(5k^2-1)\right] \tag{22}$$

$$Da_2B_3x^k = \frac{k(k+1)}{(k-1)^3}\left[(k^2-1)(\ln x)^2 - 4(k^2-2)\ln x + 4(k^2-5)\right] \tag{23}$$

$$Da_1Da_2(B_1+B_2+B_3)x^{1+k} = (k+1)\left[(\ln x)^2 - \frac{4}{k^2}(k^2+3k+1)\right] \tag{24}$$

$$Da_1(1+\varepsilon B_1)x = \frac{k+1}{k(k-1)^2}\left[k(k+1)\ln x - (k^2+5k+2)\right] \tag{25}$$

$$Da_2(1+\varepsilon B_3)x^k = \frac{k+1}{(k-1)^2}\left[k(k+1)\ln x - (2k^2+5k+1)\right] \tag{26}$$

$$Da_1Da_2[1+\varepsilon(B_1+B_2+B_3)]x^{1+k} = (k+1)\ln x - \frac{1}{k}(2k+1)(k+2) \tag{27}$$

As before, a redundancy condition can be derived after expressing Da_1x, Da_2x^k and $Da_1Da_2x^{1+k}$ as function of ε and lnx (k having already been specified). Naming the right hand side of (22)-(27) a,b,c,d,e,f respectively we have:

$$Da_1 x = d - a\varepsilon \tag{28}$$

$$Da_2 x^k = e - d\varepsilon \tag{29}$$

$$Da_1 Da_2 x^{1+k} = f - c\varepsilon \tag{30}$$

hence,

$$(d - a\varepsilon)(e - b\varepsilon) = f - c\varepsilon \tag{31}$$

Equation (31) is a quadratic in ε with coefficients which are quadratic in lnx. Thus for every lnx, there exist at most two roots for ε. The strategy is to vary lnx in the neighborhood of the seventh order contact (eqn. (9)), evaluate ε by (31) and then evaluate the remaining parameters by (28) - (30). It should be noted that two solution branches of (31) can be obtained, one of which originate from the unphysical root of (17). For convenience this unphysical branch is discarded. The remaining solution branch gives the expected cupsoid shape when projected onto any two parameter plane ((ε,B_3) chosen here).

Within the cusp in the neighborhood of the apex, the swallowtail points ($f = \partial f/\partial x = \partial^2 f/\partial x^2 = \partial^3 f/\partial x^3 = 0$) are now calculated and the solution projected onto the (Da_1, Da_2) plane. The plot can resemble the shape of a butterfly (Brocker and Lauder, (1975)). The resulting equations (see appendix A) can be written as:

$$B_1 Da_1 x = A_7 + A_8 Da_2 x^k \quad (32)$$

$$B_2 Da_1 Da_2 x^{1+k} = A_5 + A_6 Da_2 x^k \quad (33)$$

$$Da_1 (1 + \varepsilon B_1) x = A_3 - A_4 Da_2 x^k \quad (34)$$

$$Da_1 Da_2 [1 + \varepsilon(B_1 + B_2 B_3)] x^{1+k} = -A_1 + A_2 Da_2 x^k \quad (35)$$

where:

$$A_1 = \frac{1}{k^2} [2k + 3 - (1 + k)\ln x]$$

$$A_2 = \frac{1}{k^2} \{(1 + \varepsilon B_3)[(k - 1)^2 \ln x - (k - 1)(k - 3)] - B_3(k - 1)^2\}$$

$$A_3 = \frac{1}{k^2} [(1 + k)^2 \ln x - (k^2 + 4k + 3)]$$

$$A_4 = \frac{1}{k^2} \{(1 + \varepsilon B_3)[(k - 1)\ln x + (3-2k)] - B_3(k - 1)\}$$

$$A_5 = \frac{1}{k^3} \{(1 + k)[k(\ln x)^2 + 2(1 - k)\ln x - 6]\}$$

$$A_6 = \frac{1}{k^3} \{(1 + \varepsilon B_3)(k - 1)[k(k - 1)(\ln x)^2 - 2(1 - 2k)\ln x + 6] - B_3(k - 1)^2[(k + 2) + k\ln x]\}$$

$$A_7 = \frac{(k + 1)}{k^3} \{k(1 + k)(\ln x)^2 - 2(2k + 1)\ln x + 6\}$$

$$A_8 = \frac{1}{k^3} \{B_3[k(k - 1)\ln x + 2 - 3k] + (1 + \varepsilon B_3)(k - 1)[- k(\ln x)^2 + 2(k + 1)\ln x - 6]\}$$

Combining (32)-(35) a single quadratic equation in $Da_2 x^k$ is obtained:

$$(Da_2x^k)^2(\varepsilon A_8 + A_4) + (Da_2x^k)[\varepsilon(A_7 - A_6) + A_2 - A_3] + (A_1 + \varepsilon A_5) = 0 \tag{36}$$

With k, ε and B_3 already specified equation (36) can be solved for each lnx. Only one solution of eqn. (36) gives parameter values that are in the neighborhood of the singularity. The other solution will be ignored. A butterfly shape is obtained in (Da_1, Da_2) plane (or any other combination of two parameters among the four left).

The final stage of this procedure is the calculation of the bifurcation points ($f = \partial f/\partial x = 0$) for specific values of Da_1 and Da_2 chosen from inside the tail. Here, only two equations and two unknowns are left, which we solve in appendix B using Kramer's rule to get:

$$B_1 = \frac{C_1[1 + k - \varepsilon/(1 - \varepsilon y)] - C_2}{k(1 - \varepsilon y)Da_1 \exp(y)} \tag{37}$$

$$B_1 + B_2 + B_3 = \frac{C_2 - C_1[1 + \varepsilon\ (y + 1)]/(1 - \varepsilon y)}{k(1 - \varepsilon y)Da_1Da_2 \exp(k + 1)y} \tag{38}$$

where C_1 and C_2 (give in appendix B) are function of lnx, and y is lnx itself. The expected star structure in the (B_1, B_2) plane is obtained. Seven roots of the steady state eqn. (4) can be shown to obtain for appropriate choices of B_1 and B_2 within the star.

The results of these calculations will be discussed in the next section.

2.3 RESULTS AND DISCUSSIONS

As we have proven in the last section, it is sufficient to consider only $1/2 < k^2 < 1$. For $k = 0.9$, the star singularity given by (9) - (15) exists at parameter values

$$\varepsilon = 0.03991585,\ Da_1=5.1988\times10^{-5},\ Da_2=4.9443,$$

$$B_1= 8.90468144\times10^6, B_2=27.409-B_1,\ \ B_3=-9.1855.$$

The loci of the wigwam points emanating from this singularity are calculated using (22)-(27) and projected onto the (ε,B_3) plane. This is shown in Fig.1 where the cusp shape is evident. It is important to note that the lower solution branch eventually crosses the feasibility boundary where Da_1 becomes negative, as indicated by the dotted line in Fig. 1. In the neighborhood of the apex, however, both branches are feasible as evidenced in Fig. 2 where the swallowtail points calculated for $B_3 = -9.11$ and $\varepsilon = 0.03938,\ 0.03940,\ 0.03942$ are plotted on the (Da_1, Da_2) plane. This figure shows the expected trend for the problem (Brocker and Lander, 1975). Fixing $\varepsilon = 0.03942$, $Da_1 = 3.38\times10^{-6}$, $Da_2 = 4.26$, the bifurcation set is then calculated and shown in Fig. 3. Seven solutions are now obtainable in region 1. This is verified in fig. 4 where $f(x)$ is plotted versus x for $B_1 = 1.17318645\times10^7$, $B_2 = 28.7906-B_1$. Alternatively, in fig. 5, a bifurcation diagram (with B_1 chosen arbitrarily as the bifurcation parameter) is shown. This plot also verifies the existence of seven roots for (4).

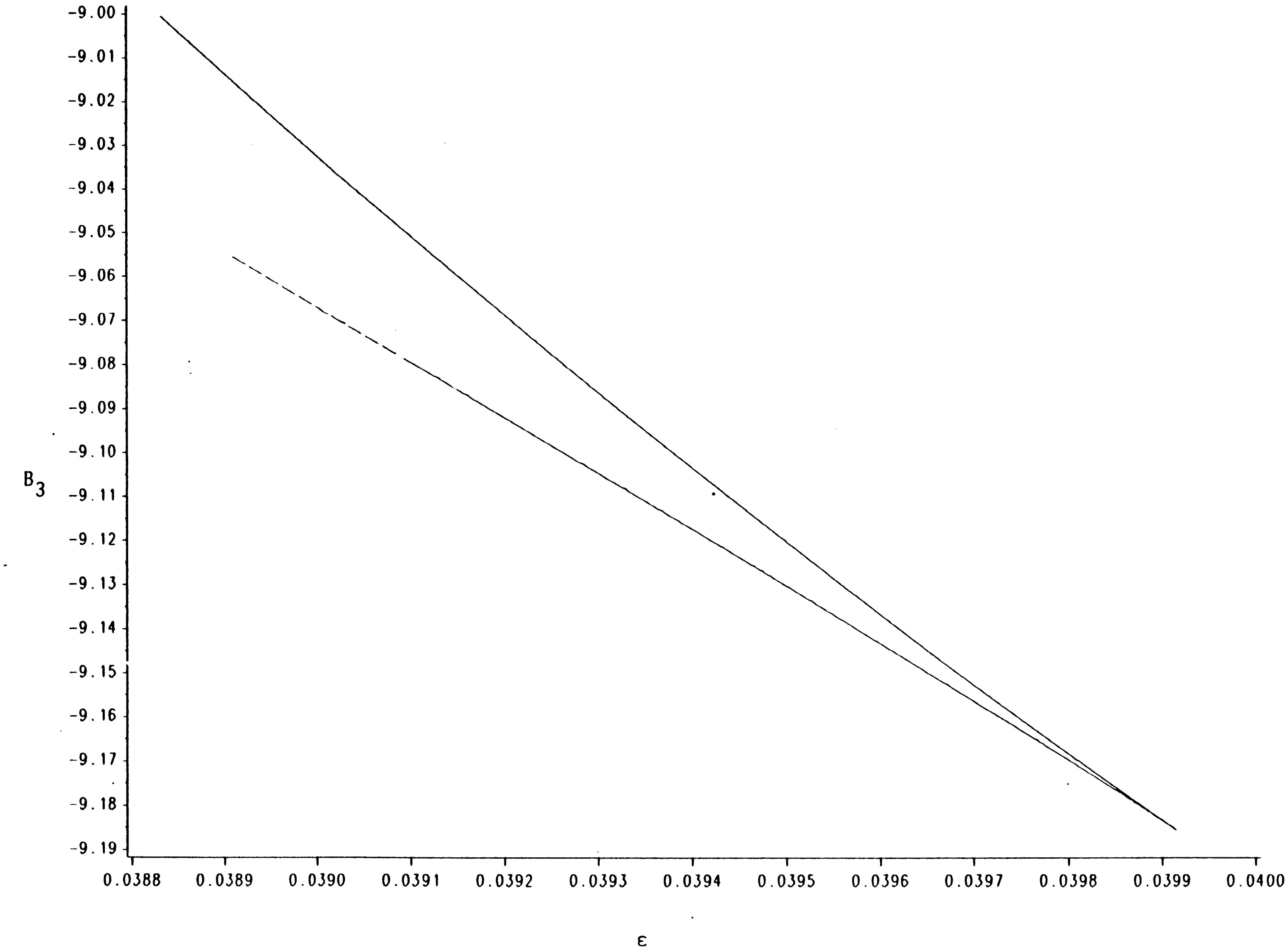

Fig. 1 Wigwam Branches on (ε, B_3), $k=0.9$.
________, $Da_1>0$; _ _ _ _, $Da_1<0$

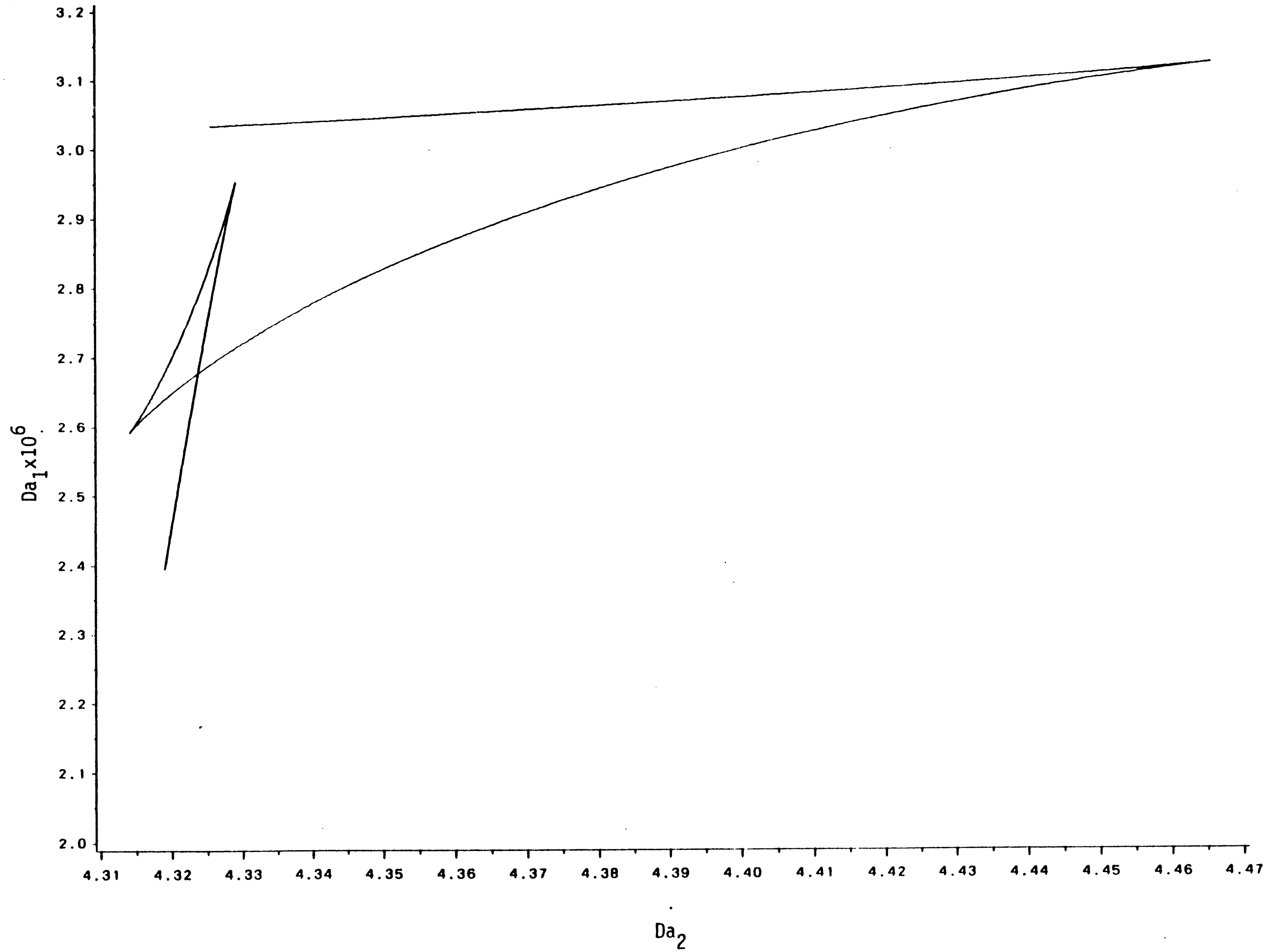

Fig. 2a Swallowtail Points on (Da_1, Da_2), k=0.9, B_3 = -9.11, ε = 0.03940

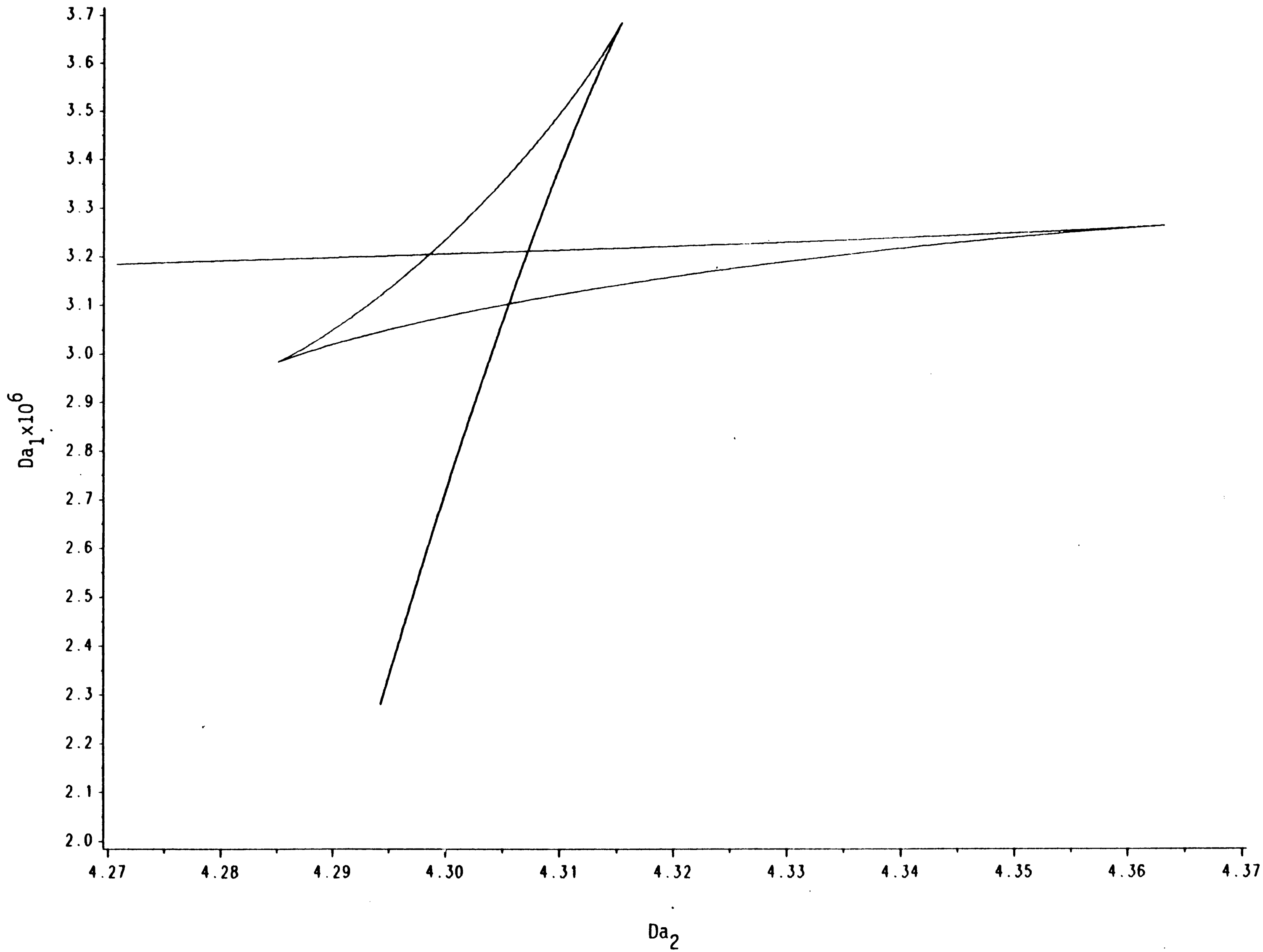

Fig. 2b Swallowtail Points on (Da_1, Da_2), k=0.9, B_3 = -9.11, ε = 0.03940

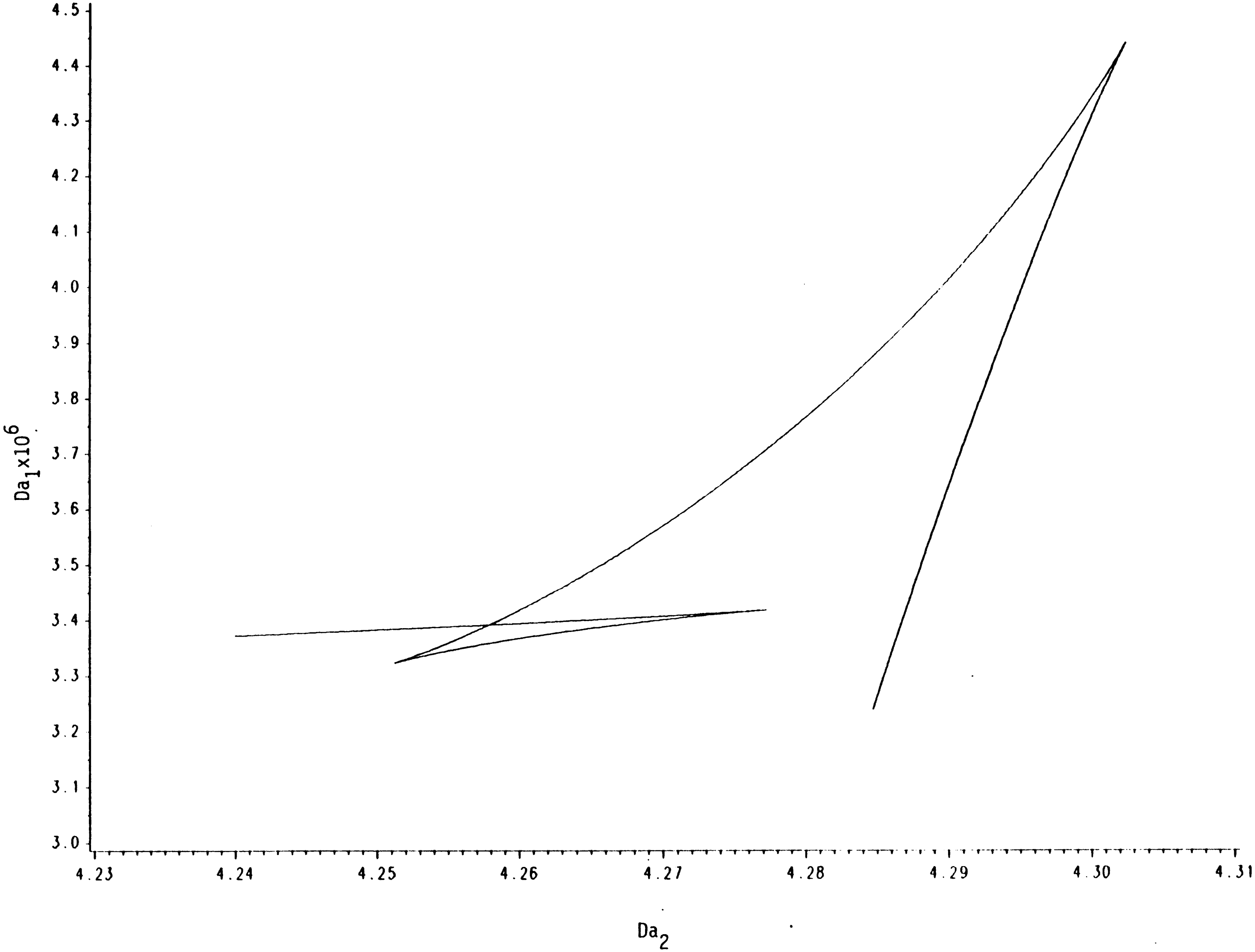

Fig. 2c Swallowtail Points on (Da_1, Da_2), $k = 0.9$, $B_3 = -9.11$, $\varepsilon = 0.03942$

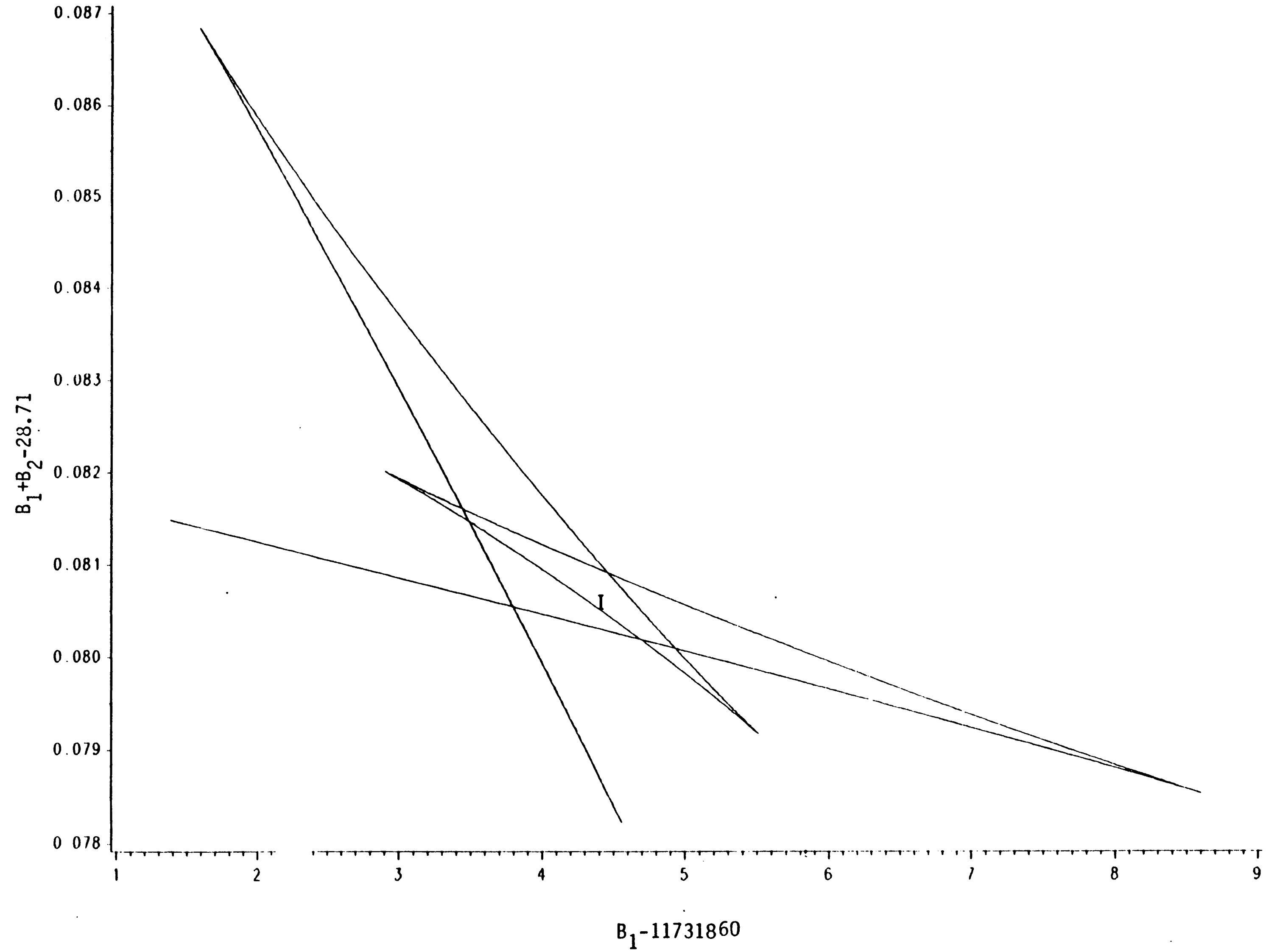

Fig. 3 Bifurcation Set on (B_1, B_2), $k = 0.9$, $B_3 = -9.11$, $\varepsilon = 0.03942$, $Da_1 = 3.38 \times 10^{-6}$, $Da_2 = 4.26$

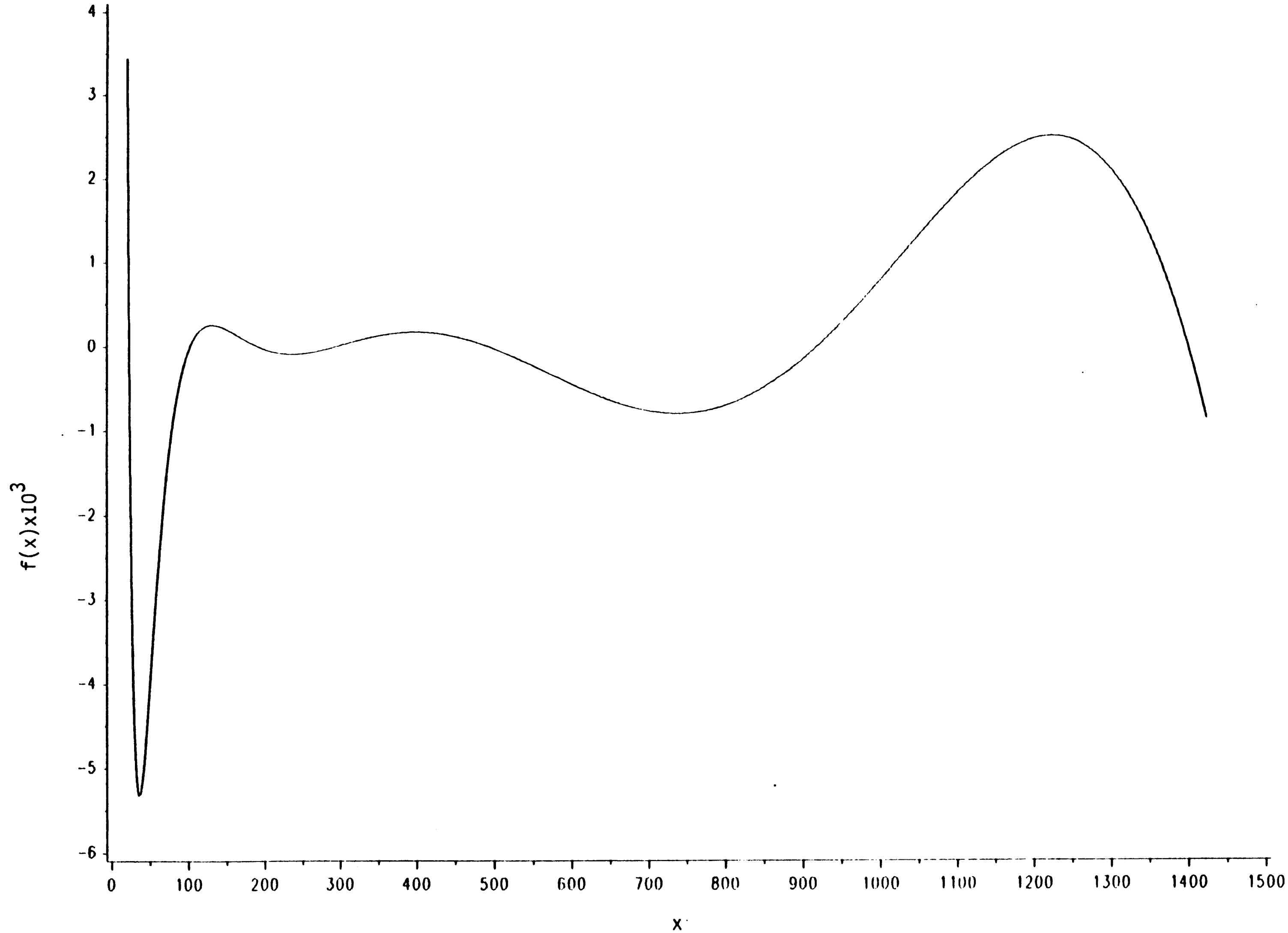

Fig. 4 $f(x)$ versus x, $B_1 = 1.17318645 \times 10^7$, $B_2 = 28.8906 - B_1$

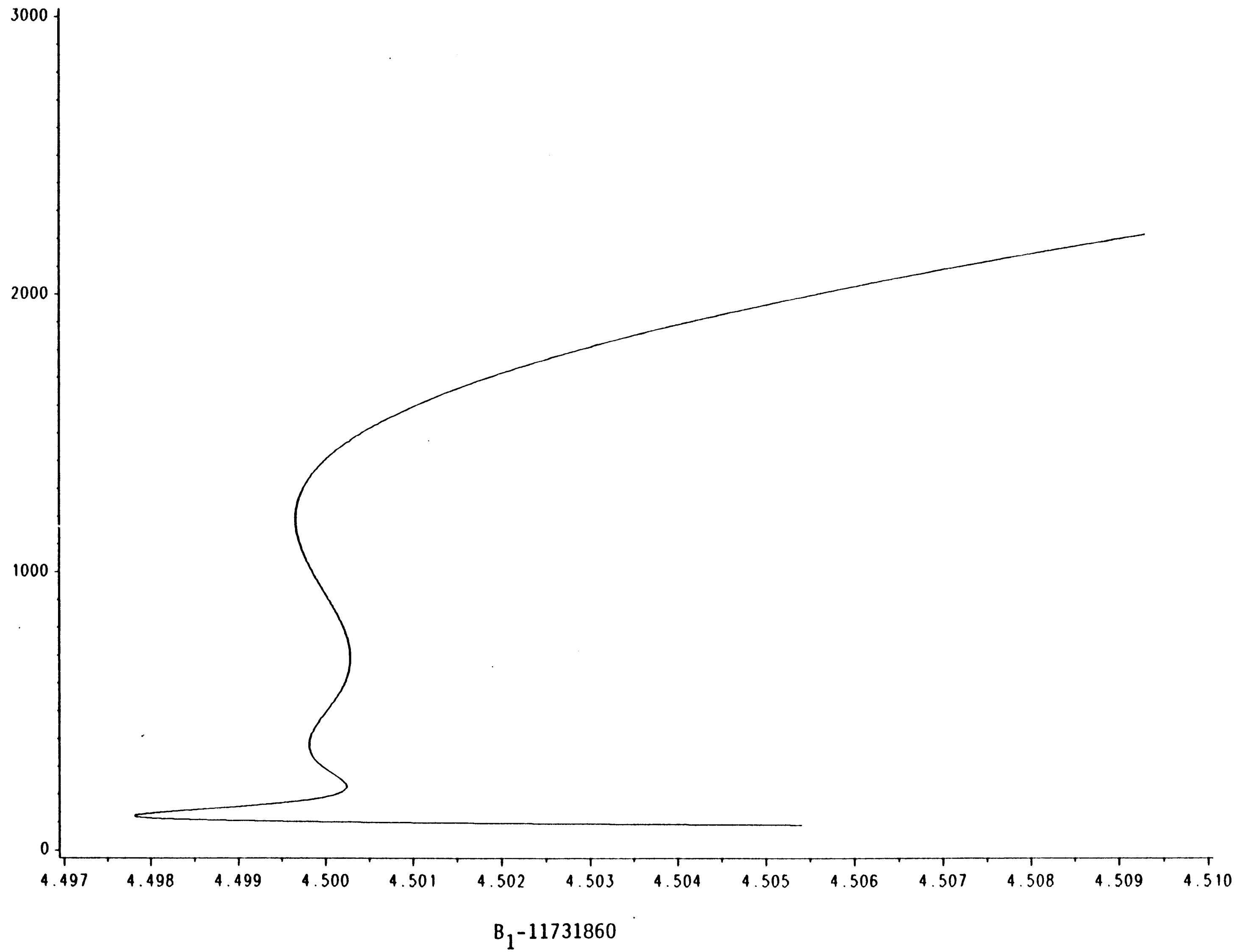

Fig. 5 Bifurcation Diagram, x versus B_1, $B_2 = -1.17318357094x10^7$

For k = 0.752, the same analyses yield similar results which are plotted in figs. 6-13. In this case, however the feasible region ($Da_1 > 0$) appears to be much smaller as the lower wigwam branch is unphysical even at parameter values quite close to the star singularity. In a small neighborhood of that point, seven roots can still be obtained by following the same procedures (Figs. 7-10),

To confirm the accuracy of our numerical results, we have also considered $\varepsilon = 1/15$, $B_3 = 0$ which were chosen by Farr and Aris (1986) in their unfolding of a wigwam singularity. As expected, this point lies very close to the upper wigwam branch of Fig. 6. By choosing the other parameters as in their calculation, an unfolding of our star singularity can in fact be achieved (Figs. 11 and 12). Obviously, the previous results by Farr and Aris (1986) is only a special case of our analyses.

Keeping $B_3 = 0$ and varying ε in Fig.6, it is observed that as ε decreases, the Da_1 values calculated for the fourth order contact also decreases until they cross the feasibility boundary to become negative as expected (Fig. 13). It is worthwhile to observe that Da_2 remains finite nevertheless, which proves that the scaling was chosen correctly.

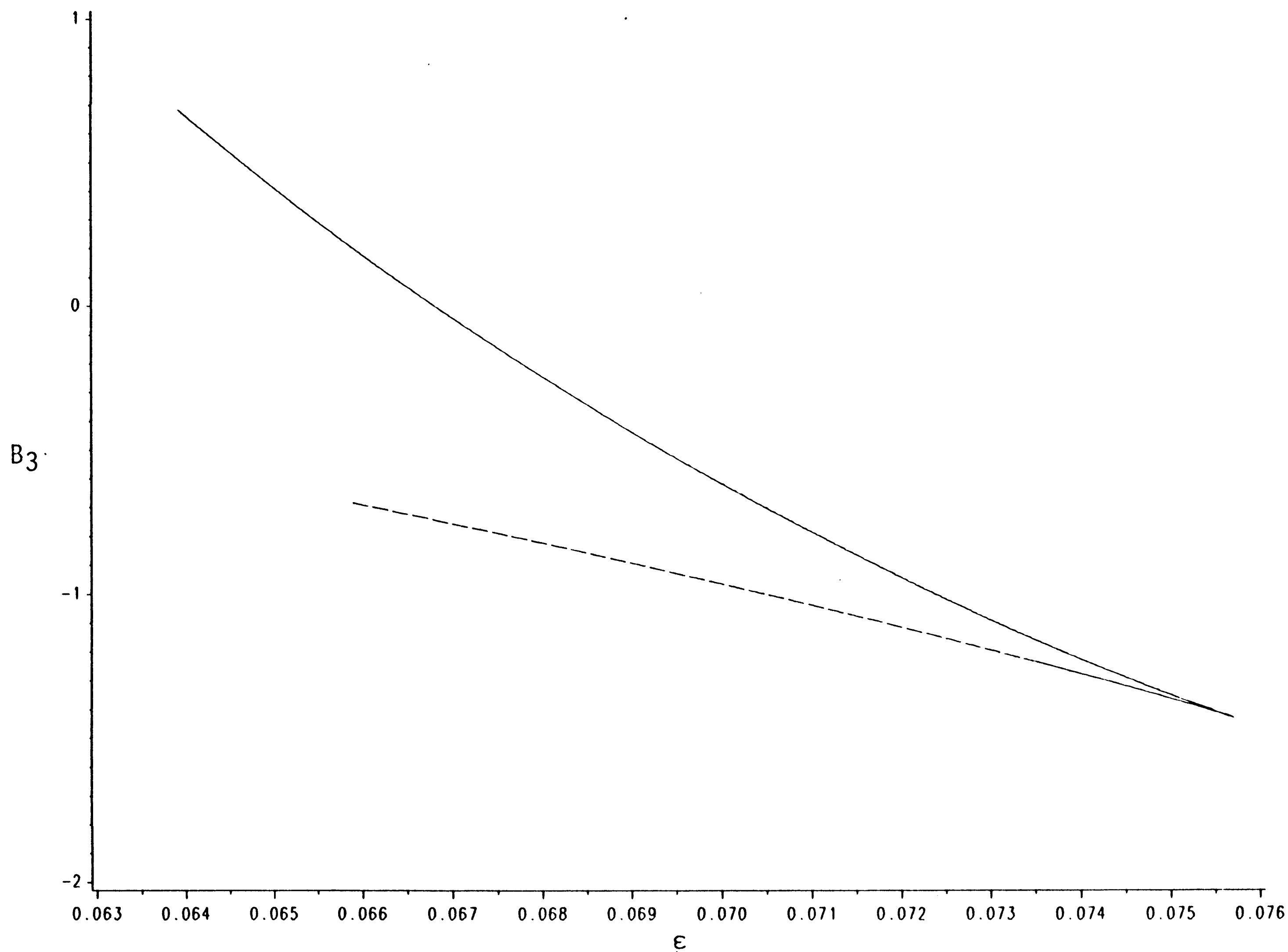

Fig. 6 Wigwam Branches on (ε, B_3), k = 0.752
_______, $Da_1>0$; _ _ _ _, $Da_1<0$

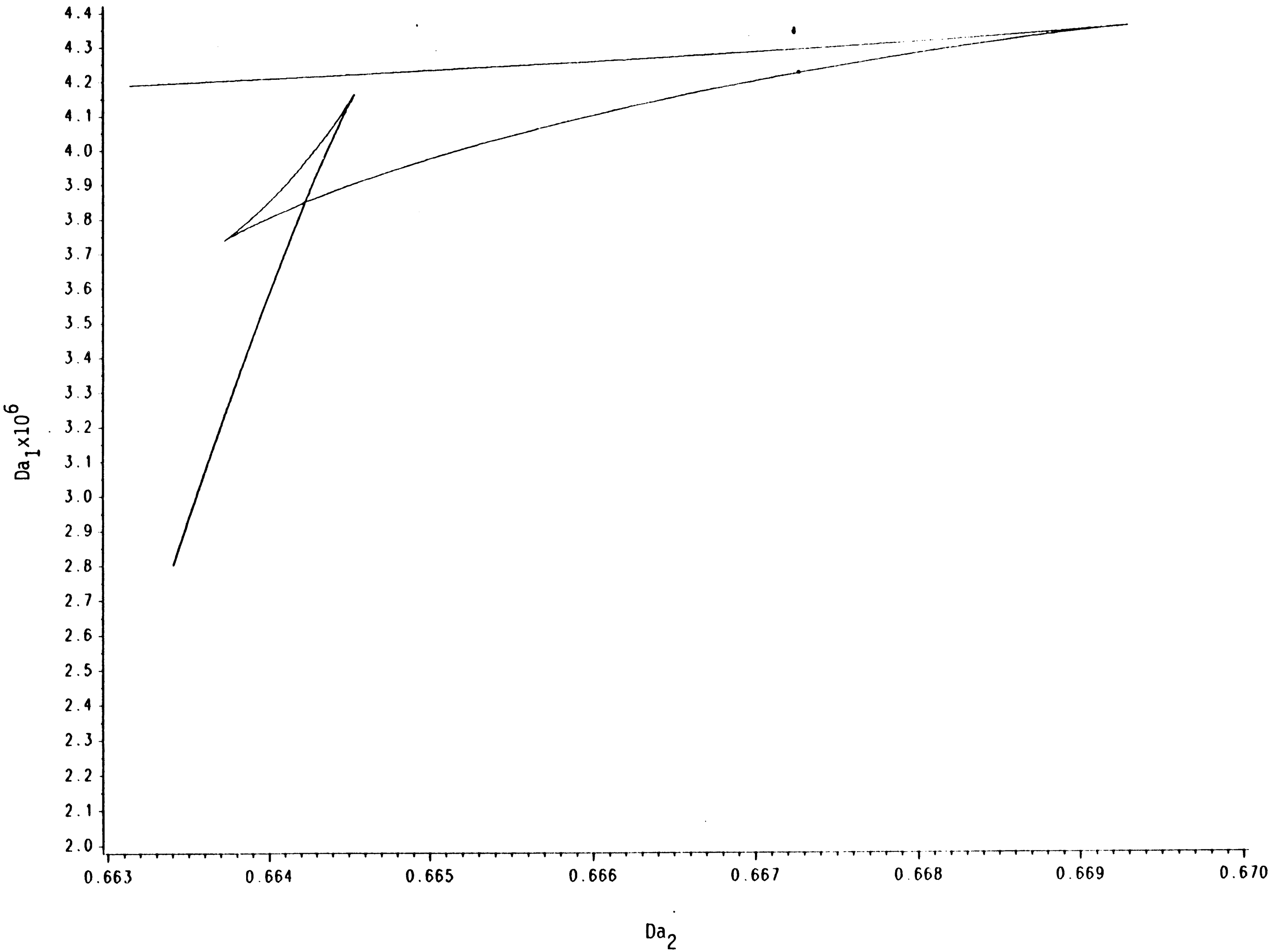

Fig. 7a   Swallowtail Point on (Da_1, Da_2), $k = 0.752$, $B_3 = -1.3$, $\varepsilon = 0.07441$

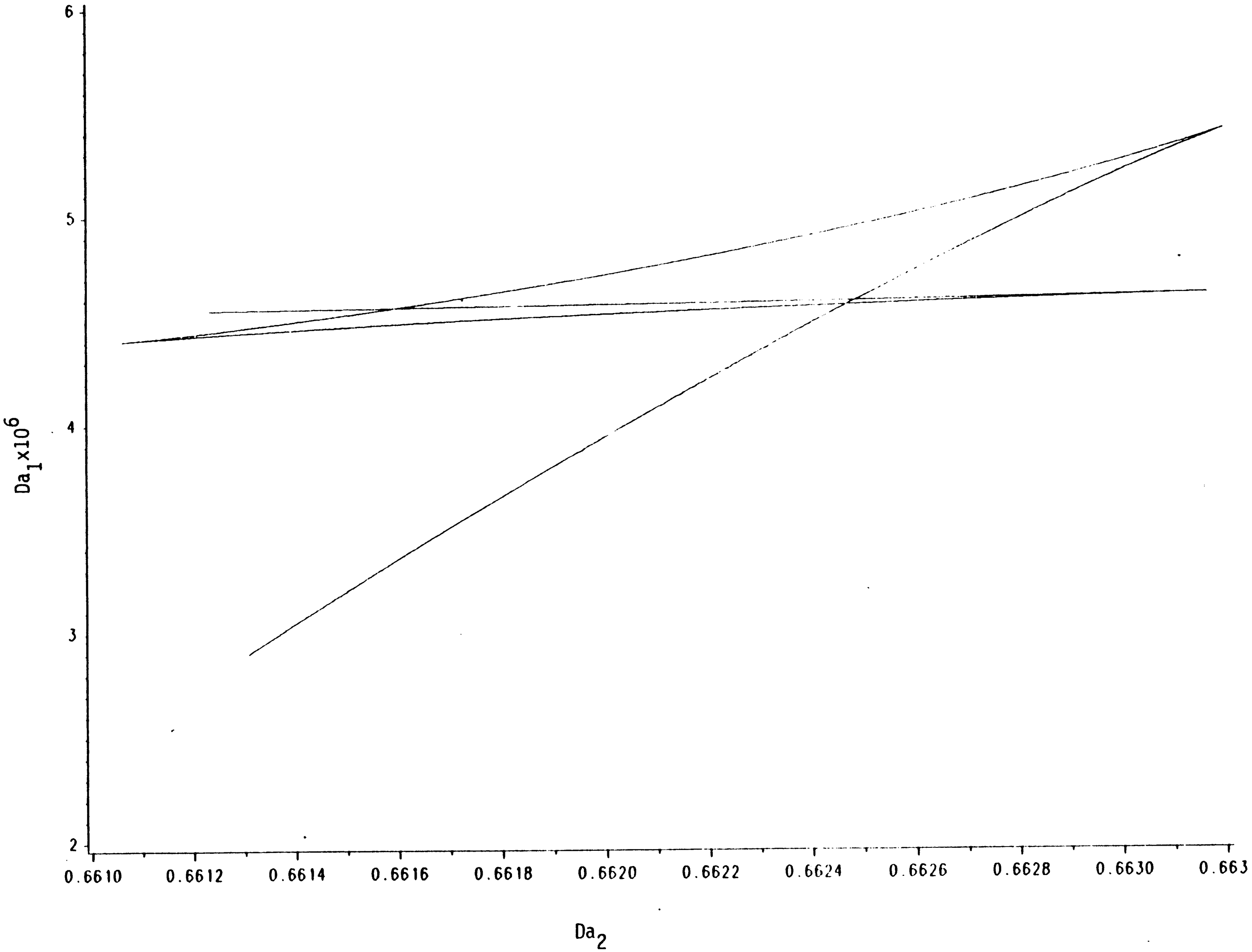

Fig. 7b Swallowtail Points of (Da_1, Da_2), k = 0.752
$B_3 = -1.3$, $\varepsilon = 0.07450$

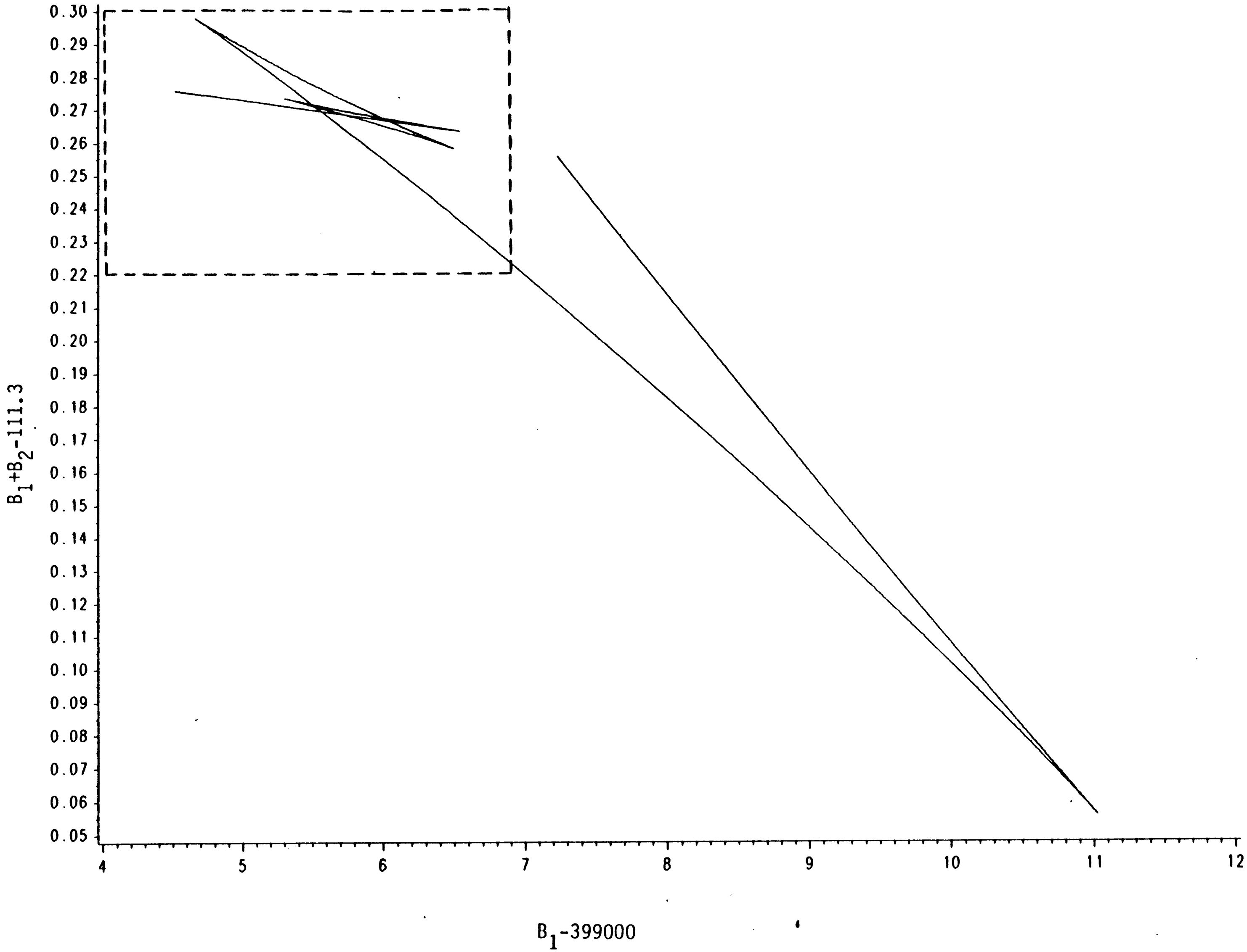

Fig. 8a Bifurcation Set on (B_1, B_2), $k = 0.752$, $B_3 = -1.3$,

$\epsilon = 0.0745$, $Da_1 = 6.55 \times 10^{-6}$, $Da_2 = 0.6618$

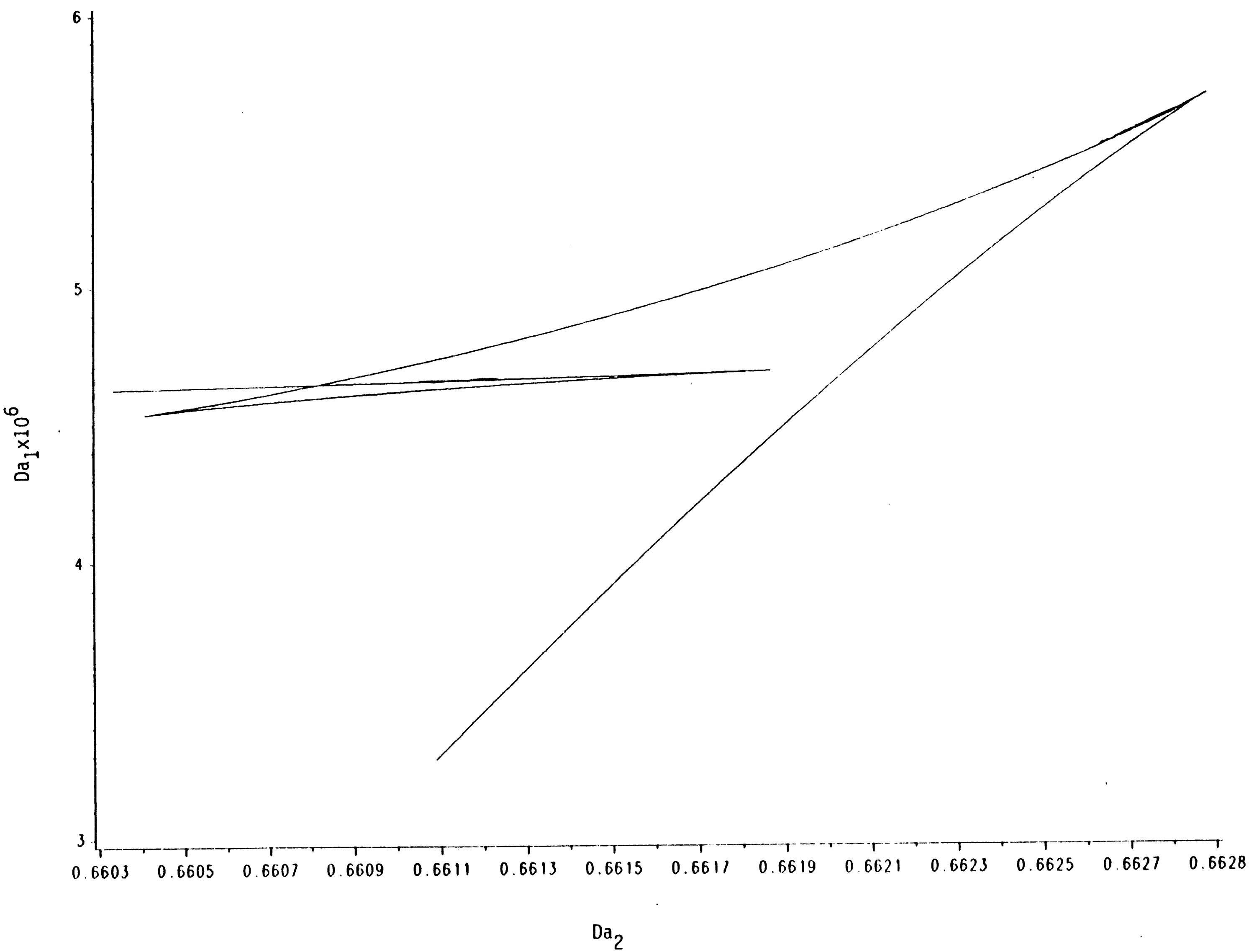

Fig. 7c Swallowtail Points on (Da_1, Da_2), k = 0.752, B_3 = -1.3, ε = 0.07452

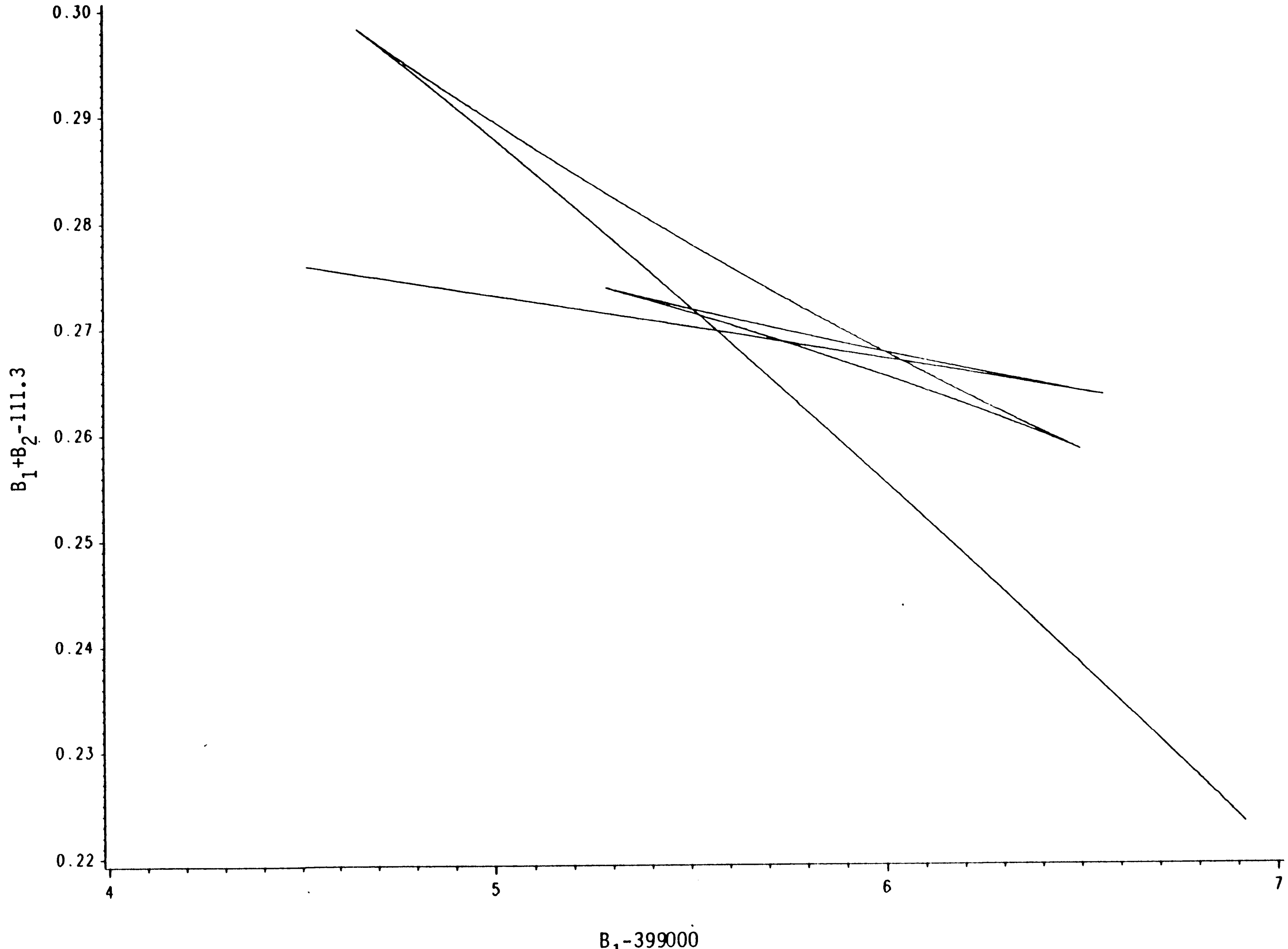

Fig. 8b Blow-up of dotted region of Fig. 8a

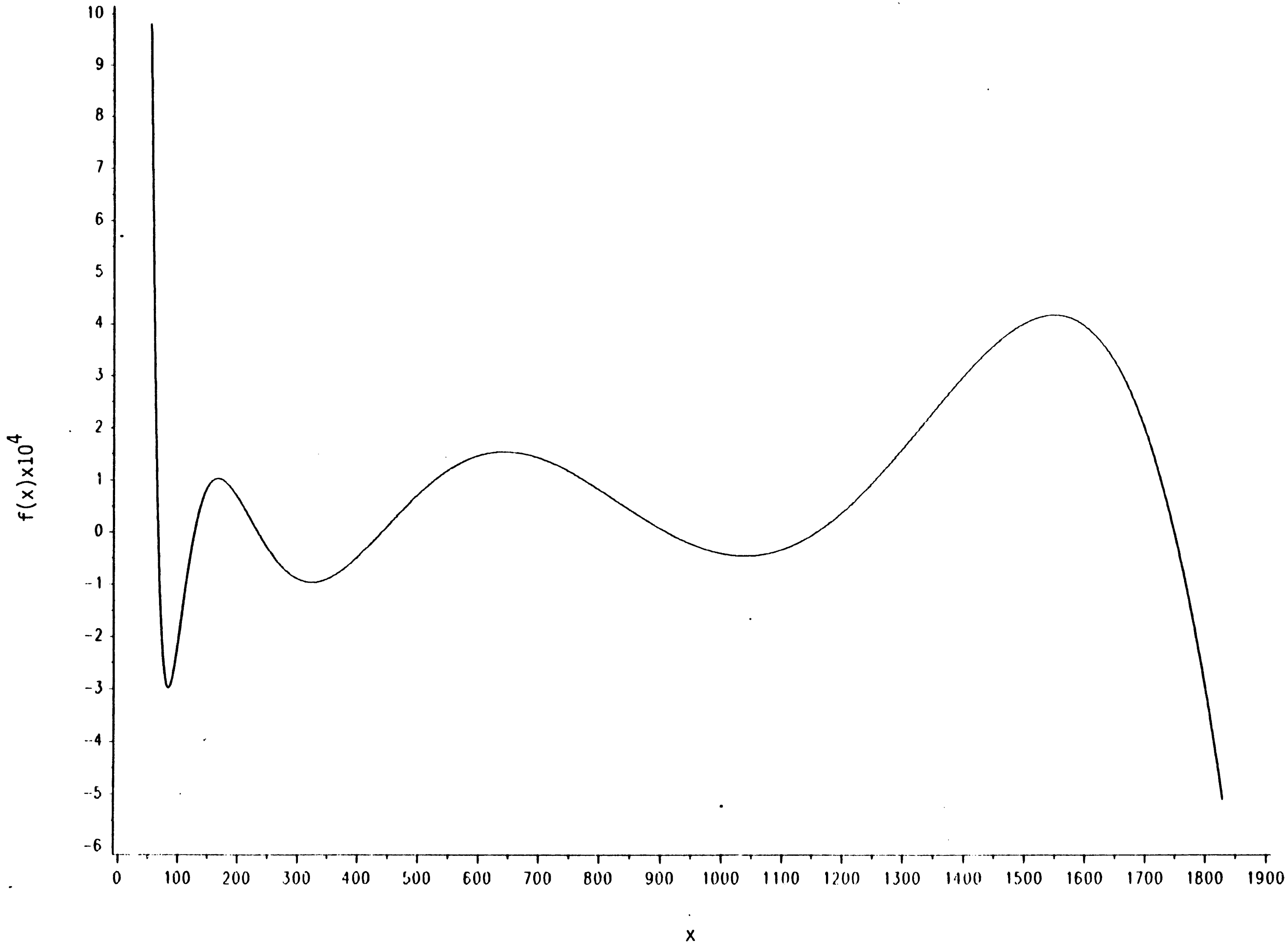

Fig. 9 $f(x)$ versus x, $B_1 = 3.990058 \times 10^5$, $B_2 = 111.569 - B_1$

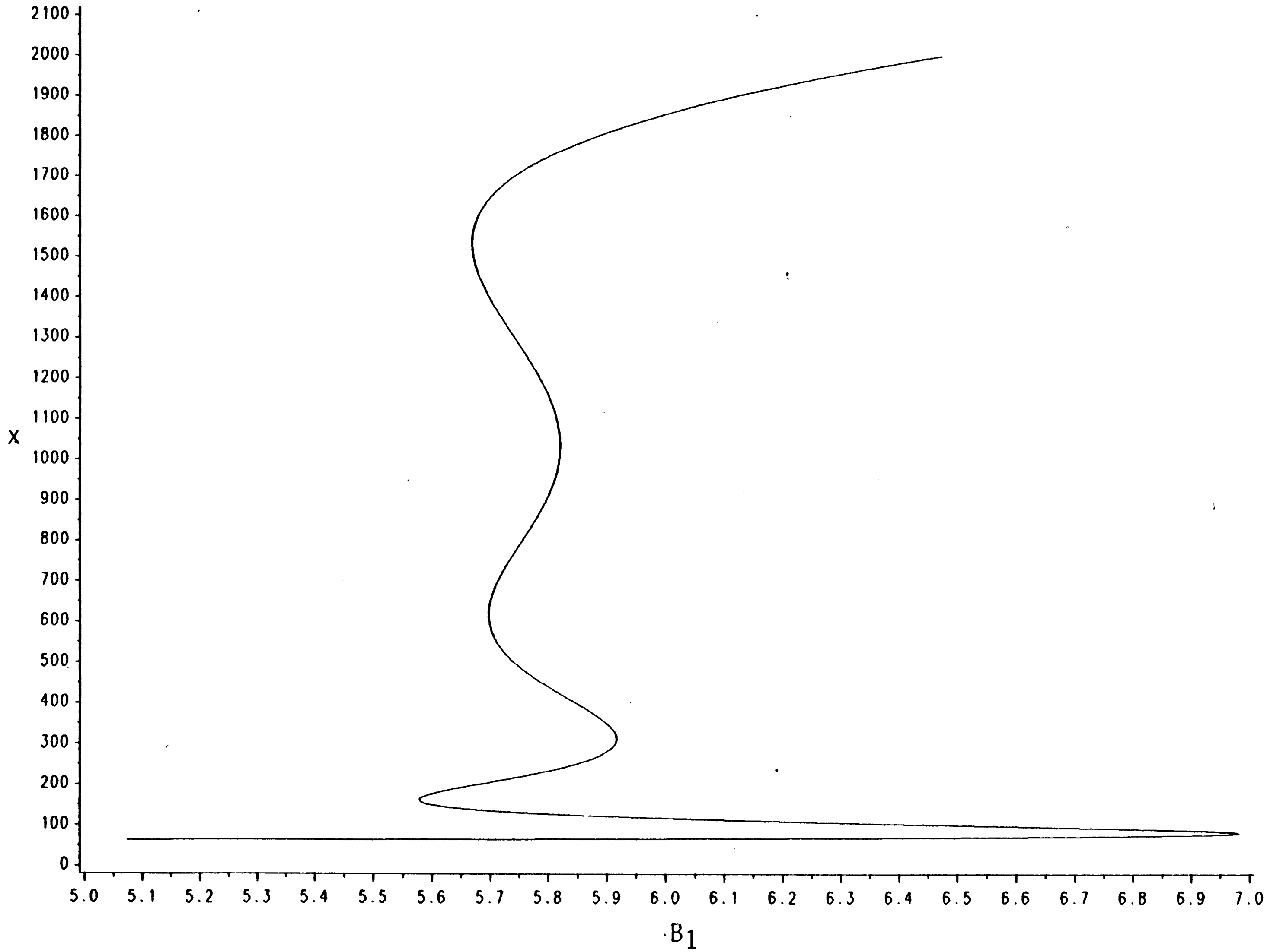

Fig. 10 Bifurcation Diagram, x versus B_1, $B_2 = -3.98894231 \times 10^5$

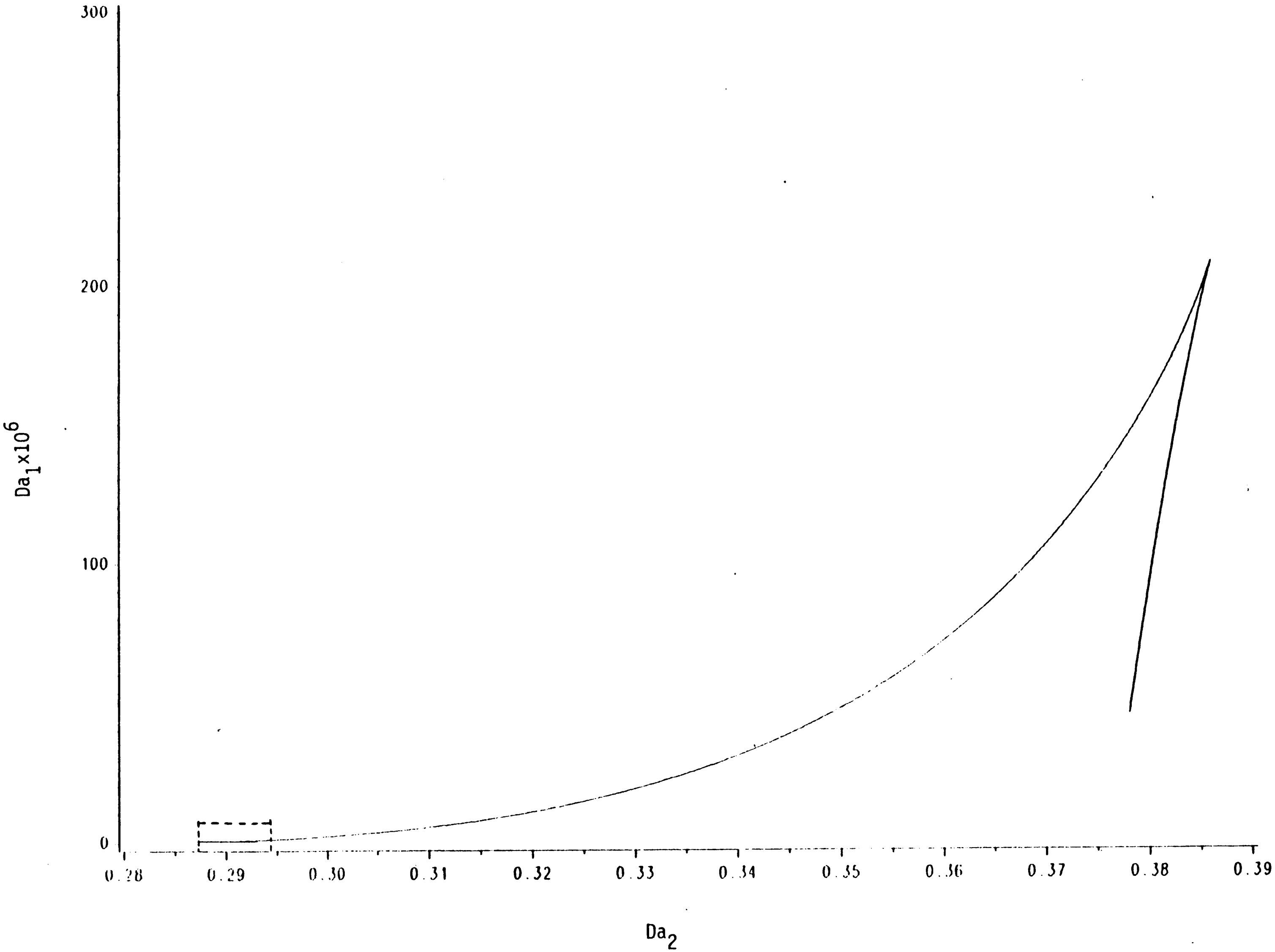

Fig. 11a Swallowtail Points on (Da_1, Da_2), $k = 0.752$,
$B_3 = 0$, $\varepsilon = 1/15$

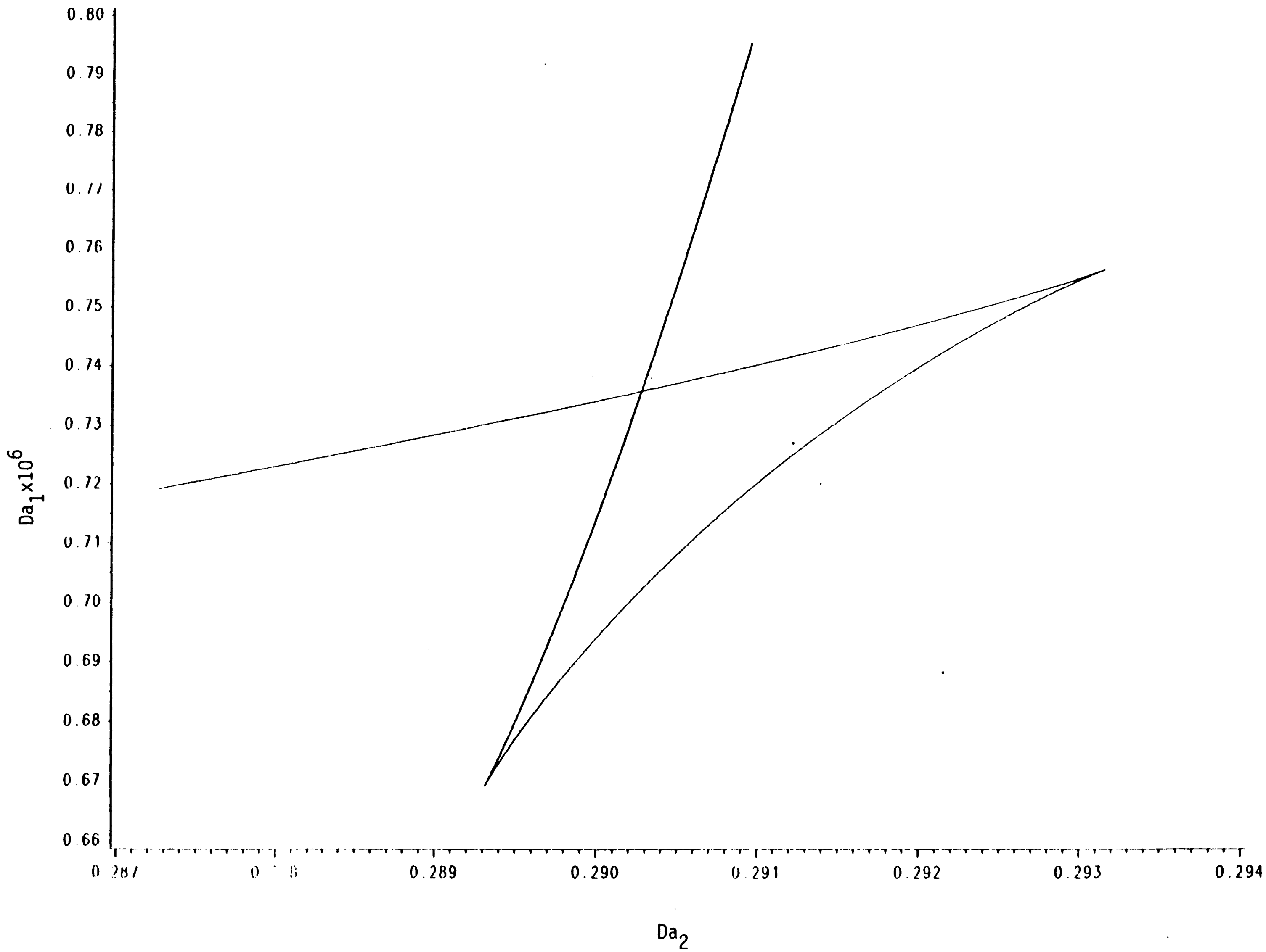

Fig. 11b Blow-up of dotted region of Fig. 11a

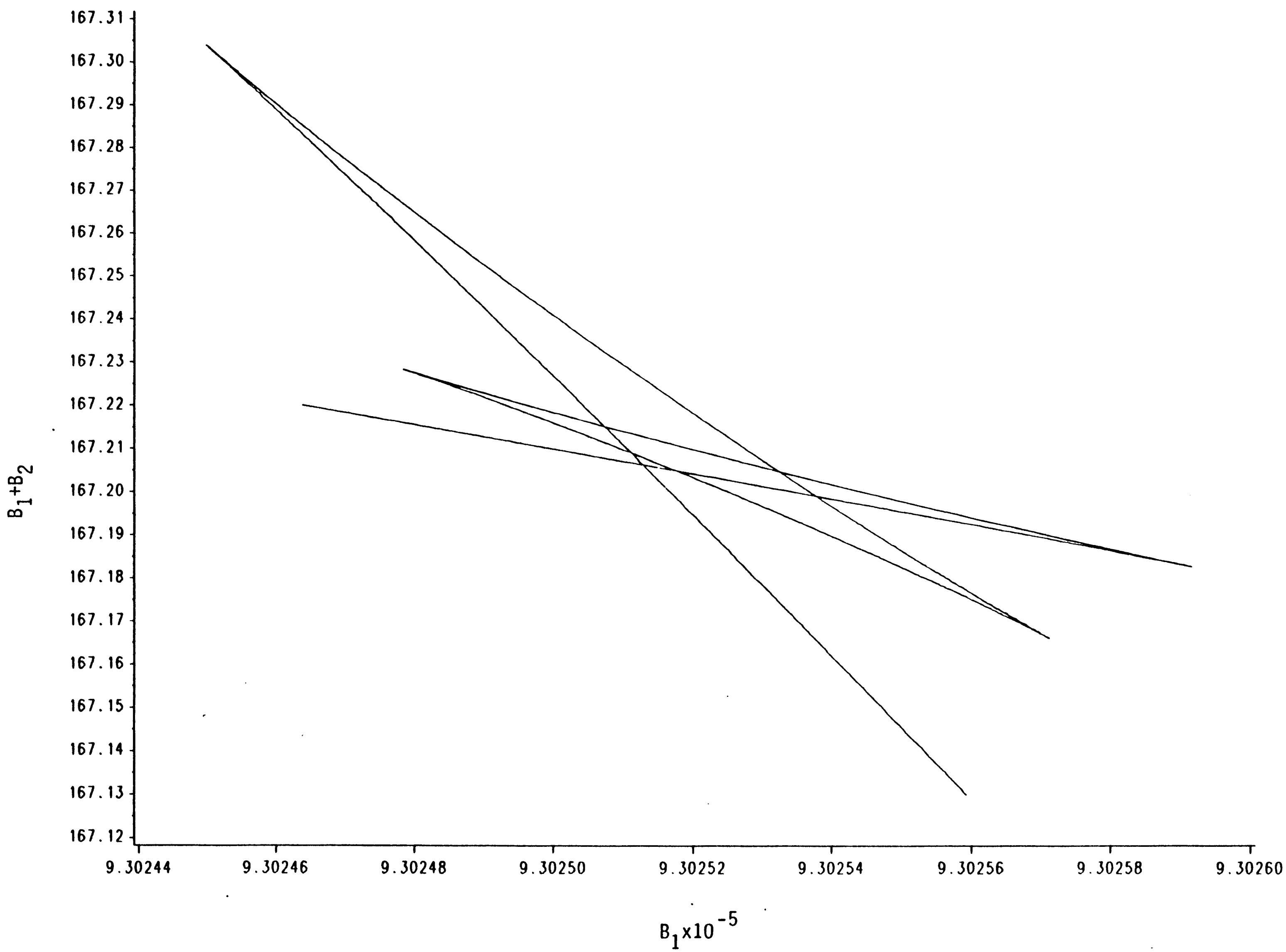

Fig. 12 Bifurcation Set on (B_1, B_2), $k = 0.752$, $\varepsilon = 1/15$, $Da_1 = 0.729 \times 10^{-6}$, $Da_2 = 0.29705$

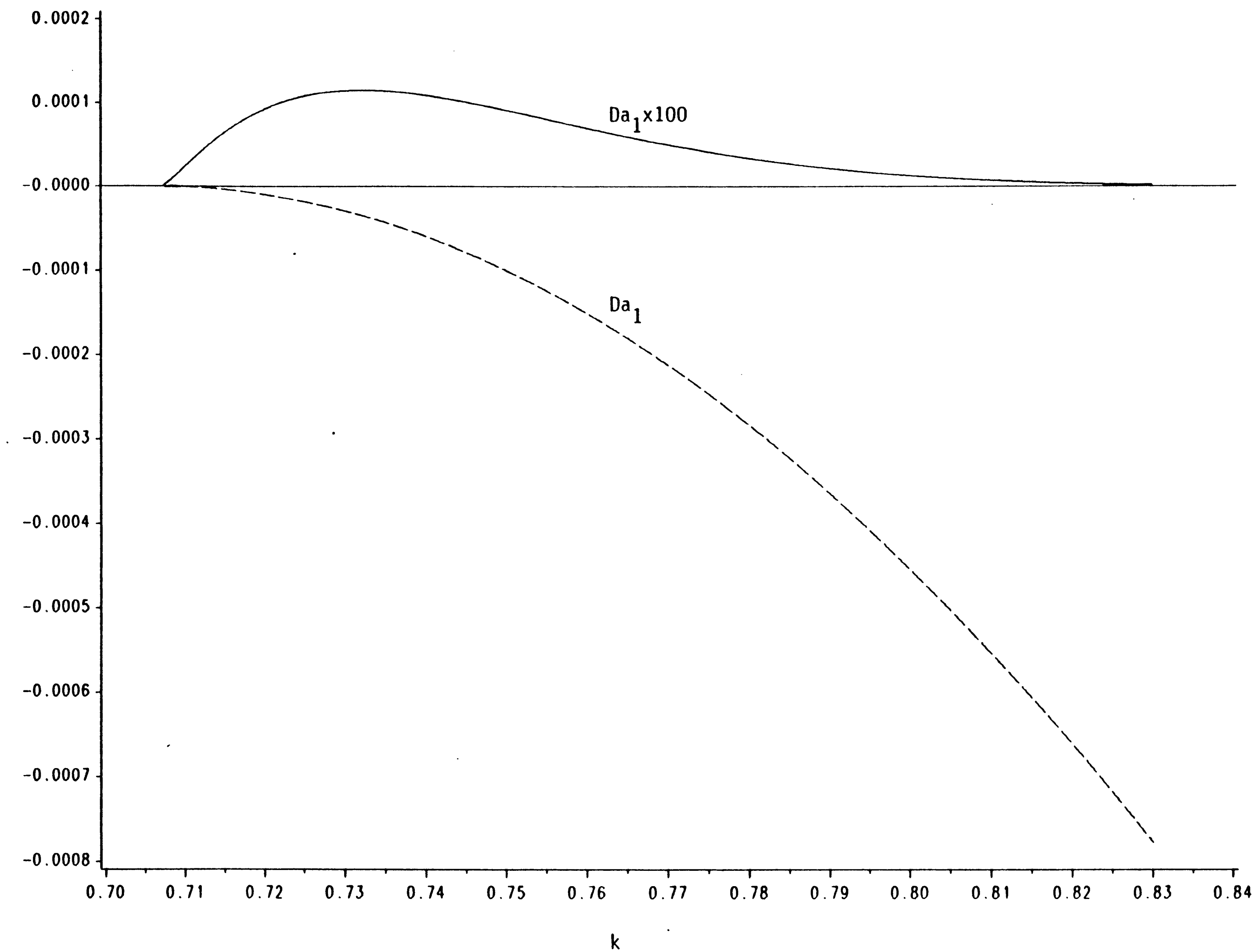

Fig. 14 Wigwam Branches on (k, Da_1), $B_3 = 0$

In Farr and Aris (1986), $B_3 = 0$ was assumed a priori (rather than fixing k as we have done here). As a result, the seventh order contact that is obtained is unfeasible ($Da_1 = 0$ in (19)) and apparently its unfolding as a star singularity fails. This problem will be examined in more detail. We first calculate the wigwam points from (22)-(27) when $B_3 = 0$. In particular, (23) gives lnx in terms of k, i.e.

$$\ln x = \frac{2}{k^2-1}\left[(k^2 - 2) \pm \sqrt{2k^2-1}\right] \tag{39}$$

As expected, a double root occurs at $k^2=1/2$, in agreement with (19). Substituting (28) into the remaining equations, we obtain

$$\varepsilon = \frac{k^2(-16k^6 + 69k^4 - 30k^2 - 7) \pm (26k^6 - 9k^4 - 1)(2k^2-1)^{1/2}}{4(k^2-1)(-8k^6 + 93k^4 - 6k^2 + 1)} \tag{40}$$

$$Da_1 x = \frac{2k^2-1}{k^2}\;\frac{2k^2(2k^2-1)(k^2-5) \pm (-5k^2+1)(k^2+1)(2k^2-1)^{1/2}}{(-8k^6 + 93k^4 - 6k^2 + 1)} \tag{41}$$

$$Da_2 x^k = \frac{k+1}{(k-1)^3}\left[-3k^2 + 1 \pm 2k(2k^2-1)^{1/2}\right] \tag{42}$$

These equations can also be written in quadratic forms with coefficients that are functions of k. For $1/2 < k^2 < 1$, the signs of these coefficients are such that both Da_2 values in (42) are positive (hence feasible), whereas the Da_1 values in (41) are always one positive, one negative. In Fig. 14 Da_1 is plotted versus k. The region where Da_1

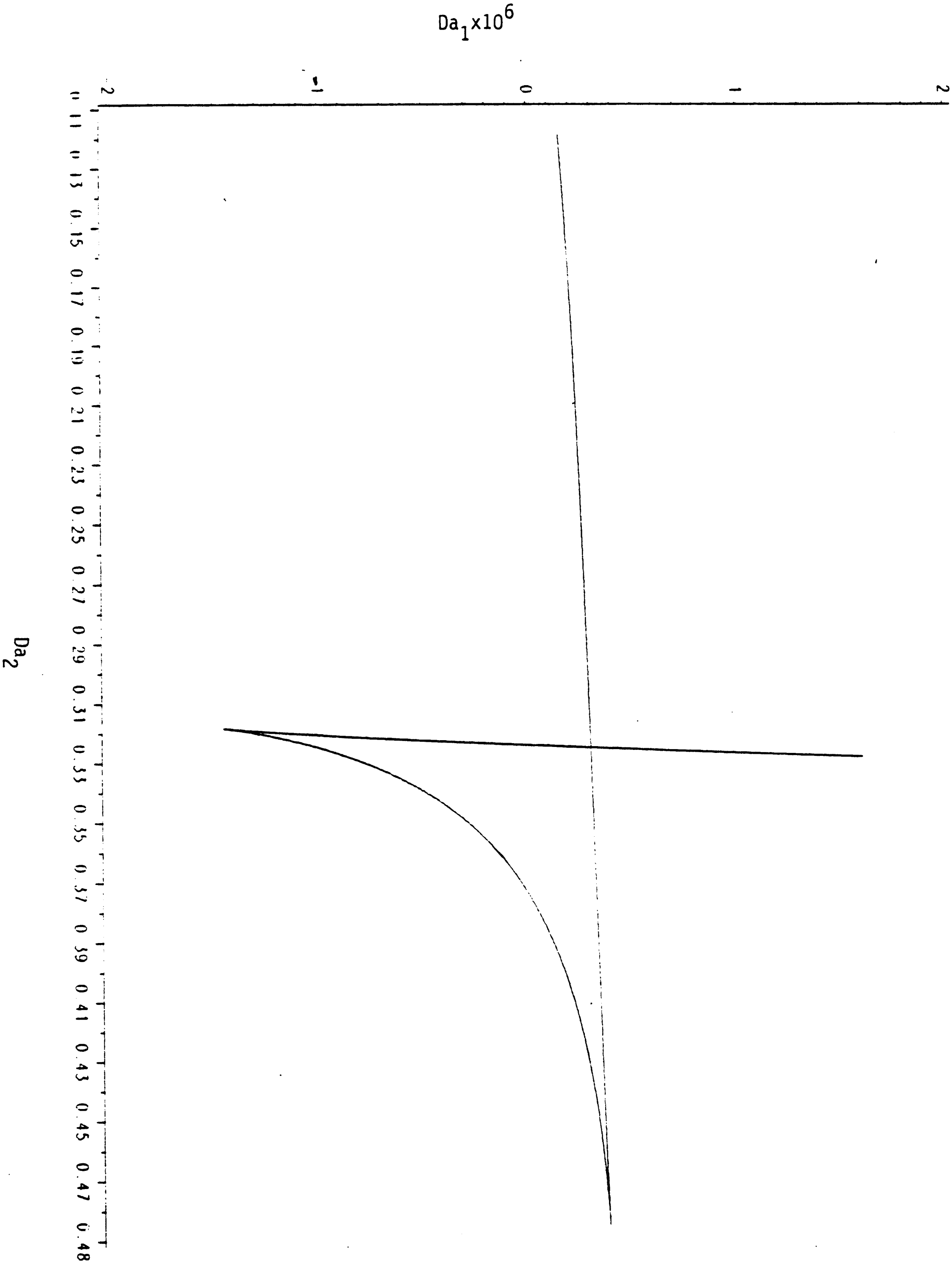

Fig. 13 Swallowtail Points on (Da_1, Da_2), k= 0.752, B = 0, ε= 0.0656

is positive has been magnified hundredfold. It is obvious that for $k \geq 0.82$, the feasible region is so small that even double precision arithmetic may fail to give the desired accuracy. Therefore, in order to guarantee that seven feasible solution are obtained, it seems prudent in this case to choose Da_1 first. Fixing $k = 0.752$ and $Da_1 = 3.38 \times 10^{-6}$, seven roots have indeed been obtained.

When B_3 is chosen to be positive near the upper wigwam branch in Fig. 6, the same unfolding procedure still gives B_2 values that are negative. From the definitions of B_2 and B_3, it then follows that C_{Af} and C_{Bf} must be of opposite signs, which is an unphysical result. Our numerical computations in fact indicate that for $1/2 < k^2 < 1$, the parameter region $B_3 > 0$ must be excluded if the unfolding is to give seven feasible solutions. It appears therefore that the second reaction is always endothermic. By similar arguments, it can be shown that the first reaction is always exothermic. These restrictions apply to $1/2 < k^2 < 1$. For $1 < k^2 < 2$, the requirements are reversed due to (6).

III. NORMAL FORM

3.1 MATHEMATICAL REFORMULATION

The choice of the bifurcation parameter is very important in practice as the predictions of the mathematical model are to be subjected to experimental verification. In this chapter the flow rate (an operating variable which is easy to measure and control) will be chosen as the bifurcation parameter. This choice has been known to give the most degenerate singularity for similar problems (Balakotaiah and Luss, 1983). We recall that in chapter II all the parameters except for k contain the flow rate in their definitions. This is clearly inconvenient for the present calculations, so that new variables must be defined. In doing so, the model equations become slightly more complicated as the number of parameters increases by two. Fortunately the chain rule will allow us to use the results obtained in the last chapter. We chose the bifurcation parameter to be:

$$H = \frac{hA}{F\rho C_p}$$

and define:

$$G = \frac{T_f}{T_c}$$

it is easily verified that:

$$\varepsilon B_1 = \frac{(-\Delta H_A)C_{Af}}{\rho C_p T_c} \frac{1}{G+H}$$

$$\varepsilon B_2 = \frac{(-\Delta H_B)C_{Af}}{\rho C_p T_c} \frac{1}{G+H}$$

$$\varepsilon B_3 = \frac{(-\Delta H_B)C_{Bf}}{\rho C_p T_c} \frac{1}{G+H}$$

$$Da_1 x = k_{oA} \frac{V\rho C_p}{hA} H \exp(\frac{-E_A}{RT})$$

$$Da_2 x = k_{oB} \frac{V\rho C_p}{hA} H \exp(- \frac{kE_A}{RT})$$

$$T_m = T_c \frac{G+H}{1+H}$$

$$\varepsilon = \frac{RT_c}{E_A} \frac{G+H}{1+H}$$

$$x = \exp(- \frac{E_A}{RT}) \exp(\frac{1}{\varepsilon})$$

Note that the choice of the new parameters is such that the only one that contains the flow rate is H.

3.2 THE MOST DEGENRATE SINGULARITY

The bifurcation problem is given by (4). For convenience however, we consider εf instead, ie:

$$\begin{aligned} \varepsilon f = {} & \varepsilon B_1 Da_1 x + \varepsilon B_3 Da_2 x^k + Da_1 Da_2 \varepsilon (B_1 + B_2 + B_3) x^{1+k} \\ & - \varepsilon \ln x \{1 + Da_1(1 + \varepsilon B_1)x + Da_2(1 + \varepsilon B_3)x^k \\ & + Da_1 Da_2 [1 + \varepsilon(B_1 + B_2 + B_3)] x^{1+k}\} = 0 \end{aligned} \quad (4')$$

The most degenrate singularity is characterized by the parameter values which satisfy the equations

$$\varepsilon f = \partial \varepsilon f/\partial x = \ldots = \partial^p \varepsilon f/\partial x^p = \ldots = \partial \varepsilon f/\partial H = \ldots =$$
$$\partial^q \varepsilon f/\partial H^q = \partial^2 \varepsilon f/\partial x \partial H = \ldots = \partial^{r+s} \varepsilon f/\partial x^r \partial H^s = 0$$

with the parameter p, q, and r + s being maximized in succession.

By identities such as:

$$\partial \varepsilon f/\partial x = \varepsilon \partial f/\partial x + f \partial \varepsilon/\partial x = \varepsilon \partial f/\partial x$$

it is easily seen that equations (9) through (15) are still valid when $p = 6$.

For the derivatives of εf with respect to H it can be shown that:

$$\partial \varepsilon B_i/\partial H = -\varepsilon B_i/(G+H) \qquad \text{for } i=1,2,3$$

$$\partial Da_1 x/\partial H = Da_1 x/H$$

$$\partial Da_2 x^k/\partial H = Da_2 x^k/H \tag{43}$$

$$\partial Da_1 Da_2 x^{1+k}/\partial H = 2Da_1 Da_2 x^{1+k}/H$$

$$\partial \varepsilon \ln x/\partial H = (1 - \varepsilon \ln x)[(1/(1+H) - 1/(G+H)]$$

Equations (43) are used in appendix D to get the following results:

$$\partial \varepsilon f/\partial H = g_1 + g_2 + g_3 \tag{44}$$

where:

$$g_1 = \frac{\varepsilon f}{H} + \frac{\varepsilon \ln x}{H} + \frac{\varepsilon}{H}\{(B_1+B_2+B_3)Da_1 Da_2 x^{1+k} - \ln x[1+\varepsilon(B_1+B_2+B_3)]Da_1 Da_2 x^{1+k}\} \tag{45}$$

$$g_2 = \frac{1}{G + H} (1-\varepsilon\ln x)(1+Da_1x+Da_2x^k+Da_1Da_2x^{1+k}) \quad (46)$$

$$g_3 = -\left(\frac{1-\varepsilon\ln x}{1+H}\right) \{1 + Da_1(1 + \varepsilon B_1)x + Da_2(1 + \varepsilon B_3)x^k$$
$$+ Da_1Da_2[1 + \varepsilon(B_1 + B_2 + B_3)]x^{1+k}\} \quad (47)$$

Equations (44) - (47) are then used in the same appendix to obtain $\partial^2\varepsilon f/\partial x\partial H$ which is a very straightforward calculation. Solving the equations $\partial\varepsilon f/\partial H = \partial^2\varepsilon f/\partial x\partial H = 0$ simultaneously at the parameter values given by (9) - (15) yeilds the following unique solution:

$$\frac{G + H}{1 + H} = 2(1 - \varepsilon\ln x) \quad (48)$$

$$\frac{1 + H}{H} = \frac{k^2 + 1}{(k - 1)^2} \frac{(1 - \varepsilon\ln x)}{\varepsilon\ln x} \quad (49)$$

The following relations can also be derived from (48)-(49):

$$\frac{G}{H} = 2 \frac{k^2 + 1}{(k - 1)^2} \frac{(1 - \varepsilon\ln x)^2}{\varepsilon\ln x} \quad (50)$$

$$H = \frac{(k - 1)^2\varepsilon\ln x}{k^2+ 1 - 2(k^2- k + 1)\varepsilon\ln x} \quad (51)$$

$$\frac{G + H}{H} = 2 \frac{(1 - \varepsilon\ln x)^2}{\varepsilon\ln x} \frac{k^2 + 1}{(k - 1)^2} \quad (52)$$

Appendix D shows the details of these calculations. Furthermore, we were able to obtain:

$$\partial^2\varepsilon f/\partial H^2 = -4 \frac{(1 - \varepsilon\ln x)^2(k^2+ 1)}{H(G + H)(1 + H)H} \frac{k^2+ 1}{(k - 1)^2} \quad (53)$$

and

$$\partial^3 \varepsilon f/\partial x^2 \partial H \quad = \quad (D19) \tag{54}$$

where (D19) is presented in appendix D.

It appears then that the most degenerate singular point is given by:

$$\varepsilon f = \partial \varepsilon f/\partial x = \ldots = \partial^6 \varepsilon f/\partial x^6 = \partial \varepsilon f/\partial H = \partial^2 \varepsilon f/\partial x \partial H = 0 \tag{55}$$

whose solution is given by (9) - (15) and two additional equations chosen appropriately from (48) - (52).

3.3 THE RECOGNITION PROBLEM

Keeping in mind that singularity theory only predicts local behavior, we consider the recognition problem for the normal form of the steady state equation (4) or (4'). A more precise mathematical definition of germs and their analysis is given in Brocker and Lander (1975). Essentially, a germ is an equivalence class of mappings that are up to contact equivalent in the neighborhood of a certain point. The recognition problem consists of finding the conditions that a given function must satisfy to be equivalent to a simpler polynomial function (normal form) in the neighborhood of the most degenerate singularity.

The uniqueness of the solution of (55) together with the derivative conditions (53) - (54) and the following result obtained by Retzloff et al. (1987) (at the most degenerate singular point):

$$\partial^7 f/\partial x^7 \quad = \quad - k^2(k + 1)^2 x^{-7} \tag{56}$$

suggest a normal form as follows:

$$h(x,H) \quad = \quad -x^7 + Hx^2 - H^2 \tag{57}$$

<u>Remarks</u>:

i) The positive sign of Hx^2 is determined by numerically calculating (D19) in appendix D for all k.

ii) The term xH^2 does not appear in (57) since it can be absorbed by a change of variable in x.

Balakotaiah and Luss (1983) obtained, for two parallel reactions under the positive exponential approximation, the normal form $h = -x^5 + Hx^2 - H^2$. Two of their derivative conditions were similar to (53) - (54).

The mathematical method for solving the recognition problem for a given normal form has been developed by Golubitsky and Shaeffer (1985). This systematic method consists of three stages. Here we present its main results when applied to our problem. The restricted tangent space RT(h) is:

$$RT(h) \quad = \quad M^8 + M^3\langle\lambda\rangle + M\langle\lambda^2\rangle + \{h,\ x\partial h/\partial x\} \tag{58}$$

1) <u>lower order terms</u>

$$L(h) \quad = \quad M^7 + M^2\langle\lambda\rangle + \langle\lambda^2\rangle \tag{59}$$

The complementary space to L(h) is:

$$L'(h) = \langle x^6, x^5, x^4, x^3, x^2, x, 1, \lambda, x\lambda \rangle \tag{60}$$

hence, for any function strongly equivalent to h it must satisfy (55).

2) Higher order terms

$$P(h) = M^8 + M^3\langle\lambda\rangle + M\langle\lambda^2\rangle \tag{61}$$

monomials in P(h) do not affect equivalence.

3) Intermediate order terms

Any function strongly equivalent to h is given by:

$$f = ax^7 + b\lambda x^2 + c\lambda^2 + p(x,\lambda) \tag{62}$$

where a,b, and c are nonzero real numbers and $p(x,\lambda)$ should belong to:

$$M^8 + M^3\langle\lambda\rangle + M\langle\lambda^2\rangle$$

This is exactly the right hand side of (61)!

Consequences:

a) By requiring strong equivalence another equation must be satisfied by the function, namely:

$$\frac{(\partial^7 f/\partial x^7)^2}{(7!)^2}\frac{(\partial^2 f/\partial x^2)^5}{(2!)^5} = -\frac{(\partial^3 f/\partial x^2\partial\lambda)^7}{(3!)^7} \tag{63}$$

b) When the problem is considered in the context of general equivalence the restraint (63) disappears and the recognition problem is completely solved by

(55) and the following:

$$\partial^2 f/\partial\lambda^2 \quad < \quad 0$$

$$\partial^3 f/\partial x^2 \partial\lambda \quad > \quad 0$$

$$\partial^7 f/\partial x^7 \quad < \quad 0$$

Hence, the normal form (57) is to be retained for our steady state equation (4) or (4').

c) Universal unfolding

Once the restricted tangent of space is identified (eqn. (58)) one needs only to use linear algebra to obtain the universal unfolding. By following the procedure of Golubitsky and Shaeffer (1985) we obtain this final result:

One of the universal unfoldings of the steady state equation (4') has a basis given by $\langle 1, x, x^2, x^3, x^4, x^5, x^6 \rangle$. The codimension is therefore 7.

$$\varepsilon f = -x^7 + Hx^2 - H^2 + \sum_{i=0}^{6} \alpha_i x^i$$

3.4 NUMERICAL ANALYSIS:

For the numerical analysis of the steady state equation (4') we define the following new variables:

$$\overline{\overline{\varepsilon B_i}} = (G + H)\, \varepsilon B_i \quad \text{for } i = 1,2,3$$

$$\overline{Da_1}\,\overline{x} = \frac{Da_1 x}{H}$$

$$\overline{Da_2}\,\overline{x}^k = \frac{Da_2 x^k}{H}$$

$$\bar{\varepsilon} = \frac{1 + H}{G + H} \varepsilon \tag{64}$$

where

$$\bar{x} = \exp(- \frac{E_A}{RT})$$

$$\bar{\varepsilon}\ln\bar{x} = (\varepsilon\ln x - 1) \frac{1 + H}{G + H}$$

It can be shown that (4') can be transformed into an equivalent equation (for the number of steady states) and is derived in appendix C as:

$$-(1 + H)\varepsilon f = A_3H^3 + A_2H^2 + A_1H + A_0 \tag{65}$$

This is a cubic in H with coefficients A_i (i= 0,1,2,3) that are functions of $\bar{x}$ and $\ln\bar{x}$ (appendix C).

The strategy used in the numerical analysis of equation (65) is as follows:

1. Calculate the parameter values given by (9) - (15) for a fixed k.
2. Evaluate H and G at the most degenerate singularity by (50) and (51).
3. Evaluate the new variables by (64).
4. Evaluate for each lnx the coefficients in (65) and solve for H by setting (65) equal to zero.
5. Graph $\bar{x}$ versus H to get the bifurcation diagram next to the most degenerate singularity.

The results of this calculation is that in the neighborhood of the most degerate singular point there exist two positive H-branches (feasible solution) as function of lnx and another one that is always negative (unfeasible solution). Figure 15 shows the corresponding bifurcation diagram of equation (65). This is to be compared to figure 16 which is the bifurcation diagram of equation (57). The equivalence is without doubt striking.

The numerical values of paramenters and state variable (the most degenerate singularity) in these calculations are:

k	$= 0.752$	G	$= 1.12534$
$\overline{B}_1$	$= 3.940247 \times 10^5$	B_2	$= -13.938989 \times 10^5$
$\overline{B}_3$	$= -1.855836$	$\overline{Da}_1$	$= 1.123525 \times 10^2$
$\overline{Da}_2$	$= 4.620856 \times 10^5$	ε	$= 0.6751724 \times 10^{-1}$
H	$= 0.3175279 \times 10^{-1}$	$\overline{x}$	$= 0.6078093 \times 10^{-3}$

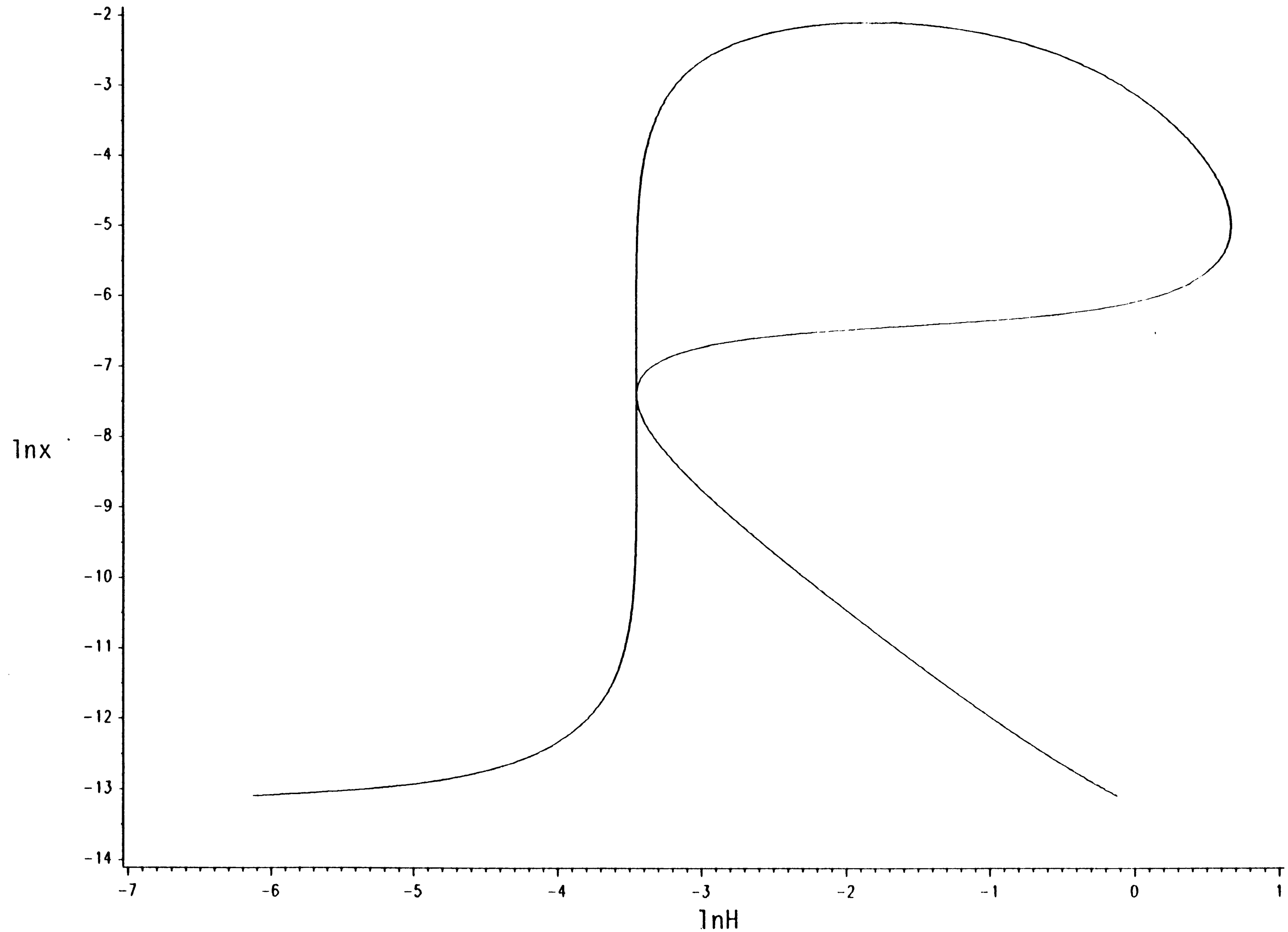

Fig. 15 Bifurcation Diagram of the original function lnx versus lnH

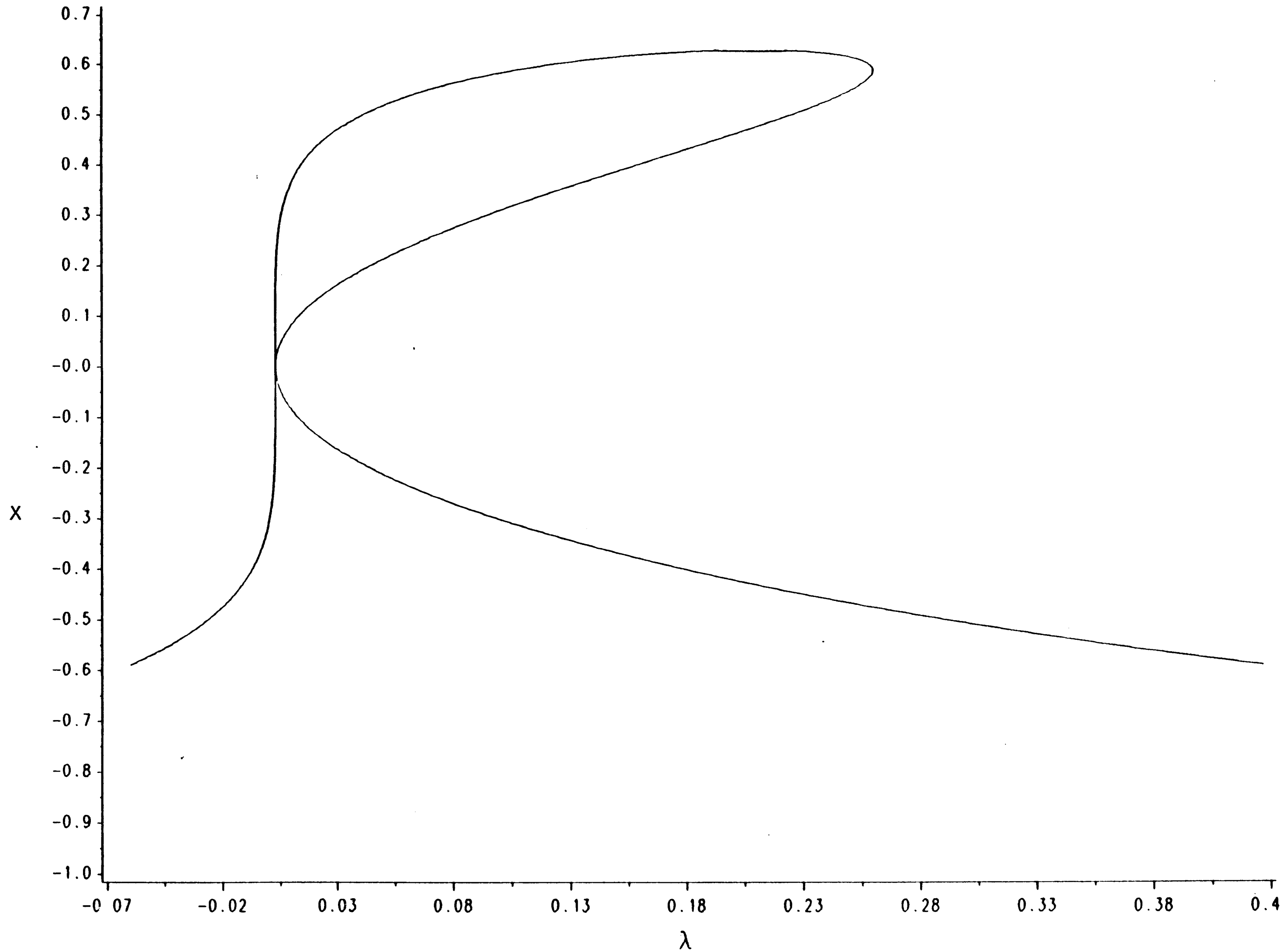

Fig. 16 Bifurcation Diagram of the Normal Form x versus λ

IV CONCLUSION

In this work we have shown that for two consecutive reactions in a CSTR seven steady state solutions can be obtained in a systematic manner in the neighborhood of a star singularity. The parameter values for which this occurs can be restricted to feasible parameter space. The effects of various assumptions made by previous authors are considered. It is seen that the analysis presented here is the most gèneral one thus far. A procedure exists to obtain all the qualitive different local bifurcation diagrams that can be found in the neighborhood of an organizing center. This is outlined in Golubitsky and Shaeffer (1985), and consists of calculating the hystersis, isola and double limit varieties of the universal unfolding. The number of bifurcation diagrams that can be found in this problem is huge (in the range of one hundred) and obtaining all of them is tedious.

Using the flow rate as the bifurcation parameter, a normal form suitable for experiments was obtained in chapter III, together with one of its universal unfoldings. It is worthwhile noting that the question of obtaining maximal multiplicity is independent of the choice of the bifurcation parameter. However the choice does play a very important role in the normal form and the bifurcation diagrams that can be obtained. The bifurcation parameter of chapter II results in a strong equivalent normal form of codimension 5 ($-x^7 + B_3$; Retzloff et al, 1987), choosing a different bifurcation parameter in chapter III augments the number of parameters by two, and results in a slightly more complicated normal form of codimension 7, obtained in the context of general equivalence this is not a serious handicap since at the level of universal unfolding all that is needed is equivalence. Moreover, in more complicated problems one has to deal with moduli and Lee groups algebra (Golubbitsky and Sheaffer (1985)).

For three consecutive reactions, the maximum number of solutions is predicted by Chicone and Retzloff (1982) to be no greater than fifteen. However the number of parameters for this problem is only eleven in their nondimensionalization, so that the maximum number of local solutions obtainable by singularity theory is twelve (globally, thirteen). It remains an extremly tedious problem to see whether fifteen solution in fact exist for this case.

REFERENCES

Balakotaiah V. and Luss D., Chemical Engineering Science 1982, 37, 1611.

Balakotaiah V. and Luss D., Chemical Engineering Science 1983, 38, 1709.

Balakotaiah V. and Luss D., Chemical Engineering Science 1984, 39, 865.

Brocker Th., and Lander L., Differentiable Germs and Catastrophes, 1975, Cambridge University Press.

Chan P. C-H., Retzloff D.G., Mohamed R., Berdouzi, B., Chicone C. and Offin D., The Dynamic Behavior and Chaos for Two Parallel Reactions in a Continuous Stirred Tank Reactor, Chem. Engr. Comm., 1987, in print.

Chicone C. and Retzloff D.G., Nonlinear Analyzes, Theory, Methods and Applications, 1982, 6, 983.

Farr W.W. and Aris R., Chemical Engineering Science 1986, 41, 1385.

Golubitsky M. and Schaeffer D., Comm. Pure App. Math. 1979, 32, 21.

Golubitsky M. and Schaeffer D., Singularities and Groups in Bifurcation Theory, Vol. 1, 1985, Springer, New York.

Retzloff D.G., Chan P. C-H., Mohamed R., Offin D. and Chicone C., J. Math. Anal. and Appl., 1987, 124, 327.

Retzloff D.G. and Chicone C., Chem. Engr. Comm. 1981, 12, 365.

NOMENCLATURE

A: heat transfer area

B_1, B_2, B_3: dimensionless heats of reaction

C: concentration

C_p: specific heat

Da_1, Da_2: Damkohler numbers

E: activation energy

F: flowrate

G: dimensionless coolant temperature

$(-\Delta H)$: heat of reaction

H: dimensionless inverse flow rate

h: heat transfer coefficient

k: activation energy ratio

k_0: pre-exponential factor

m, N, n, p, q, r, s: positive integers

R: gas constant

T: temperature

T_m: reference temperature

t: time

V: reactor volume

x: dimensionless temperature

Greek Symbols

ε: reciprocal of dimensionless activation energy

ρ: density

λ: bifurction parameter

α_i: constants

Subscripts

A, B, C: species

c: coolant

f: feed

APPENDIX A: Swallowtail Points

We present here the six relevant equations from which the wigwam, butterfly and bifurcation branches of chapter II were calculated. Letting $B_2' = B_1+B_2+B_3$ they are:

$$B_1Da_1x+Da_1Da_2B_2'x^{1+k}+Da_2B_3x^{k}-\ln x\ [1+Da_1(1+\varepsilon B_1)x$$
$$+Da_2(1+\varepsilon B_3)x^{k}+Da_1Da_2(1+\varepsilon B_2')x^{1+k}] = 0 \qquad \text{(A1)}$$

$$B_1Da_1x+Da_1Da_2B_2'x^{1+k}(1+k)+Da_2B_3kx^{k}-1-Da_1(1+\varepsilon B_1)$$
$$(x\ln x+x)-Da_2(1+\varepsilon B_3)x^{k}(k\ln x+1)-Da_1Da_2(1+\varepsilon B_2')x^{1+k}$$
$$[(k+1)\ln x+1] = 0 \qquad \text{(A2)}$$

$$Da_1Da_2B_2'(1+k)kx^{1+k}+Da_2B_3k(k-1)x\ +1-Da_1(1+\varepsilon B_1)x$$
$$-Da_2(1+\varepsilon B_3)x^{k}[k(k-1)\ln x+2k-1]+Da_1Da_2(1+\varepsilon B_2')x^{1+k}$$
$$[(k+1)k\ln x+2k+1] = 0 \qquad \text{(A3)}$$

$$Da_1Da_2B_2'(1+k)k(k-1)x^{1+k}+Da_2B_3k(k-1)(k-2)x^{k}-2$$
$$+Da_1(1+\varepsilon b_1)x-Da_2(1+\varepsilon B_3)x^{k}[k(k-1)(k-2)\ln x+3k^2-6k+2]$$
$$-Da_1Da_2(1+\varepsilon B_2')x^{1+k}[(k+1)k(k-1)\ln x+3k^2-1] = 0 \qquad \text{(A4)}$$

$$Da_1Da_2B_2'(1+k)k(k-1)(k-2)x^{1+k}+Da_2B_3k(k-1)(k-2)$$
$$(k-3)x^{k}+6-2Da_1(1+\varepsilon B_1)x-Da_2(1+\varepsilon B_3)x^{k}[k(k-1)(k-2)$$
$$(k-3)\ln x+4k^3-18k^2+22k-6)-Da_1Da_2(1+\varepsilon B_2')x^{1+k}$$
$$[(k+1)k(k-1)(k-2)\ln x+4k^3-6k^2-2k+2] = 0 \qquad \text{(A5)}$$

$$Da_1Da_2B_2'(1+k)k(k-1)(k-2)(k-3)x^{1+k}+Da_2B_3k(k-1)$$
$$(k-2)(k-3)(k-4)x^{k}-24+6Da_1(1+\varepsilon B_1)x-Da_2(1+\varepsilon B_3)x^{k}$$
$$[k(k-1)(k-2)(k-3)(k-4)\ln x+5k^4-40k^3+105k^2-100k+24]$$
$$-Da_1Da_2(1+\varepsilon B_2')x^{1+k}[(k+1)k(k-1)(k-2)(k-3)\ln x+5k^4$$
$$-20k^3+15k^2+10k-6] = 0 \qquad \text{(A6)}$$

The simultaneous solution of (A1), (A2), (A3), (A4), (A5), and (A6) has been carried out by Chan et al. (1987) to get eqns. (22)-(27).

To obtain the swallowtail points, we solve (A1), (A2), (A3) and (A4). The algebraic manipulations are:

(A2) - (A1)	= (A2a)
(1+k)(A2a) - (A3)	= (A3a)
(k-1)(A3) - (A4)	= (A4a)
(A4a) - (A3a)	= (A3b)

(A3b) is solved to obtain $Da_1 Da_2(1 + \varepsilon B_1)x^{1+k}$.
Substituting back into (A2a), (A3a), (A4a) yields equations (32) - (35).

APPENDIX B: Bifurcation Points

For the bifurcation points ($f = \partial f/\partial x = 0$) we solve equations (A1) and (A2) of appendix A for the two unknowns B_1 and B_2'. These two equations can be written as:

$$A_{11}B_1 + A_{12}B_2' = C_1 \tag{B1}$$

$$A_{21}B_1 + A_{22}B_2' = C_2 \tag{B2}$$

where:

$$A_{11} = Da_1 x(1 - \varepsilon \ln x) \tag*{(B2)}$$

$$A_{12} = Da_1 Da_2 x^{1+k}(1 - \varepsilon \ln x) \tag{B3}$$

$$A_{21} = Da_1 x(1 - \varepsilon \ln x - \varepsilon) \tag{B4}$$

$$A_{22} = Da_1 Da_2 x^{1+k}[(1 + k)(1 - \varepsilon \ln x) - \varepsilon] \tag{B5}$$

$$C_1 = -Da_2 B_3 x^k + \ln x[1 + Da_1 x + Da_2 x^k(1 + \varepsilon B_3) + Da_1 Da_2 x^{1+k}] \tag{B6}$$

$$C_2 = -Da_2 B_3 k x^k + 1 + Da_1 x(\ln x + 1) + Da_2(1 + \varepsilon B_3)x^k(k\ln x + 1) + Da_1 Da_2 x^{k+1}[(k + 1)\ln x + 1] \tag{B7}$$

Letting $y = \ln x$ and solving by Kramer's rule, we get

$$B_1 = \frac{C_1 \frac{A_{22}}{A_{11}} - C_2 \frac{A_{12}}{A_{11}}}{k(1 - \varepsilon y)\, Da_1 Da_2 \exp(k + 1)y} \tag{B8}$$

$$B_2 = \frac{\left(C_2 - \frac{A_{21}}{A_{11}} C_1\right)}{k(1 - \varepsilon y) Da_1 Da_2 \exp(k + 1)y} \tag{B9}$$

Evaluating and simplifying the quotients $\frac{A_{12}}{A_{11}}$ and $\frac{A_{21}}{A_{11}}$ results in equations (41) and (42) of chapter II.

APPENDIX C: A Bifurcation Equation

We derive here an alternate form of the steady state equation (4) or (4') in terms of the new variables defined in section 3.3:

$$
\begin{aligned}
\varepsilon f = {} & \bar{\varepsilon}\bar{B}_1\overline{Da}_1\bar{x}\,\frac{H}{G + H} + \bar{\varepsilon}\bar{B}_3\overline{Da}_2\bar{x}^k\,\frac{H}{G + H} \\
& + \bar{\varepsilon}(\bar{B}_1 + \bar{B}_2 + \bar{B}_3)\overline{Da}_1\overline{Da}_2\bar{x}^{1+k}\,\frac{H^2}{G + H} \\
& - \left(\bar{\varepsilon}\,\frac{G + H}{1 + H}\ln\bar{x} + 1\right)\Big\{1 + H\overline{Da}_1\bar{x} + H\overline{Da}_2\bar{x}^k \\
& + H^2\overline{Da}_1\overline{Da}_2\bar{x}^{1+k} + \overline{Da}_1\bar{x}\bar{\varepsilon}\bar{B}_1\,\frac{H}{G + H} + \overline{Da}_2\bar{x}^k\bar{\varepsilon}\bar{B}_3\,\frac{H}{G + H} \\
& + \overline{Da}_1\overline{Da}_2\bar{x}^{1+k}\bar{\varepsilon}(\bar{B}_1 + \bar{B}_2 + \bar{B}_3)\,\frac{H^2}{G + H}\Big\}.
\end{aligned}
$$

Rearranging and multiplying through by $-(1 + H)$, we get a cubic in H which can be written as:

$$-(1 + H)\varepsilon f = A_3H^3 + A_3H^2 + A_1H + A_0$$

where:

$$A_3 = \overline{Da}_1\overline{Da}_2\bar{x}^{1+k}(\bar{\varepsilon}\ln\bar{x} + 1)$$

$$
\begin{aligned}
A_2 = {} & \bar{\varepsilon}\ln\bar{x}[\overline{Da}_1\bar{x} + \overline{Da}_2\bar{x}^k + \overline{Da}_1\overline{Da}_2\bar{x}^{1+k}(G + \bar{\varepsilon}\bar{B}_1 + \bar{\varepsilon}\bar{B}_2 \\
& + \bar{\varepsilon}\bar{B}_3)] + \overline{Da}_1\bar{x} + \overline{Da}_2\bar{x}^k + \overline{Da}_1\overline{Da}_2\bar{x}^{1+k}
\end{aligned}
$$

$$
\begin{aligned}
A_1 = {} & \bar{\varepsilon}\ln\bar{x}[1 + \overline{Da}_1\bar{x}(G + \bar{\varepsilon}\bar{B}_1) + \overline{Da}_2\bar{x}^k(G + \bar{\varepsilon}\bar{B}_3)] \\
& + 1 + \overline{Da}_1\bar{x} + \overline{Da}_2\bar{x}^k
\end{aligned}
$$

$$A_0 = G\bar{\varepsilon}\ln\bar{x} + 1$$

APPENDIX D: Recognition Problem

In this appendix we derive the equation used in chapter III for the recognition problem. Differentiating (4') with respect to H term by term and applying (43), we obtain:

$$\begin{aligned}
\partial\varepsilon f/\partial H = {} & \varepsilon B_1 Da_1 x\left(\frac{1}{H} - \frac{1}{G+H}\right) + \varepsilon B_3 Da_2 x^k\left(\frac{1}{H} - \frac{1}{G+H}\right) \\
& + \varepsilon(B_1 + B_2 + B_3) Da_1 Da_2 x^{1+k}\left(\frac{2}{H} - \frac{1}{G+H}\right) \\
& -(1 - \varepsilon \ln x)\left(\frac{1}{1+H} - \frac{1}{G+H}\right)\{\ -\ \} \\
& - \varepsilon \ln x\{(1 + \varepsilon B_1)\frac{Da_1 x}{H} - \varepsilon B_1 \frac{Da_1 x}{G+H} \\
& + (1 + \varepsilon B_3)\frac{Da_2 x^k}{H} - \varepsilon B_1 \frac{Da_2 x^k}{G+H} \\
& + \frac{2}{H} Da_1 Da_2 [1 + \varepsilon(B_1 + B_2 + B_3)] x^{1+k} \\
& - \varepsilon(B_1 + B_2 + B_3) Da_1 Da_2 \frac{x^{1+k}}{G+H}\ \}
\end{aligned} \qquad \text{(D1)}$$

where { - } is the term between bracket in (4'). Rearranging (D1), it can be written as:

$$\partial\varepsilon f/\partial H = g_1 + g_2 + g_3 \qquad \text{(D2)}$$

where g_1, g_2 and g_3 are given by (45) - (47). Using (D2) we have:

$$\partial^2\varepsilon f/\partial x\partial H = \partial g_1/\partial x + \partial g_2/\partial x + \partial g_3/\partial x \qquad \text{(D3)}$$

and for a better subsequent use of eqn. (9) - (15) we have:

$$x\partial g_1/\partial x = x\,\frac{\varepsilon}{H}\partial f/\partial x + \frac{\varepsilon}{H}(1 + k)x^{1+k}Da_1Da_2\{(B_1 + B_2 + B_3)$$

$$- \ln x\,[1 + \varepsilon(B_1 + B_2 + B_3)]\} \tag{D4}$$

$$- \varepsilon Da_1Da_2\,\frac{x^{1+k}}{H}\,[1 + \varepsilon(B_1 + B_2 + B_3)]$$

$$x\partial g_2/\partial x = -\frac{\varepsilon}{G+H}\,(1 + Da_1x + Da_2x^k + Da_1Da_2x^{1+k}) \tag{D5}$$

$$+ \frac{1-\varepsilon\ln x}{G + H}\,[Da_1x + kDa_2x^k + (k+1)\,Da_1Da_2x^{1+k}]$$

$$x\partial g_3/\partial x = \frac{\varepsilon}{1+H}\,\{1 + Da_1x(1+\varepsilon B_1) + Da_2x^k(1+\varepsilon B_3)$$

$$+ Da_1Da_2x^{1+k}\,[1+ \varepsilon(B_1 + B_2 + B_3)]\} \tag{D6}$$

$$- \frac{1 - \varepsilon\ln x}{1+H}\,\{Da_1x\,(1 + \varepsilon B_1) + kDa_2x^k(1 + \varepsilon B_3)$$

$$+ (k+1)\,Da_1Da_2x^{1+k}\,[1 + \varepsilon(B_1 + B_2 + B_3)]\}$$

At any singularity given by (9) - (15), these equations simplify to:

$$g_1 = \frac{2\varepsilon\ln x}{H} \tag{D7}$$

$$g_2 = \frac{4(1 - \varepsilon\ln x)^2}{G + H}\;\frac{k^2 + 1}{(k - 1)^2} \tag{D8}$$

$$g_3 = -4\left(\frac{1 - \varepsilon\ln x}{1 + H}\right)\;\frac{k^2 + 1}{(k - 1)^2} \tag{D9}$$

$$x\partial g_1/\partial x = \frac{(1 + k)\varepsilon\ln x}{H} \tag{D10}$$

$$x\partial g_2/\partial x = \frac{2(k^2 + 1)}{(k - 1)^2}\;\frac{(1 - \varepsilon\ln x)}{G + H}\,[(k + 1)\,(1 - \varepsilon\ln x) - 4\varepsilon] \tag{D11}$$

$$x\partial g_3/\partial x = \frac{2(k^2 + 1)}{(k - 1)^2(1 + H)} [2\varepsilon - (k + 1)(1 - \varepsilon \ln x)] \tag{D12}$$

letting $g_1 + g_2 + g_3 = 0$, we obtain:

$$\frac{\varepsilon \ln x}{H} = \frac{2(k^2 + 1)}{(k - 1)^2}(1 - \varepsilon \ln x)\left[\frac{1}{1 + H} - \frac{1 - \varepsilon \ln x}{G + H}\right] \tag{D13}$$

Furthermore, letting $x(\partial g_1/\partial H + \partial g_2/\partial H + \partial g_3/\partial H) = 0$ and use equation (D13), eqn. (48) through (52) are obtained.

The uniqueness of G and H determined by these calculations suggests that the most degenerate singularity is already obtained.

We now derive the signs of higher derivatives. Using (D2) we have:

$$\partial^2 \varepsilon f/\partial H^2 = \partial g_1/\partial H + \partial g_2/\partial H + \partial g_3/\partial H \tag{D14}$$

It can be shown that at the most degenerate singularity:

$$\partial g_1/\partial H = -\frac{2\varepsilon \ln x(1 - \varepsilon \ln x)}{H(G + H)} \tag{D15}$$

$$\partial g_2/\partial H = \frac{g_2}{H} - \frac{g_2}{1 + H} - 2\varepsilon \ln x \frac{(1 - \varepsilon \ln x)}{H(G + H)} \tag{D16}$$

$$\partial g_3/\partial H = -\frac{2g_3}{1 + H} + \frac{g_3}{G + H} + \frac{g_3}{H} \tag{D17}$$

$$+ \frac{1 - \varepsilon \ln x}{(1 + H)(G + H)} \left[4\varepsilon \ln x \frac{k^2 + 1}{(k - 1)^2}\right]$$

Using (D14) - (D17) and (D7) - (D9) it is easy to get eqn. (53).

The other higher derivative can be written as:

$$\partial^3\varepsilon f/\partial x^2\partial H = \partial^2(g_1 + g_2 + g_3)/\partial x^2 \tag{D18}$$

Here again, it is more convenient to evaluate $x^2\partial^2(g_1 + g_2 + g_3)/\partial x^2$. Straightforward algebra starting from eqn. (45) - (47) yields the most degenerate point:

$$\partial^3\varepsilon f/\partial x^2\partial H = \frac{a}{H} - \frac{\varepsilon b}{G + H} + \frac{c(1 - \varepsilon \ln x)}{G + H} + \frac{d\varepsilon}{1 + H} - \frac{\varepsilon(1 - \varepsilon \ln x)}{1 + H} \tag{D19}$$

where:

$$a = (k + 1)(k\varepsilon \ln x - 2\varepsilon)$$

$$b = \frac{(4k)(k^2 + 1)}{(k - 1)^2} - 2(2k + 1)\varepsilon \ln x - 4\varepsilon \frac{k + 1}{k(k - 1)^2}(5k^2 + 3k - 1)$$

$$c = \frac{k(k + 1)^2}{k - 1} - \frac{4\varepsilon(2k^2 - 1)(k + 1)}{(k - 1)^2} + k(1 + k)(1 - 2\varepsilon \ln x)$$

$$d = \frac{2k^3 + 3k^2 + 4k - 1}{(k - 1)^2}$$

$$e = 2k^2 \frac{(k + 1)}{k - 1}$$

VITA

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The undersigned, appointed by the Dean of the Graduate Faculty, have examined a dissertation entitled

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FIRST ORDER REACTIONS

presented by BRAHIM BERDOUZI

a candidate for the degree of DOCTOR OF PHILOSOPHY

and hereby certify that in their opinion it is worthy of acceptance.

[redacted]