A Singularity Theory Analysis of a Thermal-Chainbranching Model for the Explosion Peninsula

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0. Introduction

In this paper we investigate multiple steady-state solutions in a thermal-chainbranching model proposed by Gray and Yang [12], [20]. Specifically we study, from a qualitative point of view, how the number of solutions varies with the concentration of the reactants. We employ new mathematical techniques (cf. [10]) based on singularity theory; by virtue of these methods we obtain our results analytically, without recourse to the computer. (The basics of the required singularity theory are summarized in Section 2 of the present paper.) We emphasize that these techniques may also be applied to analyze multiple steady states in other models. Indeed reference [9] analyzed a single reaction in a continuous-flow stirred tank in this way; the analytical methods led to the discovery of certain bifurcation diagrams which had not been observed in the numerical explorations. Our analysis proceeds by focusing on a sort of worst case, here called the *organizing center*. Of course careful treatment of the singularities in a problem is often required for solution on the computer, and our analysis complements numerical methods quite neatly.

The thermal-chainbranching model provides a unified, mathematical treatment of the three explosion limits in the reaction of H_2 with O_2 in a closed container. Figure 1 summarizes typical experimental data for this reaction. For a given mixture of hydrogen and oxygen initially at pressure P and temperature θ_0 and immersed in a bath of the same temperature, the reaction will take place at a slow speed or explosively fast according to whether (P, θ_0) lies to the left or right of the curve in Figure 1. Along the separating curve, P cannot be expressed as a function of θ_0; in particular this implies that the overall reaction must contain a number of elementary reactions. (Similar phenomena are seen in other reactions, such as the oxidation of carbon monoxide (cf. [4], [7], [16]), the oxidation of

Communications on Pure and Applied Mathematics, Vol. XXXIV, 433–463 (1981)

CCC 0010-3640/81/040433-31$03.10

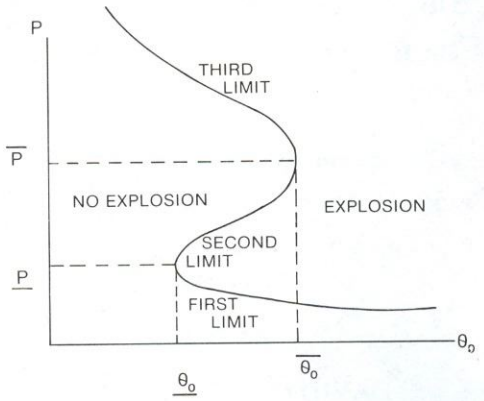

Figure 1

phosphorous vapor (cf. [3]), or certain hydrogen-halogen reactions (cf. [1], [15]).) The thermal-chainbranching model retains only four elementary reactions, presumably slow reactions—the hypothesis that fast reactions are in approximate equilibrium may be used to eliminate them from the equations. However, even after reduction the model still contains nine dimensionless parameters. Although this paper was motivated by an interest in the explosion peninsula in the H_2-O_2 reaction, we do not attempt to adjust the parameters in the model to give the best fit with data for this specific reaction. Rather we conduct a parameter exploration, searching for the values which give the most interesting behavior.

The steady state approximation (i.e., neglecting the consumption of fuel) is one of the hypotheses of the thermal-chainbranching model; thus the model admits true equilibrium solutions. We study the number of such equilibrium solutions as a function of the pressure P. Our main result is Theorem 4.2, which lists the bifurcation diagrams we have shown to occur in the thermal-chainbranching model. By a bifurcation diagram, we mean a graph of the equilibrium temperature θ against P, the other parameters, including θ_0, being held fixed. We treat the pressure as a distinguished parameter because the explosion peninsula concerns the lack of monotonicity of the explosion limit curve with respect to this variable. No claim is made that bifurcation diagrams not enumerated in Theorem 4.2 cannot occur—we have only explored a five-dimensional subspace of the nine-dimensional parameter space. Even within this five-dimensional subspace our methods indicate the presence of higher-order singularities than those considered here—indeed in Section 3 our restrictions on the parameter γ_3 are related to such higher-order singularities.

In Figure 2(iii) we have shown a sample bifurcation diagram from the list of Theorem 4.2. This diagram should be interpreted as in any equilibrium theory of explosions; i.e., whether the reaction is *subcritical* (slow, a fizzle) or *supercritical* (fast, an explosion) depends on whether the equations admit a low temperature or high temperature equilibrium. (The intermediate temperature equilibria,

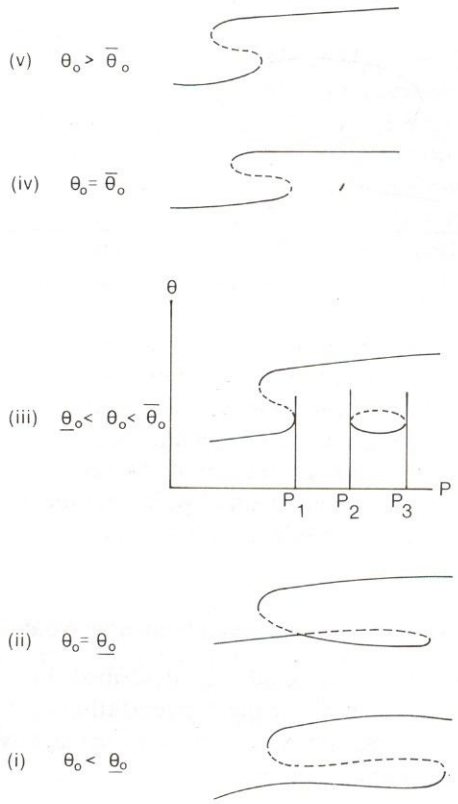

Figure 2

shown as dotted, are typically unstable.) Thus in the figure there are three explosion limits P_i, and the reaction is subcritical in the two pressure ranges $0 < P < P_1$ and $P_2 < P < P_3$. Of course this corresponds with Figure 1 at an intermediate temperature θ_0, as our labels suggest. The neighboring diagrams in Figure 2 outline a possible mechanism for the changes in the topology of the bifurcation diagram as the bath temperature θ_0 varies. Thus we propose that the transitions (ii) and (iv) occur by traditional bifurcation and isola formation, respectively. Other mechanisms are certainly possible. For example, a bifurcation as in Figure 3 could explain the three limit sections of the explosion peninsula. However, to describe the formation and destruction of the peninsula would require a longer sequence of diagrams than the one given in Figure 2. We note that diagrams like those in Figure 3 do appear in the thermal-chainbranching model. The relation of these two mechanisms is discussed in more detail at the end of Section 4.

In Section 1, we present the equations of the thermal-chainbranching model and non-dimensionalize them. Section 2 is a brief summary of the singularity

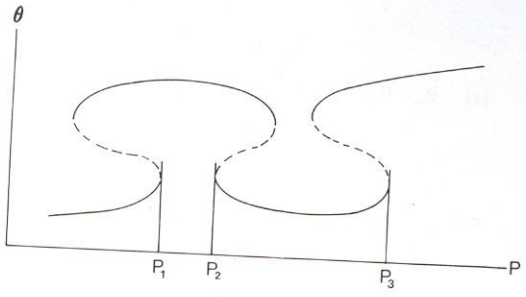

Figure 3

theory background from [9] and [10] which is necessary to understand our application. We also give in this section the analytic description of the singular bifurcation problem which is the basis of our results. In Section 3, we perform the calculations on the thermal-chainbranching model which allow us to apply the results of Sections 2 and 4. Section 4 contains the classification of all bifurcation diagrams which occur as small perturbations of the singular bifurcation problem appearing in the model and described in Section 2.

1. The Thermal-Chainbranching Model

The thermal-chainbranching model is described by the pair of ordinary differential equations (1.1) below for the concentration c of an active radical and the temperature θ. These equations are derived in the steady-state approximation which neglects the consumption of fuel:

$$\frac{dc}{dt} = k_i + \left[(n-1)k_b - k_w - k_g\right]c, \tag{1.1a}$$

$$\frac{d\theta}{dt} = h_i k_i + \left[h_b k_b + h_w k_w + h_g k_g\right]c - l(\theta - \theta_0). \tag{1.1b}$$

It is supposed that concentration and temperature are uniform within the reaction vessel; the term $l(\theta - \theta_0)$ represents a lumped parameter approximation for heat loss at the boundary to a bath at temperature θ_0. The four terms k_i, k_b, k_w, k_g are (temperature and pressure dependent) reaction rates for the four reactions included in this model—an initiation step, a branching step, and two termination steps, one at the wall and one in the interior (g for gaseous). The parameters h_i, etc. are the corresponding heats of reaction, partially non-dimensionalized. Briefly the effect of the four reactions may be described as follows. In the initiation reaction fuel is converted into the active radical; in the branching step one molecule of the active radical produces n such molecules; in the termination steps the radical is eliminated from the system by the formation of inert products. The concentration P of the fuel does not appear explicitly in

(1.1), but it does occur implicitly in the various reaction rates, which we now proceed to discuss.

Few if any realistic reactions are as simple as (1.1), but (1.1) can be a useful approximation if fast reactions are eliminated from a realistic system through the usual equilibrium assumption. In particular, Gray and Yang [20] argue that, for an appropriate parameter choice, (1.1) models the reaction of H_2 with O_2, and they propose a correspondence between certain slow, rate controlling reactions in the set of reactions for the H_2-O_2 reaction with the four reactions included in (1.1). (See the appendix for a summary of the reactions used in formulating their model.) We use their correspondence in formulating our hypotheses on the reaction rates as follows. Assuming Arrhenius kinetics, the general forms of the reaction rates in the thermal-chainbranching model are listed in Table I, where P denotes the concentration of the reactants (the stoichiometry is fixed); for a gas this concentration may be taken proportional to the initial pressure. The various activation energies E_i, etc. and pre-exponential factors Z_i, etc. are assumed constant, and we suppose $\alpha_w = 0$ throughout. The rate controlling reactions proposed by Gray and Yang lead to the following values for the orders of the various reactions:

$$\alpha_i = 2, \quad \alpha_b = 1, \quad \alpha_g = 2. \tag{1.2}$$

Henceforth we assume this. In particular, it is vital for the explosion peninsula that the order of the branching reaction be intermediate to the orders of the two termination reactions. After our non-dimensionalization below, (1.2) amounts to assuming prescribed values for two of the nine non-dimensional parameters in the full model.

TABLE I

$$k_i = Z_i \exp\{-E_i/R\theta\} P^{\alpha_i}$$
$$k_b = Z_b \exp\{-E_b/R\theta\} P^{\alpha_b}$$
$$k_w = Z_w \exp\{-E_w/R\theta\} P^{\alpha_w}$$
$$k_g = Z_g \exp\{-E_g/R\theta\} P^{\alpha_g}$$

We assume that $n > 1$ in (1.1a), i.e., that radical multiplication through repeated branching is possible. Therefore with an appropriate rescaling of k_b and h_b we may eliminate the factor $n - 1$ from (1.1a).

Consider the equilibrium equations associated to (1.1), obtained by equating the right-hand sides to zero. On solving the first equation for c and substituting into the second, we obtain the relation

$$k_i \left\{ \frac{(h_w + h_i)k_w + (h_b - h_i)k_b + (h_g + h_i)k_g}{k_w - k_b + k_g} \right\} = l(\theta - \theta_0). \tag{1.3}$$

To simplify this equation, we shall assume that

$$h_w + h_i = h_g + h_i = 0. \tag{1.4}$$

This has approximate validity for the H_2-O_2 reaction assuming the mechanisms of Gray and Yang's model (described in the appendix), in that h_i is large negative, h_w and h_g, which involve radical recombination, are large positive, and h_b is approximately zero. However, the main reason for (1.4) is mathematical convenience.

Let us introduce non-dimensional variables into (1.3) by defining

$$T = R\theta/E_i, \qquad v = 3(Z_w/Z_b)P^{-1}.$$

Then (1.3) may be rewritten as

$$\mathcal{E}_3(T)v^3 - 3\mathcal{E}_2(T)v^2 + Z\mathcal{E}_1(T)v = \frac{a}{T - T_0}, \tag{1.5}$$

where we make the following definitions:

$$T_0 = R\theta_0/E_i, \tag{1.6}$$

$$Z = 9Z_wZ_g/Z_b^2, \tag{1.7}$$

$$a = 27RZ_i\left(\frac{Z_w}{Z_b}\right)^2\left(\frac{h_b - h_i}{lE_i}\right), \tag{1.8}$$

and

$$\mathcal{E}_j(T) = \exp\{+\gamma_j/T\}, \qquad j = 1, 2, 3,$$

where

$$\gamma_1 = (E_i + E_b - E_g)/E_i, \tag{1.9a}$$

$$\gamma_2 = 1, \tag{1.9b}$$

$$\gamma_3 = (E_i + E_b - E_w)/E_i. \tag{1.9c}$$

Our final equation (1.5), defining T as a function of v, contains five auxiliary parameters in addition to the bifurcation parameter v, namely T_0, Z, a, γ_1, and γ_3. This is reduced from the nine of the full model by assumptions (1.2) and (1.4). Three of these five may be readily varied in an experiment—obviously T_0 is subject to control; Z includes the ratio of a surface reaction rate to a volume reaction rate and may therefore be controlled by changing the vessel size or

adding dilutants; a represents a ratio of heat produced to heat lost and may be controlled by changing the vessel size or its insulating properties. The scaled activation energies γ_1 and γ_3 can of course only be varied experimentally by consideration of several different reactions simultaneously. We shall study (1.5) when all the γ_j are approximately equal to 1; this is motivated by our original interest in the H_2-O_2 reaction where E_i is much larger than any of the other activation energies.

2. The Organizing Center

Let $F(T, v; a, T_0, Z, \gamma_1, \gamma_3)$ be the function defined by (1.5), i.e.,

$$F = \mathfrak{S}_3 v^3 - 3\mathfrak{S}_2 v^2 + Z\mathfrak{S}_1 v - \frac{a}{T - T_0}. \tag{2.0}$$

We shall show in Section 3 that there exist values of the parameters a, T_0, Z, γ_1, γ_3 such that the system of six equations

$$F = F_T = F_v = F_{TT} = F_{Tv} = F_{vv} = 0 \tag{2.1}$$

admits a simultaneous solution (T^0, v^0), where subscripts of F denote partial derivatives. This fact is fundamental to our analysis.

To see the significance of (2.1), let us recall that we want to solve (1.5) for T as a function of v. More specifically, we are interested in how the number of values of T which satisfy (1.5) varies with v. At a point where $F_T \neq 0$ we may conclude from the implicit function theorem that locally the equation $F = 0$ defines T as a smooth function of v—in particular, there can be no contribution to a change in the number of solutions. Thus the first case involving a possible change in the number of solutions occurs at a point (T^0, v^0) where

$$F = F_T = 0.$$

Provided that F_{TT} and F_v are both nonzero, it can be shown rather easily that (T^0, v^0) is a limit point, i.e., for $v < v^0$ (or $v > v^0$ respectively) there are two values of T solving (1.5) which meet at T^0 as $v \to v^0$ and for $v > v^0$ (or $v < v^0$ respectively) there are no solutions near T^0. A hierarchy of cases of increasing degeneracy suggests itself, and obviously (2.1) is fairly far down on the list. Indeed because of its complexity, the general theory of [10] provides useful guidance. (See also the summary of this material in [9], Section 2.)

Balanced against this complexity is the fact that we can analyze (1.5) with local, analytic methods. Intuitively the reason for this is as follows. If the parameter values are such that (2.1) cannot be solved, the association bifurcation diagrams contain up to six limit points—see for example the diagrams of Theorem 4.2. Choosing parameter values so that (2.1) admits a solution corre-

sponds to adjusting the parameters until all the limit points coalesce into a single, highly degenerate point. We may then discuss perturbations of this singular case *via* the universal unfoldings of [10], a purely local problem. Moreover, since effectively all singularities have already been taken into account, this local representation is often valid in a much larger region than might be *a priori* expected.

This section contains three propositions of significance, Propositions 2.6, 2.13, and 2.15. The first provides an answer to the following question. If (2.1) is satisfied, then the first non-zero terms in the Taylor expansion of F at (T^0, v^0) are cubic; do the quartic and higher terms affect the qualitative properties of the bifurcation? Proofs of these propositions are sketched at the end of the section—the proofs assume a knowledge of [10]. We now briefly review the fundamental concepts of the singularity theory approach to bifurcation.

A *bifurcation problem* is defined as an equation

$$G(x,\lambda) = 0, \tag{2.2a}$$

where (x,λ) is near 0 in $\mathbb{R}\times\mathbb{R}$ and G is (the germ of) a C^∞ mapping of $\mathbb{R}\times\mathbb{R}\to\mathbb{R}$ defined near 0. Two such bifurcation problems are *contact equivalent* if

$$H(x,\lambda) = T(x,\lambda)\cdot G(X(x,\lambda),\Lambda(\lambda)), \tag{2.2b}$$

where $T(0,0)\neq 0$, $X(0,0) = \Lambda(0) = 0$, $\partial X(0,0)/\partial x > 0$, and $\partial\Lambda(0)/\partial\lambda > 0$. In words, two bifurcation problems are contact equivalent if they differ only by a change of coordinates.

For a bifurcation problem $G(x,\lambda)$, x is assumed to measure the state of a system while λ measures some externally controlled parameter which is to be varied quasistatically by an experimenter. In our intended application, x represents (an appropriate function of) the temperature of a chemical reaction while λ measures the concentration of a reagent.

The special form of the changes of coordinates $(x,\lambda)\to(X,\Lambda)$ in (2.2)—that is, Λ is independent of x—is based on the fact that λ is externally controlled and should not depend on the state of the system. It should be clear that the solutions of $H = 0$ differ from the solutions of $G = 0$ only by a change of coordinates preserving λ.

Our first task will be to give the beginnings of a classification of bifurcation problems of the form

$$G(x,\lambda) = P(x,\lambda) + \cdots, \tag{2.3}$$

where

$$P(x,\lambda) = Ax^3 + 3Bx^2\lambda + 3Cx\lambda^2 + D\lambda^3 \tag{2.4}$$

and $\cdots$ indicates terms of degree four or higher. Associate to P the following polynomial in one variable:

$$p(z) = Az^3 + 3Bz^2 + 3Cz + D. \tag{2.5}$$

We call G of type (2.3) *non-degenerate* if $A \neq 0$ and the polynomial p has no multiple roots, i.e., $p = \partial p/\partial z = 0$ has no common solution. We shall show first that under the assumption of non-degeneracy G and P are contact equivalent. More specifically, we have:

PROPOSITION 2.6. *A non-degenerate bifurcation problem G of type* (2.3) *is contact equivalent to*

$$H(x,\lambda) = x^3 - 3\bar{C}x\lambda^2 + 2\bar{D}\lambda^3, \tag{2.7}$$

where

$$\bar{C} = \left(\frac{B}{A}\right)^2 - \frac{C}{A} \quad \text{and} \quad 2\bar{D} = \frac{D}{A} - 3\frac{B}{A}\frac{C}{A} + 2\left(\frac{B}{A}\right)^3. \tag{2.8}$$

Note that dividing (2.3) by A and changing coordinates by $x \to x - (B/A)\lambda$ one can write the lowest-order terms of (2.3) in the form (2.7). The content of Proposition 2.6, whose proof is sketched below, is that the higher-order terms may also be eliminated by an appropriate change of coordinates.

If $\bar{D} \neq 0$, G is contact equivalent to

$$H(x,\lambda) = x^3 - 3m\lambda^2 x \pm 2\lambda^3, \tag{2.9}$$

where

$$m = \bar{C}/\bar{D}^{2/3}, \tag{2.10}$$

this last equivalence being obtained by replacing λ by $\lambda/|\bar{D}|^{1/3}$. We shall consider only the case of a "+" sign in (2.9).

H in (2.7) is degenerate precisely when $\bar{C}^3 = \bar{D}^2$ and thus degeneracy for (2.9) occurs when $m = 1$. Moreover, observe that there is an obvious difference between the zero set of H in (2.9) when $m < 1$ and $m > 1$. In the second case, the zero set consists of three lines while in the first case it consists of one line (the other two lines in $H = 0$ having become complex). When $m = 1$ the two lines which are to become complex have merged, thus causing the degeneracy.

Following the usage of singularity theory, we call the parameter m a *modal* parameter, since it cannot be scaled from (2.9) by a contact equivalence. As we shall see in Section 4, m plays a distinguished role in perturbations of (2.9).

Suppose that F is the bifurcation problem defined by (2.0), the values of the parameters a, T_0, Z, γ_1, γ_3 being such that (2.1) has a solution (T^0, v^0). The cubic terms in the Taylor series of F around (T^0, v^0) have the form (2.4) with coefficients

$$A = \tfrac{1}{6}F_{TTT}, \quad B = \tfrac{1}{6}F_{TTv}, \quad C = \tfrac{1}{6}F_{Tvv}, \quad D = \tfrac{1}{6}F_{vvv}, \tag{2.11}$$

where we identify x with $T - T^0$ and λ with $v - v^0$ in (2.4). Now compute m from the combination of (2.8) and (2.10), namely

$$m = \frac{2^{2/3}(B^2 - AC)}{(2B^3 - 3ABC + A^2D)^{2/3}}. \tag{2.12}$$

Provided $m \neq 1$, one may apply Proposition 2.6 to obtain the normal form (2.9); in particular, the quartic terms of F do not affect the qualitative properties of the bifurcation. Also observe that if one regards (2.1) as a system of six equations in the seven variables T, v and the five parameters, then generically one expects a one-parameter family of solutions, that parameter being equivalent to m. We verify this for (2.0) in Section 3.

Our second task of this section is to describe a method for finding all small perturbations of the singular bifurcation problem that we have just discussed. The singularity theory language is as follows: Given $G(x,\lambda)$, a k-parameter family $F(x,\lambda,\alpha)$ is called an *unfolding of* G if $F(x,\lambda,0) = G(x,\lambda)$. A *universal unfolding of* G is an unfolding F of G which classifies up to contact equivalence *all* small perturbations of G. More precisely, let $G_\epsilon(x,\lambda) = G(x,\lambda) + \epsilon Z(x,\lambda)$ be a small perturbation of G; then there is a smooth function $\alpha(\epsilon)$ such that, for each small ϵ, G_ϵ is contact equivalent to $F(\cdot,\cdot,\alpha(\epsilon))$. For example, we have the following, proposition whose proof is given at the end of the section.

PROPOSITION 2.13.

$$F(x,\lambda,\alpha,\beta,\gamma,\delta,\epsilon) = x^3 - 3\gamma(\lambda^2 + \delta\lambda + \epsilon)x + 2(\lambda^3 + \alpha\lambda + \beta)$$

and

$$F(x,\lambda,a,b,c,d,e) = x^3 - 3ex\lambda^2 + 2\lambda^3 + ax^2 + bx + c\lambda + d$$

are each universal unfoldings of (2.9) *where* $\alpha, \beta, \delta, \epsilon, a, b, c, d$ *are near zero and* γ, e *are near* m.

The *codimension* of a bifurcation problem G is the minimum number of parameters necessary in a universal unfolding. From Proposition 2.13, one sees that the codimension of (2.9) is five. Thus to analyze all bifurcation diagrams

near (2.9) one need only analyze $F = 0$ for fixed values of the five unfolding parameters. In Section 4, we shall describe the classification of the bifurcation diagrams given by the above function F.

The next proposition will allow us to verify in Section 3 that the five parameters a, T_0, Z, γ_1, γ_3 provide a universal unfolding of (2.0) in the neighborhood of parameter values where (2.1) is soluble. We state the proposition in terms of a general unfolding $F(x,\lambda,\boldsymbol{\alpha})$ where $\boldsymbol{\alpha} \in \mathbb{R}^5$, supposing that $F(\cdot,\cdot,\boldsymbol{\alpha}_0)$ is contact equivalent to (2.9) near (x_0,λ_0). Given a function $Q(x,\lambda)$, let $j(Q)$ denote the vector in $\mathbb{R}^{10}$:

$$(2.14) \qquad (Q, Q_x, Q_\lambda, \tfrac{1}{2}Q_{xx}, Q_{x\lambda}, \tfrac{1}{2}Q_{\lambda\lambda}, \tfrac{1}{6}Q_{xxx}, \tfrac{1}{2}Q_{xx\lambda}, \tfrac{1}{2}Q_{x\lambda\lambda}, \tfrac{1}{6}Q_{\lambda\lambda\lambda})$$

evaluated at $(x_0,\lambda_0,\boldsymbol{\alpha}_0)$.

PROPOSITION 2.15. *$F(x,\lambda,\boldsymbol{\alpha})$ is a universal unfolding of $F(x,\lambda,\boldsymbol{\alpha}_0)$ near (x_0,λ_0) if the determinant of the 10×10 matrix J whose rows are given by*

$$(2.16) \qquad \begin{aligned} &j(F),\ j(F_x),\ j(F_\lambda),\ j((x-x_0)F_x),\ j((\lambda-\lambda_0)F_x),\\ &j(F_\alpha),\ j(F_\beta),\ j(F_\gamma),\ j(F_\delta),\ j(F_\epsilon) \end{aligned}$$

is non-zero.

We shall now prove the various propositions stated above. The reader who is not familiar with singularity theory or one of the papers [9], [10] will probably want to skip the following material.

First we recall some notation. Let $\tilde{TG} = \langle G, G_x \rangle$ be the ideal in $\mathcal{E}_{x,\lambda}$ generated by G and G_x. Let $TG = \tilde{TG} + \mathcal{E}_\lambda\{G_\lambda\}$, where "+" means vector space sum and $\mathcal{E}_\lambda\{G_\lambda\}$ denotes the vector space spanned by $G_\lambda, \lambda G_\lambda, \lambda^2 G_\lambda, \cdots$. Let $\mathfrak{M}$ be the ideal of real-valued function germs $f(x,\lambda)$ which vanish at the origin. Note that by Taylor's theorem $\mathfrak{M}$ is just the ideal generated by x and λ. Then $\mathfrak{M}^k$ denotes the ideal generated by homogeneous polynomials of degree k. The ideal $\tilde{TG}$ has *finite codimension* if $\tilde{TG} \supset \mathfrak{M}^k$ for some k. We always assume that $\tilde{TG}$ has finite codimension. Note that if G and H are contact equivalent and $\mathfrak{M}^k \subset \tilde{TG}$, then $\mathfrak{M}^k \subset \tilde{TH}$. (A similar statement holds for TG and TH.)

The main technique used in proving contact equivalence is the following: let $G_t(x,\lambda)$ be a curve of bifurcation problems depending smoothly on t. Suppose that $\tilde{TG}_t = \tilde{TG}_0$ for $0 < t \leqq 1$; then G_1 is contact equivalent to G_0.

Nakayama's lemma is a useful algebraic tool for computing $\tilde{TG}$. Let $\mathcal{I} = \langle p, q \rangle$ be the ideal generated by $p(x,\lambda)$ and $q(x,\lambda)$. Let p' and q' be in the ideal $\mathfrak{M}\mathcal{I}$ generated by xp, λp, xq, λq. Then the ideal $\langle p + p', q + q' \rangle$ equals $\mathcal{I}$.

LEMMA 2.17. *Let G be a nondegenerate bifurcation problem of type* (2.3). *Then $\mathfrak{M}^4 \subset \mathfrak{M}\tilde{TG} \subset \tilde{TG}$.*

Proof: Using a change of coordinates of the form $x = \bar{x} + A\bar{x}^2 + B\bar{x}\lambda + C\bar{\lambda}^2$, $\lambda = \bar{\lambda} + D\bar{\lambda}^2$, we may write G in the form

$$G(x,\lambda) = x^3 - 3mx\lambda^2 + 2\lambda^2 + N\lambda^4 + \cdots, \tag{2.18}$$

where $+ \cdots$ indicate terms of degree five or higher and $m \neq 1$. Now define

$$G_t(x,\lambda) = x^3 - 3mx\lambda^2 + 2\lambda^3 + t(N\lambda^4 + \cdots). \tag{2.19}$$

Note that

$$\tilde{T}G_t = \langle x^3 - 3mx\lambda^2 + 2\lambda^3 + p', 3x^2 - 3m\lambda^2 + q' \rangle, \tag{2.20}$$

where p' and q' are in $\mathfrak{M}^4$. Consider the ideal

$$\mathfrak{I} = \langle x^3 - 3mx\lambda^2 + 2\lambda^3, x^2 - m\lambda^2 \rangle. \tag{2.21}$$

The homogeneous terms of degree four contained in $\mathfrak{I}$ are

$$\begin{gathered} x^4 - 3mx^2\lambda^2 + 2x\lambda^3, \quad x^3\lambda - 3mx\lambda^3 + 2\lambda^4, \quad x^4 - mx^2\lambda^2, \\ x^3\lambda - mx\lambda^3, \quad x^2\lambda^2 - x\lambda^4. \end{gathered} \tag{2.22}$$

When $m \neq 1$, the polynomials in (2.22) form a basis for the homogeneous polynomials of degree four. Noting further that the polynomials of (2.22) are actually in $\mathfrak{M}\mathfrak{I}$, we see that $\mathfrak{M}^4 \subset \mathfrak{M}\mathfrak{I}$. Thus we may apply Nakayama's lemma to see that $\tilde{T}G_t = \mathfrak{I}$ for all t. Hence $\mathfrak{M}^4 \subset \mathfrak{M}\tilde{T}G \subset \tilde{T}G$.

We have, of course, proved more, namely Proposition 2.6, since $\tilde{T}G_t = \tilde{T}G_0$ for all t and $G_0 = H$ in (2.9).

The results about the universal unfolding follow relatively easily from the above calculations and the unfolding theorem. Denote the space of germs of functions in x and λ by $\mathcal{E}_{x,\lambda}$. Let $\boldsymbol{\alpha} = (\alpha_1, \cdots, \alpha_k)$.

THEOREM 2.23 (cf. [10]). *Let $F(x,\lambda,\boldsymbol{\alpha})$ be a k-parameter unfolding of $G(x,\lambda)$. Then F is a universal unfolding if*

$$\mathcal{E}_{x,\lambda} = TG + \mathbb{R}\left\{ \frac{\partial F}{\partial \alpha_1}\bigg|_{\alpha=0}, \cdots, \frac{\partial F}{\partial \alpha_k}\bigg|_{\alpha=0} \right\}. \tag{2.24}$$

Knowing that $\mathfrak{M}^4 \subset \tilde{T}G \subset TG$ means that a complementary vector space to TG in $\mathcal{E}_{x,\lambda}$ may be found among the polynomials $\mathcal{P}_3$ of degree at most three in x and λ. Also, $TG \cap \mathcal{P}_3$ is spanned by the Taylor expansions up to degree three of G, G_x, xG_x, λG_x, and G_λ. (The one other possibility, λG_λ, is already in the span of these five generators.) One may check that these terms are linearly indepen-

dent. Since $\dim \mathcal{P}_3 = 10$, one sees that there is a five-dimensional complement to TG. For the canonical form (2.9) it is easy to check that $1, x, \lambda, x\lambda$, and $x\lambda^2$ span a complementary space to TG as do $1, x, \lambda, x^2$, and $x^2\lambda$. This computation along with Theorem 2.23 proves both Proposition 2.13 and Proposition 2.15.

3. Calculations for the Thermal-Chainbranching Model

The purpose of this section is to verify two facts promised in Section 2. First, we show that there is a one-parameter family of bifurcation problems (we choose γ_3 as the parameter) which are contact equivalent to (2.9) in the thermal-chainbranching model defined by (1.5). For this family the modal parameter m is less than unity so that we are dealing with the one-root case. We find that m may be either positive or negative depending on the choice of γ_3. In fact, the physically reasonable choice of $\gamma_3 = 1$ leads to the value $m = 0$, which, as we shall see in the next section, is distinguished by admitting a larger number of perturbations. Some of the calculations are also simplified for this value. In any case, the sign of m affects which perturbations are possible.

Second, we show that the five auxiliary parameters, a, T_0, Z, γ_2, γ_3, form universal unfolding parameters for the bifurcation problem described above when $m = 0$ and hence that all the perturbations described in Section 4 actually do occur.

Recall the function G defined by equation (1.5):

$$G(T, v, a, T_0, Z, \gamma_1, \gamma_3) = \mathcal{E}_3 v^3 - 3\mathcal{E}_2 v^2 + Z\mathcal{E}_1 v - \frac{a}{T - T_0} \tag{3.1}$$

$$\equiv F - \frac{a}{T - T_0}\,.$$

THEOREM 3.2. *For any γ_3 satisfying $0 < \gamma_3 < \frac{3}{2}$ there are unique values of T, v, and the other four parameters solving* (3.3) *below. Provided $0 < \gamma_3 < k$, where*

$$k = 1 + \frac{1}{2 + \sqrt[3]{12}} \approx 1.23,$$

the bifurcation problem defined locally by G with these parameter values is contact equivalent to (2.9) *with $m < 1$.*

Proof: We must solve the six equations

$$G = G_T = G_v = G_{TT} = G_{Tv} = G_{vv} = 0, \tag{3.3}$$

and verify that the cubic terms are non-degenerate there. Observe first that

$G_v = F_v$ and that the three equations

$$\text{(a)} \quad F_v = 3\mathcal{E}_3 v^2 - 6\mathcal{E}_2 v + Z\mathcal{E}_1 = 0,$$

$$\text{(3.4)} \qquad \text{(b)} \quad F_{vv} = 6\mathcal{E}_3 v - 6\mathcal{E}_2 = 0,$$

$$\text{(c)} \quad F_{vT} = 3\mathcal{E}_3' v^2 - 6\mathcal{E}_2' v + Z\mathcal{E}_1' = 0,$$

imply that

$$\text{(a)} \quad v = \mathcal{E}_2/\mathcal{E}_3,$$

$$\text{(3.5)} \qquad \text{(b)} \quad Z = 3\mathcal{E}_2^2/(\mathcal{E}_1\mathcal{E}_3),$$

$$\text{(c)} \quad \frac{3}{T}\frac{\mathcal{E}_2^2}{\mathcal{E}_3}(2\gamma_2 - \gamma_1 - \gamma_3) = 0.$$

Thus from the three equations (3.4) we deduce the relations

$$\text{(3.6)} \qquad \tfrac{1}{2}(\gamma_1 + \gamma_3) = \gamma_2 = 1, \qquad Z = 3,$$

both independent of v and T, and equation (3.5a) expressing v as a function of T. However for convenience below, we prefer to rewrite (3.4a), using (3.6), as

$$\text{(3.7)} \qquad F_v = 3\left(\mathcal{E}_3^{1/2} v - \mathcal{E}_1^{1/2}\right)^2 = 0.$$

Next observe the equations $G = G_T = 0$ can be solved for a and T_0 as functions of T:

$$\text{(3.8)} \qquad \begin{aligned} a &= -F^2/F_T, \\ \frac{1}{T - T_0} &= -F_T/F. \end{aligned}$$

Finally we consider $G_{TT} = 0$. Note that by integrating (3.7) with respect to v we have

$$\text{(3.9)} \qquad F = \frac{\left(\mathcal{E}_3^{1/2} v - \mathcal{E}_1^{1/2}\right)^3}{\mathcal{E}_3^{1/2}} + \mathcal{E}_1^{3/2}\mathcal{E}_3^{-1/2}.$$

Let $\mathcal{F}(T) = \mathcal{E}_1^{3/2}\mathcal{E}_3^{-1/2} = \exp\{3\gamma_1 - \gamma_3\}/2T$. Since the first term in (3.9) vanishes at the organizing center, we have there

$$\text{(3.10)} \qquad F = \mathcal{F}, \quad F_T = \mathcal{F}', \quad F_{TT} = \mathcal{F}''.$$

Thus

$$G_{TT} = F_{TT} - \frac{2a}{(T - T_0)^3} = \mathcal{F}'' - 2\frac{(\mathcal{F}')^2}{\mathcal{F}} = 0, \tag{3.11}$$

where we have used (3.8) and (3.10) to eliminate a and T_0. On performing the differentiations, we find that (3.11) has a unique solution T; in fact $T = \frac{1}{4}(3\gamma_1 - \gamma_3)$ which may be rewritten using (3.6) as

$$T = \tfrac{3}{2} - \gamma_3. \tag{3.12}$$

The values of the other variables at the organizing center may be obtained by back substitution into (3.5) and (3.8).

To complete the proof of Theorem 3.2, we must calculate the third derivatives of G at the organizing center. Labeling these derivatives as in (2.11), we find

$$A = \left\{ \left(\frac{1 - \gamma_3}{T^2} \right)^3 + \frac{2}{3}\frac{1}{T^3} \right\} \mathcal{E}_1^{3/2} \mathcal{E}_3^{-1/2},$$

$$B = \left(\frac{1 - \gamma_3}{T^2} \right)^2 \mathcal{E}_1,$$

$$C = \left(\frac{1 - \gamma_3}{T^2} \right) \mathcal{E}_1^{1/2} \mathcal{E}_3^{1/2},$$

$$D = \mathcal{E}_3,$$

where T is given by (3.12). Note that $A > 0$ provided $0 < \gamma_3 < k$. On substitution into formula (2.12) for the modal parameter, we obtain

$$m = -\left\{ \frac{4s}{(s-1)^2} \right\}^{1/3}, \tag{3.13}$$

where

$$s = \frac{3}{2}\left(\frac{1 - \gamma_3}{\frac{3}{2} - \gamma_3} \right)^3.$$

We claim that $m \leqq 1$; for $s \geqq 0$ this is obvious from (3.13), and if $s < 0$ we may use the inequality $|2s| \leqq 1 + s^2$ to compare the numerator and denominator. Finally, m is positive or negative according to whether $\gamma_3 > 1$ or $\gamma_3 < 1$, respectively. This completes the proof of Theorem 3.2.

The second task of this section is to show that the five parameters a, T_0, Z, γ_1, and γ_3 provide a universal unfolding for G at the points satisfying (3.3). This involves evaluating a 10×10 determinant of the form (2.16) for each value of γ_3. When $\gamma_3 = 1$ this determinant simplifies because $m = 0$ and the two coefficients B and C also vanish. An explicit calculation of the determinant in this case yields the value $2^{11} \times 3^{21} \times e^{18}$; in particular it is non-zero. Of course by continuity it is non-zero in a neighborhood of $\gamma_3 = 1$, which proves that the five physical parameters do indeed provide a universal unfolding of G near this point.

Computer calculations of the determinant for other values of γ_3 indicate that it is non-zero for $1 < \gamma_3 < k$ but that it changes sign at values of γ_3 somewhat smaller than 1. This suggests that additional physical effects may be expected for $\gamma_3 < 1$, but we do not pursue this further here.

4. Perturbations of the Organizing Center

Our purpose in this section is to classify all stable bifurcation diagrams which occur as small perturbations of a non-degenerate, one-root cubic which may be put in the normal form (see Section 2):

$$G(x,\lambda) = x^3 - 3m\lambda^2 x + 2\lambda^3 = 0, \tag{4.1}$$

where $-\infty < m < 1$. The parameter m cannot be scaled from (4.1) by a contact equivalence and is called a *modal* parameter. (The form $G(x,\lambda) = x^3 - 3m\lambda^2 x - 2\lambda^3 = 0$ can also occur; however, replacing λ by $-\lambda$ will change this form to (4.1). Studying this problem separately is not necessary.) We shall show (in two different ways) that the values $m = 0$ and $m = -\infty$ are distinguished. Our main result is the following theorem. The reader should note that in the bifurcation diagrams of this theorem the horizontal axis λ corresponds to v, *the inverse pressure*; this explains the reverse orientation of the case LLLR compared to Figure 2(iii) in the introduction.

THEOREM 4.2. (a) *Fix* $m < 1$. *Then the eleven* (*stable*) *bifurcation diagrams shown in Figure* 4 *occur as small perturbations of* (4.1).

(b) *If* $0 < m < 1$, *then precisely three other stable bifurcation diagrams, pictured in Figure* 5, *may occur as small perturbations of* (4.1).

(c) *If* $-\infty < m < 0$, *then precisely three other stable bifurcation diagrams may occur as small perturbations of* (4.1), *as shown in Figure* 6.

(d) *The seventeen bifurcation diagrams listed above occur as small perturbations of* (4.1) *when* $m = 0$. *Note that here one must perturb* m.

To clarify the notation in this theorem and to explain why $m = 0$ and $m = -\infty$ are distinguished, we recall the idea of "paths through the cusp" discussed in Sections 4 and 8 of [10].

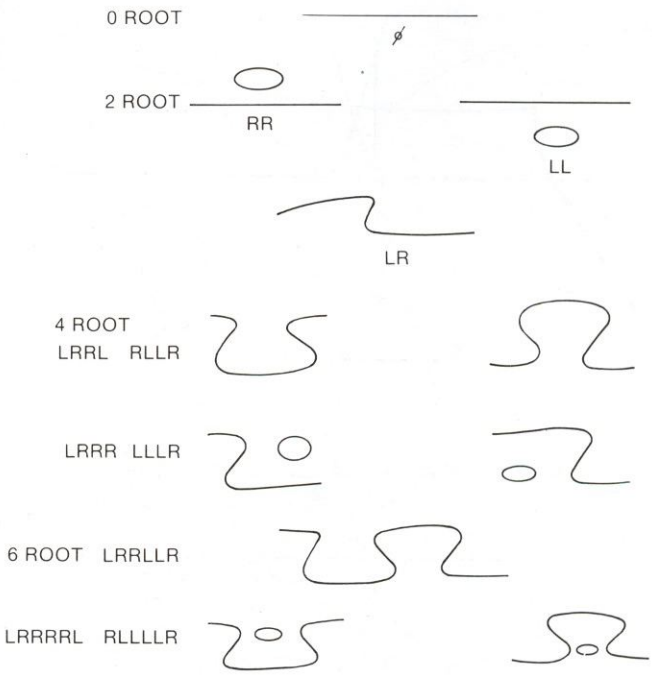

Figure 4

Figure 5

Figure 6

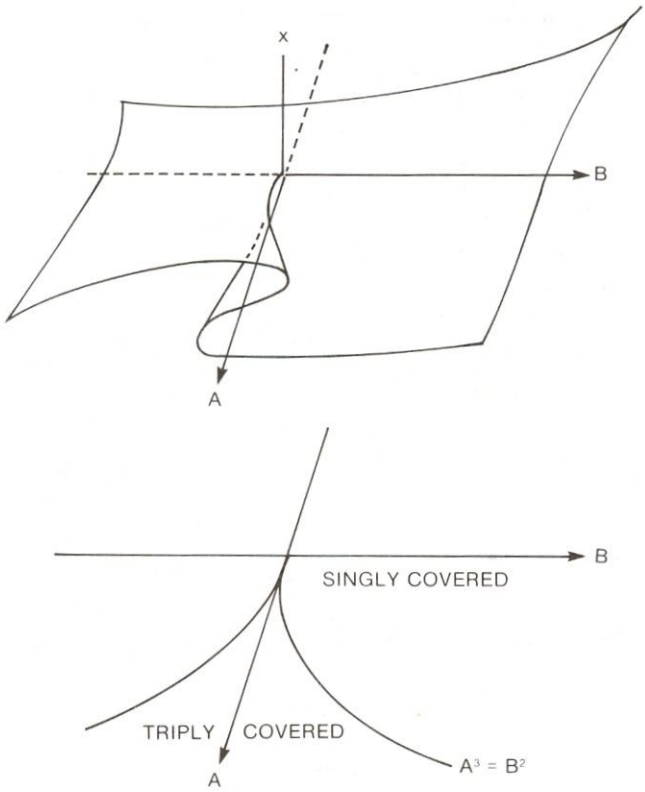

Figure 7

Consider

$$x^3 - 3Ax + 2B = 0, \tag{4.3}$$

which is the standard cusp surface pictured in Figure 7. The cusp curve $A^3 = B^2$ divides the A, B-plane into two regions; one which is triply covered by the cusp surface while the other is singly covered.

Letting

$$A(\lambda) = m\lambda^2 \quad \text{and} \quad B(\lambda) = \lambda^3, \tag{4.4}$$

we obtain a path in the A, B-plane which is also a cusp curve except where $m = 0$ and $m = -\infty$. See Figure 8.

The universal unfolding (2.13) of (4.1) shows that all small perturbations of (4.1) may be realized (up to contact equivalence) by paths

$$A(\lambda) = \gamma(\lambda^2 + \delta\lambda + \epsilon) \quad \text{and} \quad B(\lambda) = \lambda^3 + \beta\lambda + \alpha, \tag{4.5}$$

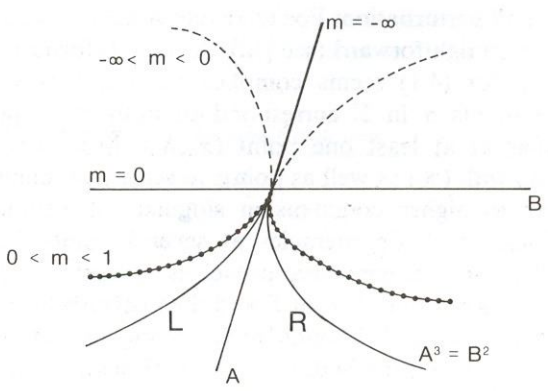

Figure 8

where α, β, δ, ϵ are near 0 and γ is near m. Moreover, as was discussed in Section 4 of [10], the number and order of intersections of the path $(A(\lambda), B(\lambda))$ with the cusp curve $A^3 = B^2$ completely determine the types of bifurcation diagrams which can occur as small perturbations of (4.1). Since $A(\lambda)^3 = B(\lambda)^2$ is a polynomial of degree six in λ, there are at most six intersections. By order we mean the order (as λ increases) in which the path crosses the left-hand (L) nappe or the right-hand (R) nappe of the cusp curve. This sequence is given in Theorem 4.2 for each of the diagrams.

The actual proof of Theorem 4.2 proceeds along a different tack. The reader should be warned that the calculations involved are long and somewhat tedious. Therefore, we shall give a detailed outline of our methods showing the essential ideas. The interested reader should be able to fill in the omitted details if he or she so desires.

In order to describe how our proof of Theorem 4.2 proceeds, we recall a result from [10]. Let $F(x, \lambda, \alpha)$ be a universal unfolding of (4.1) depending on five parameters α. Define $\Sigma = \mathcal{B} \cup \mathcal{H}$, where

$$\mathcal{B} = \{\alpha \in \mathbb{R}^5 \mid \text{there are } x_0, \lambda_0 \text{ with } F = F_x = F_\lambda = 0 \text{ at } (x_0, \lambda_0, \alpha)\}$$

and

$$\mathcal{H} = \{\alpha \in \mathbb{R}^5 \mid \text{there are } x_0, \lambda_0 \text{ with } F = F_x = F_{xx} = 0 \text{ at } (x_0, \lambda_0, \alpha)\}.$$

THEOREM 4.6. *Suppose α and β are in the same connected component of the complement of Σ in $\mathbb{R}^5$. Then $F(\cdot, \cdot, \alpha)$ and $F(\cdot, \cdot, \beta)$ are contact equivalent and thus the bifurcation diagram associated with $F(\cdot, \cdot, \alpha) = 0$ for $\alpha \notin \Sigma$ is stable.*

This theorem states that the connected components of the complement of Σ give an enumeration of the stable bifurcation diagrams which can be obtained

from (4.1) by a small perturbation. For relatively simple bifurcation problems the delineation of Σ is straightforward (see [10], Section 4, for examples). The direct computation of Σ for (4.1) seems complicated (see, however, [22]). Instead, observe that the points α in Σ correspond to bifurcation problems $F(\cdot,\cdot,\alpha)$ which are singular at at least one point (x_0,λ_0). Moreover, points α in the intersection of $(\mathcal{B})$ with $(\mathcal{H})$ as well as points in self-intersections of $(\mathcal{B})$ and $(\mathcal{H})$ correspond either to higher codimension singular bifircation problems or to bifurcation problems with degeneracies at several points. We call the latter singularities *multi-local*. Our general approach is to classify the local and multi-local singularities which occur for α in Σ and then perturb these problems to find the stable diagrams. Since Σ bounds each component of $\mathbb{R}^5 \sim \Sigma$, this is an exhaustive (and exhausting) method. Several simplifications are possible and we shall describe them shortly.

To start, observe that if $\alpha \in \Sigma$ and $(x_0,\lambda_0), \cdots, (x_k,\lambda_k)$ are singular points of $F(\cdot,\cdot,\alpha)$, then the following holds:

PROPOSITION 4.7. *The parameters α form universal unfolding parameters for each of the local bifurcation problems $F(\cdot,\cdot,\alpha)$ near (x_i,λ_i) simultaneously.*

In particular $\sum_{i=1}^{k} \operatorname{codim}(F(\cdot,\cdot,\alpha)$ near $(x_i,\lambda_i))$ is at most 5. Moreover, perturbations of $F(\cdot,\cdot,\alpha)$ can be found by perturbing $F(\cdot,\cdot,\alpha)$ arbitrarily near each (x_i,λ_i) and connecting the end points of the branches. For a bifurcation problem $G(x,\lambda)$ defined near $(0,0)$, let rank $G = n$ if the Taylor expansion of $G(x,0)$ at 0 starts with terms of degree n. Observe that if $F(x,\lambda,\alpha)$ is a universal unfolding of G, then the rank of $F(x,\lambda,\alpha)$ localized near (x_0,λ_0) is at most equal to the rank of G. Note that the rank of G in (4.1) is three.

Finally, for a bifurcation problem $G(x,\lambda)$, the codimension l of the ideal $\tilde{T}G = \langle G, G_x \rangle$ is the maximum number of (possibly degenerate) limit points (i.e., simultaneous zeros of G and G_x) which can occur in a small perturbation of G (cf. [8], [10]). (If the corresponding bifurcation diagram is stable, then $G_{xx} \cdot G_\lambda \neq 0$ and, in a neighborhood of a limit point, G is contact equivalent to $x^2 \pm \lambda$.) Proposition 4.7 also implies that, for multi-local singularities, $\sum_{i=1}^{k} l_i \leqq l$. For (4.1), $l = 6$. It is also the case that each $l_i \geqq 2$. Thus no more than three local singularities can occur in a small perturbation of (4.1).

The first step in our proof of Theorem 4.2 is to identify which local singularities can occur as small perturbations of (4.1). Each local singularity $G(x,\lambda)$ may be classified by a sequence of equalities and inequalities on the partial derivatives of G at the singular point. We call the conditions of equality the *defining conditions* for the singularity and the conditions of inequality the *non-degeneracy conditions*. For singular bifurcation problems of low codimension and rank, these two numbers define the singularity. In the notation of the following theorems, S_c^r refers to a singularity of codimension c and rank r.

THEOREM 4.8. *The following is a complete classification of local bifurcation problems $G(x,\lambda)$ of codimension less than or equal to 4 and rank less than or equal to 3.*

Singularity	*l*	*Normal Form*	*Defining Conditions*	*Non-Degeneracy Conditions*
S_0^2	1	$x^2 \pm \lambda$	$G = G_x = 0$	$G_{xx} \cdot G \neq 0$
S_1^2	2	$x^2 \pm \lambda^2$	$G = G_x = G_\lambda = 0$	$\det(d^2G) \neq 0$
S_2^2	3	$x^2 \pm \lambda^3$	$G = G_x = G_\lambda = \det(d^2G) = 0$	$(d^3G)(v,v,v) \neq 0$, where $(d^2G)v = 0$
S_3^2	4	$x^2 \pm \lambda^4$	$G = G_x = G_\lambda = \det(d^2G) = d^3G(v,v,v) = 0,$	$(d^4G)(v,v,v,v) - 6\left(d^3G\left(v,v,\frac{\partial}{\partial x}\right)\right)^2 \neq 0$
S_4^2	5	$x^2 \pm \lambda^5$	$G = G_x = G_\lambda = \det(d^2G) = (d^3G)(v,v,v) = (d^4G)(v,v,v,v) - 6\left((d^3G)\left(v,v,\frac{\partial}{\partial x}\right)\right)^2 = 0$	
S_1^3	2	$x^3 \pm \lambda$	$G = G_x = G_{xx} = 0$	$G_{xxx} \cdot G_\lambda \neq 0$
S_2^3	3	$x^3 \pm \lambda x$	$G = G_x = G_\lambda = G_{xx} = 0$	$G_{xxx} \cdot G_{x\lambda} \neq 0$
S_3^3	4	$x^3 \pm \lambda^2$	$G = G_x = G_\lambda = G_{xx} = G_{x\lambda} = 0$	$G_{xxx} \cdot G_{\lambda\lambda} \neq 0$

We shall not need the non-degeneracy conditions for S_4^2 so these are not included.

COROLLARY 4.9. *The multi-local singularities which could occur in the unfolding of* (4.1) *subject to the limitations in codimension, rank, and limit points discussed above are*:

Total codimension	*Possible Singularities*
1	S_1^2, S_1^3
2	$S_2^2, 2S_1^2, S_1^2 + S_1^3, S_2^3, 2S_1^3$
3	$S_3^3, 3S_1^2, 2S_1^2 + S_1^3, S_1^2 + 2S_1^3, 3S_1^3, S_3^3, S_2^2 + S_1^2, S_2^2 + S_1^3, S_2^3 + S_1^2, S_2^3 + S_1^3$
4	$S_4^2, S_3^2 + S_1^2, S_3^2 + S_1^3, S_3^3 + S_1^2, S_3^3 + S_1^3, 2S_2^2, S_2^2 + S_2^3, 2S_2^3.$

It is now necessary to analyze which of the multi-local singularities listed in Corollary 4.9 actually occur as small perturbations of (4.1). There are several tricks which simplify the calculations involved.

Observe that the universal unfolding of (4.1) consists of the cubic term (4.1) plus four of the six lower order terms. Also, it is much easier to calculate the defining conditions for a given singularity at the origin rather than at an arbitrary point (x_0, λ_0). Trick one is that if we add the two remaining lower-order terms to the unfolding of (4.1), i.e.,

$$F(x,\lambda) = C(x,\lambda) + ax^2 + bx\lambda + c\lambda^2 + dx + e\lambda + f, \tag{4.10}$$

then we may assume that the desired singularity is based at the origin. Indeed, these two extra parameters may be thought of as translation parameters, and translation $(x,\lambda)\to(x - x_0, \lambda - \lambda_0)$ does not change the cubic terms C in (4.10). As a result one may specify the cubic terms up to contact equivalence and also require that one singularity be at $(0,0)$ in (4.10). As we are working with a cubic with one real root, we may—by a rotation—assume that $x = 0$ is the zero set of C. Further scalings show that

$$C(x,\lambda) = x^3 - 3\beta x^2\lambda + x\lambda^2 \tag{4.11}$$

is an alternative to (4.1) in (4.10).

EXAMPLE. Does S_4^2 occur in the unfolding of (4.1)? Answer: No. We may assume from the above discussion that S_4^2 occurs at the origin and that the cubic terms in (4.10) are (4.11). The defining conditions for S_4^2 imply that $d = e = f = 0$ in (4.10) and that the quadratic terms are $a(x + \bar{c}\lambda)^2$. Moreover, $v = -\bar{c}\partial/\partial x + \partial/\partial\lambda$. Since $(d^3G)(v,v,v) = (d^3C)(v,v,v)$ at $(0,0)$, we see that $-\bar{c}$ is a root of $C(x,\lambda) = 0$ and thus $\bar{c} = 0$. Since $(d^3G)(v,v,\partial/\partial x) = C_{\lambda\lambda x} = 2 \neq 0$, we see that the defining conditions for S_4^2 are never satisfied.

Another observation is that two local singularities cannot occur for the same value of λ in a multi-local singularity (when rank is at most three). For suppose (x_0, λ_0) and (x_1, λ_0) are singularities for the same value of α. Then, at the very least, $F = F_x = 0$ at both (x_0, λ_0) and (x_0, λ_1). Fixing λ_0 and α we see that the unfolding of (4.1) is a cubic polynomial in x. Specifying $F = F_x = 0$ at two points implies that the cubic polynomial is identically zero, an impossibility.

Now suppose that (x_0, λ_0) and (x_1, λ_1) with $\lambda_0 \neq \lambda_1$ are local singularities for the same α. We can assume that $(x_0, \lambda_0) = (0,0)$. By a linear contact equivalence $x \to x + b\lambda$ we can assume that $x_1 = 0$. Scaling λ allows us to assume that $(x_1, \lambda_1) = (0, \pm 1)$. Of course, these coordinate changes alter the form of the cubic terms, but sometimes this is a preferable alternative. When two singularities are

specified, the cubic terms may be assumed to have the form

$$C(x,\lambda) = x^3 + \beta x^2\lambda + \gamma x\lambda^2 + \delta\lambda^3 \tag{4.12}$$

along with the assumption that C has one real root.

EXAMPLE. The multi-local singularity $S_2^2 + S_1^2$ cannot occur in the universal unfolding of (4.1).

Proof: Assume that S_2^2 occurs at $(0,0)$ and S_1^2 occurs at $(0,1)$. (S_1^2 could occur at $(0,-1)$ but sending $\lambda \to -\lambda$ reduces that case to the above.) The defining conditions for S_2^2 imply that (4.10) has the form

$$F(x,\lambda) = x^3 + \beta x^2\lambda + \gamma x\lambda^2 + \delta\lambda^3 + a(x + c\lambda)^2. \tag{4.13}$$

By calculation, $F = F_x = F_\lambda = 0$ at $(0,1)$ implies

$$\delta + ac^2 = 0, \quad \gamma + 2ac = 0, \quad \text{and} \quad 3\delta + 2ac^2 = 0. \tag{4.14}$$

Thus $\gamma = \delta = 0$, which implies that the cubic terms of (4.13) are $x^3 + \beta x^2\lambda$ which has zero as a double root. Hence $S_2^2 + S_1^2$ cannot occur when (4.1) is non-degenerate.

Note that in the above proof we only used the defining conditions of $S_2^2 + S_1^2$; thus $2S_2^2$ and $S_2^2 + S_2^3$ cannot occur. Calculations of the same type as those in the two examples above show:

PROPOSITION 4.15. *The multi-local singularities which do occur in the universal unfolding of* (4.1) *for* $m \neq 0$, $m \neq -\infty$ *and* $m < 1$ *are*:

Total Codimension	*Multi-local Singularites*
1	S_1^2, S_1^3
2	$S_2^2, 2S_1^2, S_1^2 + S_1^3, S_2^3, 2S_1^3$
3	$S_3^2, S_1^2 + 2S_1^3, S_3^3, S_2^2 + S_1^3,$ $S_2^3 + S_1^2, S_2^3 + S_1^3.$

Note: The multi-local singularity $S_3^3 + S_1^3$ occurs when $m = 0$ and $2S_2^3$ occurs when $m = -\infty$ and these are the only codimension four singularities which do occur. This is the second way in which $m = 0$ and $m = -\infty$ are distinguished values for the modal parameter m.

The second step in the proof of Theorem 4.2 is the observation that to find the stable bifurcation diagrams in the unfolding of (4.1) one need only look at small perturbations of the multi-local singularities of total codimension three. The proof of this statement proceeds as follows: one shows that each connected component of a singularity of codimension one or two has in its boundary a singularity of higher codimension. The calculations involve showing that among those bifurcation problems satisfying the defining conditions for a given multi-local singularity there are those which do not satisfy the non-degeneracy conditions.

We consider two examples. The defining conditions for S_1^2 are $G = G_x = G_\lambda = 0$. We may take the universal unfolding of (4.1) to be

$$F(x,\lambda) = C(x,\lambda) + ax^2 + bx + c\lambda + d. \tag{4.16}$$

The three defining conditions allow one to find b, c, and d as functions of x, λ, m, and a. Thus the defining condition for S_1^2 will give a connected set in $\mathbb{R}^5$. The trivial observation that problems of higher codimension occur in this set proves our assertion.

As a second example consider $2S_1^3$. We can assume that the two S_1^3's occur at $(0,0)$ and $(0,1)$ and that F is given by

$$F = C(x,\lambda) + ax^2 + bx\lambda + c\lambda^2 + dx + e\lambda + f = 0, \tag{4.17}$$

where C is as in (4.12). Now $G = G_x = G_{xx} = 0$ at $(0,0)$ and $(0,1)$. Thus $a = d = f = 0$ and

$$\delta + c + e = 0, \quad \gamma + b = 0, \quad 2\beta = 0. \tag{4.18}$$

Consequently,

$$F = x^3 - bx\lambda^2 - (c + e)\lambda^3 + bx\lambda + c\lambda^2 + e\lambda = 0. \tag{4.19}$$

The non-degeneracy conditions are given by $F_{xxx} \neq 0$ which is always satisfied and

$$F_\lambda = -2bx\lambda - 3(c + e)\lambda^2 + bx + 2c\lambda + e \neq 0 \tag{4.20}$$

at $(0,0)$ and $(0,1)$. That is

$$e \neq 0 \quad \text{and} \quad c + 2e \neq 0. \tag{4.21}$$

Thus, there are at least four connected components of $2S_1^3$ type singularities and each borders on a more degenerate problem (obtained by setting *one* of the non-degeneracy conditions to zero).

The other calculations used to prove the second step are similar.

There are two parts to the third step in the proof of Theorem 4.2. First one calculates—for fixed values of the modal parameter—the various curves in parameter space along which each of the six codimension three singularities listed in Proposition 4.16 occurs. They are given in

PROPOSITION 4.22.

(a) S_3^2 $\quad F = x^3 - 3\beta x^2\lambda + x\lambda^2 + ax^2,$

(b) $S_1^2 + 2S_1^3$ $\quad F = x^3 - 3mx\lambda^2 + 2\lambda^3 - \frac{1}{2}bmx^2 + bx\lambda + b(m^3 - 4)\lambda^2/6m,$

(c) $S_2^3 + S_1^2$ $\quad F = x^3 - \beta x^2\lambda + \gamma x\lambda^2 \pm \gamma x\lambda,$

(d) $S_2^3 + S_1^3$ $\quad F = x^3 - 3mx\lambda^2 + 2\lambda^3 + bx\lambda - (2b/3m)\lambda^2,$

(e) $S_2^2 + S_1^3$ $\quad F = x^3 - (\lambda \mp 1)(ax^2 + 2ac\lambda x + ac^2\lambda^2),$

(f) S_3^3 $\quad F = x^3 - 3mx\lambda^2 + 2\lambda^3 + c\lambda^2.$

The second part of this third step is to graph the actual singular bifurcation diagrams which occur in Proposition 4.22. Care must be taken in (a), (c), and (e) to find the modal parameter m as this puts restrictions on the two free parameters present. The bifurcation diagrams are shown in Figure 9.

The calculations involved in finding these diagrams are all elementary though those for case (e) are by far the most difficult. As a sample we describe the calculations for case (b).

We assume that S_1^2 is at $(0,0)$ and the two S_1^3 singularities are at (x_1,λ_1) and (x_2,λ_2) with $\lambda_1 \neq \lambda_2$. Thus

$$\text{(4.23)} \qquad \begin{aligned} &\text{(a)} \quad F = x^3 - 3mx\lambda^2 + 2\lambda^3 + ax^2 + bx\lambda + c\lambda^2 = 0, \\ &\text{(b)} \quad F_x = 3x^2 - 3m\lambda^2 + 2ax + b\lambda = 0, \\ &\text{(c)} \quad F_{xx} = 6x + 2a = 0, \end{aligned}$$

at (x_i,λ_i). From (4.23c) we see that $x_1 = x_2 = -\frac{1}{3}a$. Substituting in the first two equations yields:

$$\text{(4.24)} \qquad \begin{aligned} &\text{(a)} \quad 2\lambda^3 + (ma + c)\lambda^2 - \frac{ab}{3}\lambda + \frac{2a^3}{27} = 0, \\ &\text{(b)} \quad \lambda^2 - \frac{b}{3m}\lambda + \frac{a^2}{9m} = 0. \end{aligned}$$

Moreover these equations should have both λ_1 and λ_2 as roots. As a result, (4.24b) is a factor of (4.24a) which implies

$$\text{(4.25)} \qquad a = -\frac{1}{2}bm, \qquad c = \frac{b}{6m}(m^3 - 4).$$

This gives the form of F in Proposition 4.22(c). The non-degeneracy conditions

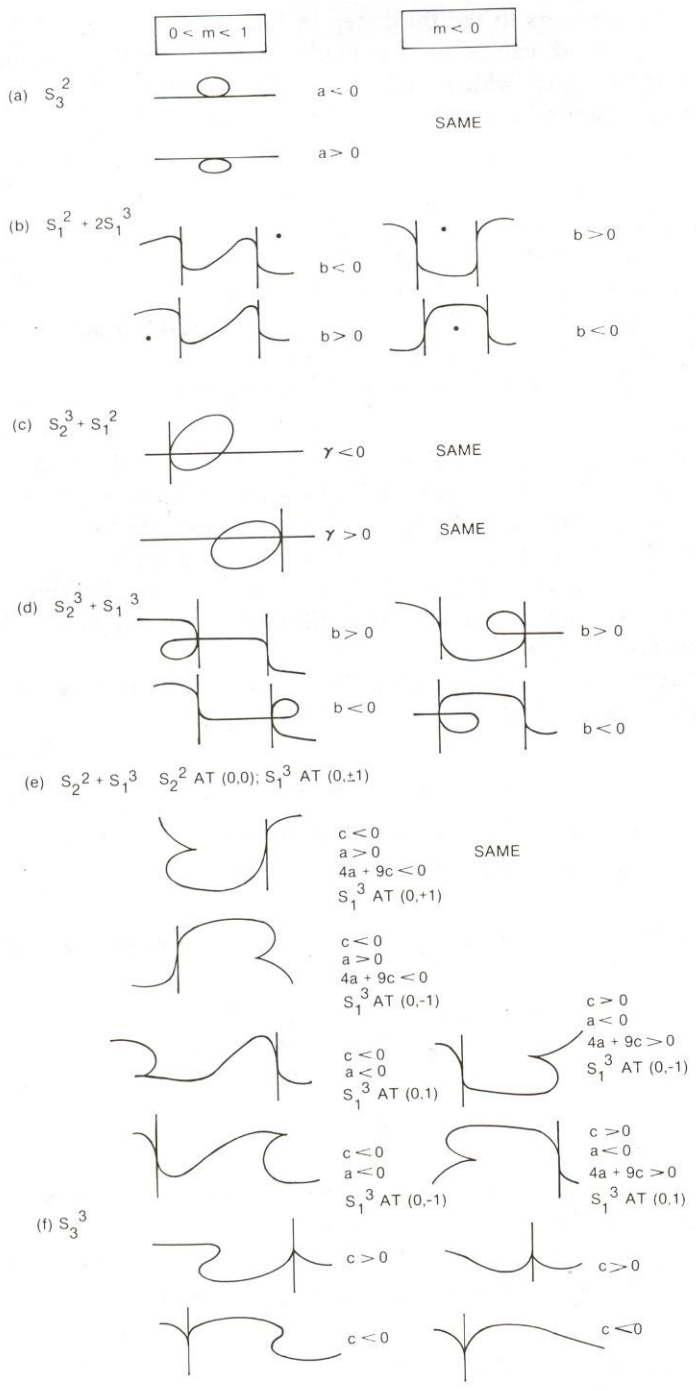
0 < m < 1
m < 0
(a) S_3^2
a < 0
SAME
a > 0
(b) $S_1^2 + 2S_1^3$
b < 0
b > 0
b > 0
b < 0
(c) $S_2^3 + S_1^2$
γ < 0
SAME
γ > 0
SAME
(d) $S_2^3 + S_1^3$
b > 0
b > 0
b < 0
b < 0
(e) $S_2^2 + S_1^3$ S_2^2 AT (0,0); S_1^3 AT (0,±1)
c < 0
a > 0
4a + 9c < 0
S_1^3 AT (0,+1)
SAME
c < 0
a > 0
4a + 9c < 0
S_1^3 AT (0,-1)
c < 0
a < 0
S_1^3 AT (0,1)
c > 0
a < 0
4a + 9c > 0
S_1^3 AT (0,-1)
c < 0
a < 0
S_1^3 AT (0,-1)
c > 0
a < 0
4a + 9c > 0
S_1^3 AT (0,1)
(f) S_3^3
c > 0
c > 0
c < 0
c < 0

Figure 9

are $G_{xx} \cdot \det(d^2G) \neq 0$ at $(0,0)$ and $G_{xxx} \cdot G_\lambda \neq 0$ at (x_i, λ_i). Now $G_{xx}(0,0) = 2a$ while $\det(d^2G)_{(0,0)} = \frac{1}{3}(1 - m^3) > 0$. Note that both eigenvalues of (d^2G) have the same sign so that, near $(0,0)$, G is contact equivalent to $x^2 + \lambda^2 = 0$ (as long as $b \neq 0$). This explains the point in the bifurcation diagrams. Since $G_{xxx} \equiv 6$, we need only compute G_λ at (x_i, λ_i). In fact,

$$G_\lambda = \frac{4b\lambda_i}{3m}(1 - m^3) \quad \text{at} \quad (x_i, \lambda_i). \tag{4.26}$$

Thus G is contact equivalent to $x^3 \pm \lambda$ near (x_i, λ_i), where the $\pm$ sign is just the sign of G_λ. This information is sufficient to draw the bifurcation diagrams.

The final step in the proof of Theorem 4.2 is to perturb each of these singular bifurcation problems to obtain the stable perturbations of (4.1). For example in case (d) a pitchfork S_2^3 and a hysteresis point S_1^3 appear. From previous calculations (cf. [9], [10]) we know that the pitchfork perturbs into four stable diagrams and the hysteresis into two. See Figure 10.

One now uses the fact that all local perturbations are possible to split case (d), $b > 0$, $0 < m < 1$, into the eight stable diagrams given in Figure 11.

If one breaks each of the diagrams in Figure 9(a)–(f) into their stable perturbations and keeps track of the intersection sequences which appear, one completes the proof of Theorem 4.2(a)–(c).

Clearly, when $m = 0$, a small perturbation will make m either positive or

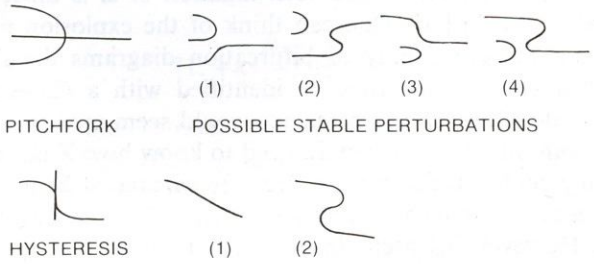

Figure 10

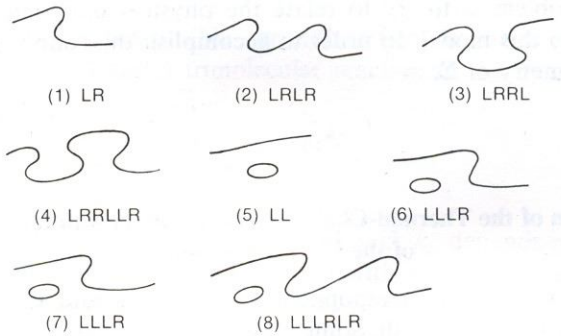

Figure 11

Figure 12

negative and thus yield all the diagrams in parts (a)–(c) as small perturbations. To see that no new diagrams are obtained, one observes that the singularity $S_1^3 + S_3^3$ occurs as a subcase of case (f), i.e., as

$$(f') \qquad F = x^3 + 2\lambda^3 + c\lambda^2$$

with associated bifurcation diagrams as shown in Figure 12. Finally note that all possible stable bifurcation diagrams obtained by perturbations of those in Figure 12 have been obtained previously.

We end this section by commenting briefly on possible sequences of bifurcation diagrams which might explain the explosion peninsula along the lines of Figure 2. For example, a sequence which includes Figure 3 would have to be more complicated than the sequence given in Figure 2. However, from the proofs given in this paper it would be impossible to choose between these sequences.

In Theorem 2.16 of [10] it was shown that for any universal unfolding $F(x, \lambda, \alpha)$ there exists a variety Σ in parameter space $\mathbb{R}^k$ (the space of α's) such that connected components of $\mathbb{R}^k \sim \Sigma$ correspond to bifurcation diagrams of a given qualitative type. In general, the determination of Σ is difficult, but some examples are calculated in [10]. One can think of the explosion peninsula as a (continuous) one-parameter family of bifurcation diagrams depending on T_0; that is, the explosion peninsula may be identified with a curve in parameter space. In order to determine which sequence would seem most reasonable (from a mathematical point of view) one would need to know how Σ is contained in $\mathbb{R}^5$ for our organizing center. I. Stewart has recently calculated Σ in the case $m < 0$ and concluded that the sequence shown in Figure 2 is the one most likely to occur; see [22]. However, his preliminary calculations for the range $0 < m < 1$ (private communication) indicate that here a sequence including the diagram of Figure 3 is a more likely explanation of the explosion peninsula.

A further problem is to try to relate the physical parameter values of the H_2-O_2 reaction to this model. In order to accomplish this, one would again have to know the geometry of Σ.

Appendix

Identification of the Thermal-Chainbranching Model with the Mechanism of the H_2-O_2 Reaction

We outline briefly the correspondences that Yang and Gray make in the application of their model in [20]. Some attempts to catalogue the complete set of elementary reactions for this reaction appear in [4], [5], and [16].

There are several versions of the initiation step, with Semenov [18] suggesting

$$H_2 + O_2 \rightarrow H + HO_2$$

and Dainton [3] preferring

$$H_2 + M \rightarrow 2H + M,$$

where M represents either a hydrogen or an oxygen molecule, while Gray and Yang follow Lewis and von Elbe's [16] mechanism, using a series of initiation steps which depend on achieving a steady-state concentration of H_2O_2. What is important for our purposes is that any of these mechanisms leads to a rate of production of H which is proportional to P^2, since it is assumed that $[H_2]$, $[O_2]$ and *a fortiori* [M] are proportional to their partial pressures and hence to [A] in the general reaction. Thus $\alpha_i = 2$.

There is substantial agreement (cf. [4], [3], [7], [16], and [17]) that the chainbranching of hydrogen atoms is accomplished *via* a series of three reactions

(A.1) $$H_2 + OH \xrightarrow{k_1} H_2O + H,$$

(A.2) $$O_2 + H \xrightarrow{k_2} OH + O,$$

(A.3) $$H_2 + O \xrightarrow{k_3} OH + H,$$

of which the middle one is rate-determining (the slowest). If one considers reaction (A.2) followed by (A.3) to convert the O radicals to H and OH, and then by (A.1) to convert the OH to H, one obtains an overall reaction

(A.4) $$H + 3H_2 + O_2 \rightarrow 3H + 2H_2O.$$

Hence, in the branching step, $n = 3$, while the rate k_b is determined by the rate, k_2, of (A.2). Thus $\alpha_b = 1$.

The two mechanisms responsible for destruction of the free radicals are recombination at the wall and a trimolecular reaction in the interior. The first, represented as

$$H + \text{Wall} \xrightarrow{k_w} \frac{1}{2} H_2$$

is supposed to be thermally neutral ($\gamma_w = 0$), although k_w depends on the size and shape of the container as well as the material with which it is coated (cf. [4]). Lewis and von Elbe [16] argue that the gaseous termination mechanism is

$$H + O_2 + M \xrightarrow{k_g} HO_2 + M,$$

followed by further reactions of the hydroperoxyl radical HO_2. Again M is some stable species and hence the reaction rate is proportional to P^2; that is, $\alpha_g = 2$.

Thus, when the model is applied to the combustion of hydrogen, the constants α_j are fixed. Values of the γ_j depend on which model is used, though E_i is large ($E_i/R > 50{,}000°\text{K}$) in all versions. The accepted value of E_b/R is about 8000°K, while E_g is zero or slightly negative. Thus, when γ_2 is normalized to be 1 in equation (A.2) the other two activation energies, γ_1 and γ_3 in (A.1) and (A.3), are approximately 1.2. This justifies the consideration, in Section 3, of an organizing center near $\gamma_1 = \gamma_3 = 1$.

Acknowledgment. The research of the first author was sponsored in part by the N.S.F. Grant MCS-7905799, that of the second by the N.S.F. Grant MCS-7704164, and that of the third by the N.S.F. Grant MCS-7902010 and the U.S. Army Contract DAA-29-78-G0127.

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Received March, 1980.