An Introduction to the Stability of Distributed Systems via a Liapunov Functional

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Liapunov's direct method is extended to determine the stability of distributed systems with single and multiple equilibrium profiles. The method is simple to apply and makes use of certain inequalities to establish the sign definiteness of the time derivative of the Liapunov functional. Two numerical examples are presented, the adiabatic catalyst particle and an empty adiabatic tubular reactor with axial diffusion.

In recent years the chemical engineering literature has dealt more and more with stability problems germane to the field. Two general types of problems have usually been discussed. The first problem concerns the question of whether there is more than one steady state solution to the system's equations; this relates to the mathematical question of uniqueness. In addition, if the solution is not unique, what perturbations in the system can a given steady state tolerate while still insuring that the transient will approach the steady state; in other words, what is the region for asymptotic stability (R.A.S.).

The second problem deals with the question of whether bounded inputs yield bounded or unbounded outputs. In this case the input variables to the system are changed and the question to be answered is whether the new steady state will be in the neighborhood of the former steady state. This is known as sensitivity analysis.

Both types of problems have been extensively treated in the literature starting with the work of Barkelew [*4*], and of van Heerden [*15, 16*]. Typical contributors have been Coste, Aris and Amundson [*7*], Wang and Perlmutter [*17*], Amundson and coworkers [*1, 5, 6, 11*], Weisz and Hicks [*20*], and Gavalas [*8*]. Our concern here is with distributed systems and the stability of a unique or multiple steady state configuration, in which case the work of Wei [*19*] and Kuo and Amundson [*10*] as applied to a catalyst particle is of direct interest. Both authors take advantage of the linearized transient equations for the catalyst particle. Wei [*19*] used an extension of the direct method of Liapunov to determine stability (see discussion later) while Kuo and Amundson [*10*] analyzed the stability of the steady states by using the theory of eigenfunctions. Essentially Kuo and Amundson's analysis of the problem is one of finding the solution of the corresponding eigenvalue problem of the linearized system of partial differential equations. The asymptotic stability of the steady state is determined by the sign of the real part of the extremal eigenvalue of the corresponding eigenvalue problem. This determination of the extremal eigenvalue required use of a variational method to approximate the eigenvalue. For the special case where the Lewis number (the Lewis Number is the ratio of heat diffusion to mass diffusion) is equal to one, Kuo showed that the linearized partial differential equations are much simpler and in fact form a self-adjoint system. Since the eigenvalues are all real for a self-adjoint system, Kuo and Amundson used the comparison theorem and Sturm's oscillation theorems to determine the stability of the steady states of this special catalyst particle.

Another large class of distributed systems which can exhibit multiple steady states is the tubular reactor with axial diffusion. Raymond and Amundson [*13*] presented a method for the backward integration of the steady state equation of the adiabatic tubular reactor with axial diffusion, which yields the multiple steady state profiles. In a later paper, Amundson [2] used the previously mentioned comparison and oscillation theorems to derive a criterion for the stability, or instability, of the steady states of the adiabatic tubular reactor with axial diffusion, subject to infinitesimal perturbations. The stability conditions are based upon steady state information alone and require the solution of a linear ordinary differential equation.

At this point a summary of the work on the stability of the steady states of distributed systems seems appropriate. The problem of showing the possibility that a distributed system can exhibit multiple steady states seems well in hand, and the steady state profiles can be generated, even in very poor situations, by backward integration. The analysis of the stability of these profiles has taken two paths:

1. The nonlinear transient partial differential equations are integrated for a given initial perturbation. This is a brute force analysis and does not yield any general region of stability about a given steady state without a manifold amount of computation.
2. The system's differential equations are linearized and the resulting equations are manipulated so that the problem becomes one of finding the limits of the real parts of eigenvalues of the corresponding eigenvalue problem. It is true that the limits of the eigenvalues may be evaluated from steady state information and that the criterion for stability or instabilty, with respect to infinitesimal perturbations, is sharp. There are two drawbacks in the eigenvalue analysis, the first is the complexity of the mathematics, and the second is the local nature of the region of stability as a consequence of linearization of the system equations.

Both of these drawbacks can be mitigated, in special cases, by Liapunov stability analysis. In the present paper we present such an analysis which, while retaining the linearization, does not require an eigenvalue solution. The analysis is applied to two distributed parameter systems, the catalyst particle modeled as a slab, and the empty adiabatic tubular reactor. The results show that in certain cases the stability characteristics of equilibrium distributions in such systems can be simply and directly calculated without resorting to the solution of the descriptive

partial differential equations. It is hoped that this analysis will motivate other workers to proceed further along this line of attack to solve these important problems.

THE FUNCTIONAL LIAPUNOV METHOD

In this section we will briefly point out some of the alien features associated with Liapunov stability. Thus for ordinary differential equations the δ, ϵ definition of stability is [9]:

An equilibrium state $\mathbf{x}_e$ of a free dynamic system is stable if for every real number $\epsilon > 0$ there exists a real number $\delta(\epsilon,t_o) > 0$ such that $||\mathbf{x}_o - \mathbf{x}_e|| \leqq \delta$ implies:

$$||\phi(t; \mathbf{x}_o, t_o) - \mathbf{x}_e|| \leqq \epsilon \qquad \text{for all } t \geqq t_o$$

In this purely mathematical definition $\mathbf{x}_o$, $\mathbf{x}_e$ are the $n \times 1$ state vectors of the system, ϕ is the solution vector of the system of differential equations and $||\cdot||$ denotes a norm, or in this case the Euclidian distance. In addition, it is necessary to realize that a free dynamic system will be one which does not have any forcing functions, and an equilibrium state of a free dynamic system is a state which is time invariant. This means that the equilibrium state is defined by a point in the phase diagram of the state variables.

Figure 1, which illustrates the simple two state variable case, will help to explain the above definition. Extending the definition to the case where the corresponding solution trajectory goes to the equilibrium state we obtain:

An equilibrium state $\mathbf{x}_e$ of a free dynamic system is asymptotically stable if

1. It is stable, and
2. Every motion starting sufficiently near $\mathbf{x}_e$ converges to $\mathbf{x}_e$ as $t \to \infty$.

This is also illustrated in Figure 1. Two further definitions for systems described by ordinary differential equations are important. If the solution trajectory tends to the equilibrium state, no matter how far the initial state is from the equilibrium, this is defined as asymptotic stability in the large. If the trajectory of the system goes out of the prescribed ϵ region this is defined as unstable behavior.

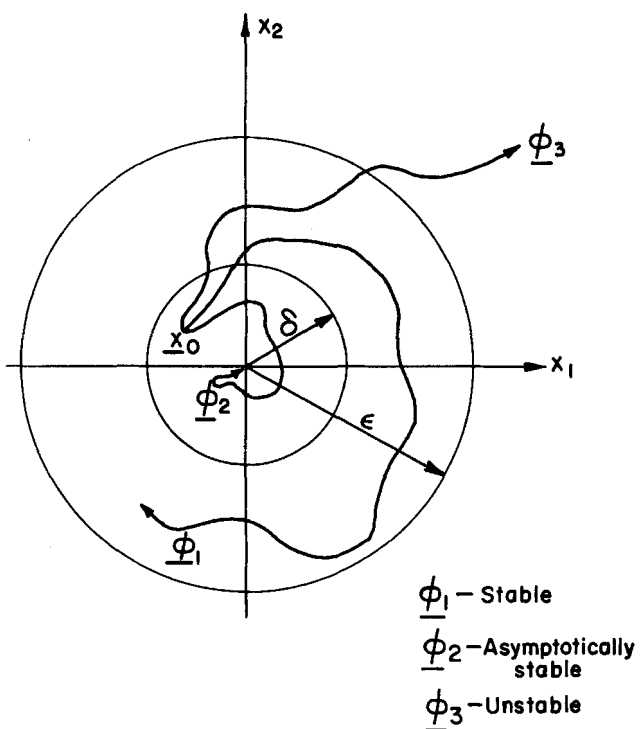

Fig. 1. Stability definitions, ordinary differential equations.

Liapunov's direct method determines if a steady state is stable based upon the sign definiteness of both a scalar function (Liapunov function) and its time derivative. However, the direct method can only supply a sufficient condition for stability. That is, if the sign definiteness criteria are met, the system will be stable, if these are not met no conclusion as to the stability or instability of the system can be made. The most important feature of the direct method is its use in determining the stability of a system without actually solving the transient equations.

The principle theorem of stability for a free dynamic system described by ordinary differential equations is stated and proved quite rigorously and succinctly in the article by Kalman and Bertram [9]. We shall not quote this theorem here.

Since the Liapunov function, $V(\mathbf{x})$, is not unique many investigators have tried to find the optimal Liapunov function which yields the largest region of asymptotic stability (R.A.S.) for a system. The search for the best Liapunov function is the main difficulty in applying the direct method. For linear stationary systems, the best Liapunov function is a quadratic form, namely

$$V(\mathbf{x}) = \mathbf{x}^T\mathbf{P}\mathbf{x}$$

where $\mathbf{P}$ is a positive definite symmetric matrix. Also if $V > 0$ and $\dot{V} < 0$ for a linear system then the system is asymptotically stable in the large. For nonlinear stationary system the methods of generating a Liapunov function are not as well developed. An excellent and current review of various generation methods for nonlinear systems is presented by Salah [*14*].

Because of the nonuniqueness of the Liapunov function it frequently may be necessary, in nonlinear systems, to construct several different Liapunov functions. Each function may show some restricted region in state space where both the conditions on the function and its derivative are satisfied. The union of all such regions then gives a class of disturbances about the equilibrium state. No disturbance in this class can result in unstable behavior. In other words, a systematic investigation of the function form may be necessary to carry out a valid stability analysis.

In the case of ordinary differential equations the concept of the phase diagram is easily visualized, and one is concerned with stability with reference to a steady state or equilibrium point. Here, stability is taken to mean that after an initial perturbation the transient response of a system will remain within a finite region of the steady state. Asymptotic stability is the case where there is stability and given sufficient time the displacement from the steady state can be made as small as desired. One is then concerned with the size of the region about the steady state point in which the initial perturbation can occur, as well as how close the transient will approach the steady state point.

The concepts of stability of a distributed parameter system are not as easy to visualize as those of a system described by ordinary differential equations. The steady state is no longer a point in state space, but it is a profile; there are now an infinite number of equilibrium points each having its own phase diagram. When this continuum of phase diagrams is joined the entire transistory is determined. In order to define the stability of the system a perturbation is made about the steady state profile, and if the system is stable, the resulting transient response will remain within a finite region or neighborhood of the steady state profile. Asymptotic stability means that the transient profile approaches the steady state profile, and given sufficient time the displacement from the steady state can be made as small as desired.

The above definitions can be put on a more mathematical

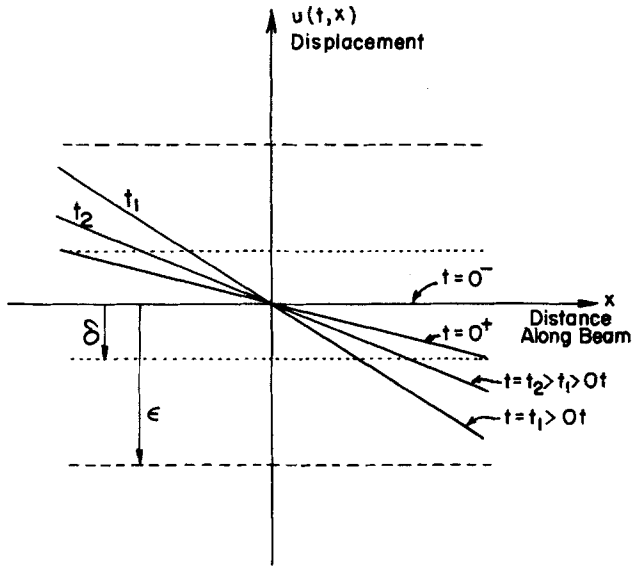

Fig. 2. Stability definitions, partial differential equations.

level by extending the stability definitions for ordinary differential equations which were credited to Liapunov [*18*]. In dealing with distributed systems we are concerned with a spatial doman Ω.The norm of the state vector is taken to be, for example, the L_2 norm, that is

$$||\mathbf{u}(t, \mathbf{x})||_\Omega = \frac{1}{2}\left[\int_\Omega \mathbf{u}^T\mathbf{u}\, d\Omega\right]^{1/2}$$

This is because the state vector, **u**, is now a function of both time and position in Ω. In this case the state solution vector will be defined as a perturbation from the equilibrium vector.

An equilibrium state $\mathbf{u}_e$ is stable if for every real number $\epsilon > 0$ there exists a real number $\delta(\epsilon, t_o) > 0$ such that

$$||\mathbf{u}(t_o, \mathbf{x})||_\Omega \leqq \delta(\epsilon, t_o)$$
$$||\mathbf{u}(t, \mathbf{x})||_\Omega \leqq \epsilon \qquad \text{for all } t > t_o$$

In the above we are not making the solution vector distinct from the state vector. Figure 2 illustrates this definition in the case of one state variable, for instance the displacement of a beam from its equilibrium configuration. Continuing with the same logic as in the case of ordinary differential equations:

An equilibrium state of a free distributed system will be asymptotically stable if

1. It is stable, and
2. Every motion starting sufficiently near $\mathbf{u}_e$ converges to $\mathbf{u}_e$ as $t \to \infty$:

$$||\mathbf{u}(t, \mathbf{x})||_\Omega \to 0 \qquad \text{as } t \to \infty$$

From the above the analogies which exist between the two types of systems are obvious as far as definitions of stability are concerned.

We can extend the previous notions concerning a Liapunov function into a more general space by defining a Liapunov functional. A functional is a correspondence which assigns a definite number to each function (or curve) belonging to some class. In the case of systems described by partial differential equations, the motion no longer takes place in an n-dimensional phase space, the phase space is now infinite in dimension. Zubov [*21*] has greatly advanced the direct method as applied to infinite dimensional spaces. In a distributed system we define a Liapunov functional which properly describes a kind of energy distribution of the system, and it is the purpose of the direct method to indicate whether the energy is always decreasing to zero, if this is the case then the system is asymptotically stable.

The necessary theorem concerning stability of a partial differential equation system has been given by Wang [*18*], and Zubov [*21*]. The essence of such a theorem is to extend the Liapunov stability theory from a finite dimensional phase space to a phase space of infinite dimensions and the realm of partial differential equations. As with the simpler n-dimensional phase space method the determination of the Liapunov functional is the main difficulty.

The technical literature gives very little guidance on what type of Liapunov functional to choose. A logical functional to attempt to use is one which describes the distance or metric of the perturbed state from the steady state whose stability is being analyzed. Zubov [*21*] has suggested that for a system of strongly parabolic partial differential equations the following Liapunov functional be used

$$V = \frac{1}{2}\int_\Omega \mathbf{u}^T(t, \mathbf{x})\mathbf{u}(t, \mathbf{x})\, d\Omega$$

The reason for this form of functional is that the usual choice of the Liapunov function is to take functions which define hyperspheres about the steady state point. In order to have asymptotic stability the transient trajectory must puncture these closed surfaces in such a manner that the value of the Liapunov function is always decreasing along the trajectory of the transitory. The above functional form is a generalization of this notion of an appropriate Liapunov function. For a linear system of ordinary differential equations the Liapunov function is a quadratic form, the above metric is the distributed analog of this quadratic form with the weighting matrix **P** equal to the identity matrix. These authors know of only one other form of the Liapunov functional which has been used successfully. This was for a very special physical system, a thin elastic plate, and was presented in an article by Movchan [*12*].

In the present paper we shall investigate the feasibility of the Liapunov functional to a number of different chemical engineering systems which can exhibit multiple steady states. While linearization of the system equations is required to test this feasibility this is not a serious disadvantage as compared to other approaches to the same problem. Thus Wei [*19*], and Wang [*18*], after linearization, change the $\dot{V} < 0$ condition into a corresponding eigenvalue problem; as a result it was necessary to evaluate an extremal eigenvalue. The advantage of the following analysis as compared with previous methods is the simplicity of the method. For the analysis of the stability of distributed systems the primary advantage of the direct method of Liapunov is that the stability of a steady state profile can be determined without computation of the trajectory of the perturbed system. The sole purpose of the Liapunov functional method is to determine stability by looking at the steady state properties of the system, and then to use these properties in the simplest manner. The main disadvantage of the Liapunov functional method is the nonuniqueness of the functional, which then leads to a lack of sharpness in the determination of the stability of the steady states. Here we shall only consider the single Liapunov functional of Zubov. As previously mentioned, more conclusive results might possibly be obtained by analyzing the results of other forms of the functional. In particular, the use of a weighting matrix in the functional may be quite significant. It is hoped that the present work will lead to such investigations.

THE CATALYST PARTICLE PROBLEM

If we consider a catalyst particle in the form of a slab,

the dimensionless mass and heat balances associated with a first-order chemical reaction [19, 20] are

$$\frac{\partial y}{\partial t} = \frac{\partial^2 y}{\partial x^2} - \phi^2 y \exp\left[\frac{\gamma(z-1)}{z}\right] \quad (1)$$

$$N_{Le}\frac{\partial z}{\partial t} = \frac{\partial^2 z}{\partial x^2} + \beta\phi^2 y \exp\left[\frac{\gamma(z-1)}{z}\right] \quad (2)$$

where

$$\phi^2 = \frac{l^2 k(T_o)}{D};\ \beta = -\frac{\Delta H\ D\ C_o}{KT_o};\ \gamma = \frac{E}{RT_o}$$

and the Lewis Number $= N_{Le} = \dfrac{\rho c_p D}{K}$. The boundary conditions are given by

$$\frac{\partial y(t,0)}{\partial x} = \frac{\partial z(t,0)}{\partial x} = 0,\ y(t,1) = z(t,1) = 1 \quad (3)$$

The derivation of these equations plus a discussion of the physical system can be found in the references above.

At steady state Equations (1) and (2) still hold but with the left hand time derivatives becoming zero; we shall designate the solution of the resulting steady state concentration and temperature balances by y^* and z^* respectively. At this condition an adiabatic balance yields

$$z^* = 1 + \beta(1 - y^*) \quad (4)$$

Assuming the possibility of multiple steady states we shall now try to analyze the stability characteristics of these steady states.

To carry out this analysis we first define a set of perturbation equations around the steady states by letting

$$\begin{aligned} y &= y^* + u \\ z &= z^* + v \end{aligned} \quad (5)$$

and by writing the nonlinear reaction rate term as

$$f(y,z) = \phi^2 y \exp\left(\frac{\gamma(z-1)}{z}\right) \quad (6)$$

Equations (1) to (3) become

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - f(y,z) + \frac{\partial^2 y^*}{\partial x^2} \quad (7)$$

$$N_{Le}\frac{\partial v}{\partial t} = \frac{\partial^2 v}{\partial x^2} + \beta f(y,z) + \frac{\partial^2 z^*}{\partial x^2} \quad (8)$$

$$\frac{\partial u(t,0)}{\partial x} = \frac{\partial v(t,0)}{\partial x} = 0,\ u(t,1) = v(t,1) = 0 \quad (9)$$

The Special Case of $N_{Le} = 1$ and an Adiabatic Perturbation

In an analysis of the stability of the steady states of the above model, Wei [19] made certain simplifying assumptions which will also be used here. He assumed that $N_{Le} = 1$ and also that the perturbation has the special form $\beta u = -v$. The assumption that the Lewis number is equal to one is special, and only occurs in certain circumstances. Assuming that the temperature perturbation is proportional to the concentration perturbation, is equivalent to the assumption that the perturbations respond in a locally adiabatic manner similar to Equation (4). With these two assumptions Equations (7)and (8) can be decoupled so that only a single equation in one dependent variable is necessary to describe the system. Thus the mass balance becomes

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - \phi^2 y \exp\left[\frac{\beta\gamma(1-y)}{1+\beta(1-y)}\right] + \frac{\partial^2 y^*}{\partial x^2} \quad (10)$$

or

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - g(y) + \frac{\partial^2 y^*}{\partial x^2} \quad (11)$$

Linearizing the nonlinear term

$$g(y) = g(y^*) + \left.\frac{dg}{dy}\right|_{y=y^*} u = g(y^*) + g_y u \quad (12)$$

and noting from the steady state equation that

$$\frac{\partial^2 y^*}{\partial x^2} = g(y^*) \quad (13)$$

the linearized transient equation becomes

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - g_y u \quad (14)$$

with boundary conditions

$$\frac{\partial u(t,0)}{\partial x} = 0 \quad u(t,1) = 0 \quad (15)$$

Remember that g_y is a function only of position and is determined from steady state information alone.

As previously described, the Liapunov functional will be defined as the following for the case of one state variable:

$$V = \frac{1}{2}\int_0^1 u^2 dx \quad (16)$$

This is positive definite except when $u = 0$. Differentiating with respect to time yields

$$\dot{V} = \int_0^1 u\frac{\partial u}{\partial t}dx = \int_0^1 \left(u\frac{\partial^2 u}{\partial x^2} - g_y u^2\right)dx \quad (17)$$

To insure stability of a given steady state it is necessary to show that $\dot{V}$ is negative definite along all the trajectories of the perturbed system. If Green's first identity is applied to the first term under the integral of Equation (17) this yields

$$\int_0^1 u\frac{\partial^2 u}{\partial x^2}dx = u\frac{\partial u}{\partial x}\Big|_0^1 - \int_0^1 \left(\frac{\partial u}{\partial x}\right)^2 dx \quad (18)$$

and thus

$$\dot{V} = -\int_0^1 \left(\frac{\partial u}{\partial x}\right)^2 dx - \int_0^1 g_y u^2 dx \quad (19)$$

Now we turn to an inequality suggested by Gavalas [8]. Consider the identity

$$u(t,x) = -\int_0^1 \frac{\partial u(t,x)}{\partial x}dx \quad \text{for } u(t,1) = 0 \quad (20)$$

It follows that

$$u^2(t,x) = \left\{\int_x^1 \frac{\partial u(t,x)}{\partial x}dx\right\}^2 \quad (21)$$

and using the Schwarz inequality

$$u^2(t,x) \leqq \int_x^1 \left(\frac{\partial u}{\partial x}\right)^2 dx \int_x^1 (1)^2 dx$$

$$\leqq (1-x)\int_0^1 \left(\frac{\partial u}{\partial x}\right)^2 dx \quad (22)$$

In the expression for $\dot{V}$, g_y may be positive and negative in the interval $0 \leqq x \leqq 1$. If we assume, which is usually the case for the systems investigated, that in the interval $\alpha' \leqq x \leqq \beta'$ $g_y \leqq 0$ and $\alpha' \nleqq x \nleqq \beta'$ $g_y \geqq 0$ then

$$\dot{V} = -\int_0^1 \left(\frac{\partial u}{\partial x}\right)^2 dx + \int_{\alpha'}^{\beta'} |g_y| u^2 dx - \int_{\substack{\alpha' \nleq x \nleq \beta'}} |g_y| u^2 dx \quad (23)$$

and thus

$$\dot{V} \leqq -\int_0^1 \left(\frac{\partial u}{\partial x}\right)^2 dx + \int_{\alpha'}^{\beta'} u^2 |g_y| dx$$

$$\leqq -\int_0^1 \left(\frac{\partial u}{\partial x}\right)^2 dx + \int_0^1 \left(\frac{\partial u}{\partial x}\right)^2 dx \int_{\alpha'}^{\beta'} |g_y|(1-x)dx \quad (24)$$

$$\dot{V} \leqq \int_0^1 \left(\frac{\partial u}{\partial x}\right)^2 dx \left\{ \int_{\alpha'}^{\beta'} |g_y|(1-x)dx - 1 \right\} \quad (25)$$

For stability a sufficient condition is

$$\dot{V} < 0 \quad (26)$$

and therefore the stability criterion is

$$\int_{\alpha'}^{\beta'} |g_y|(1-x)dx < 1 \quad (27)$$

Liapunov's direct method has led to a single, easily evaluated, stability criterion for this model of an adiabatic catalyst particle.

We will now apply this stability criterion to two examples. The first example (Case A) is of a catalyst particle which exhibits three steady states and the second (Case B) is a particle with a single steady state. Case A uses the same parameters for the system given by Wei.

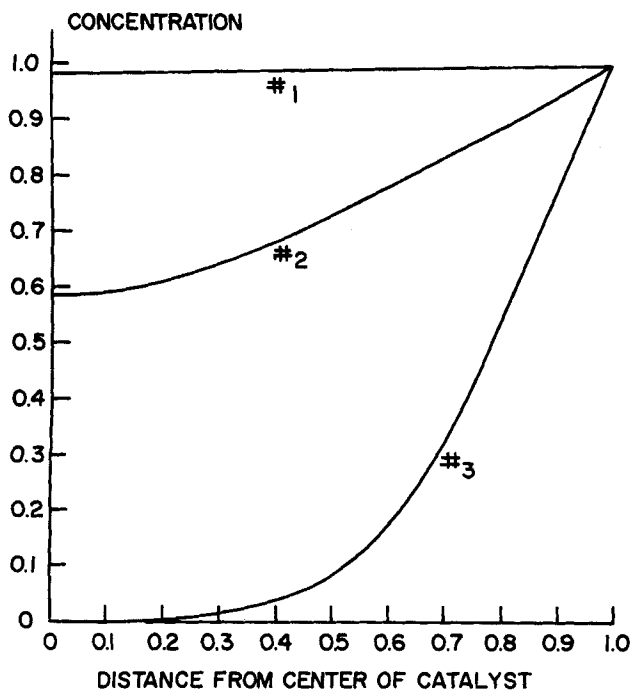

Fig. 3. Steady state concentration as a function of position case A.

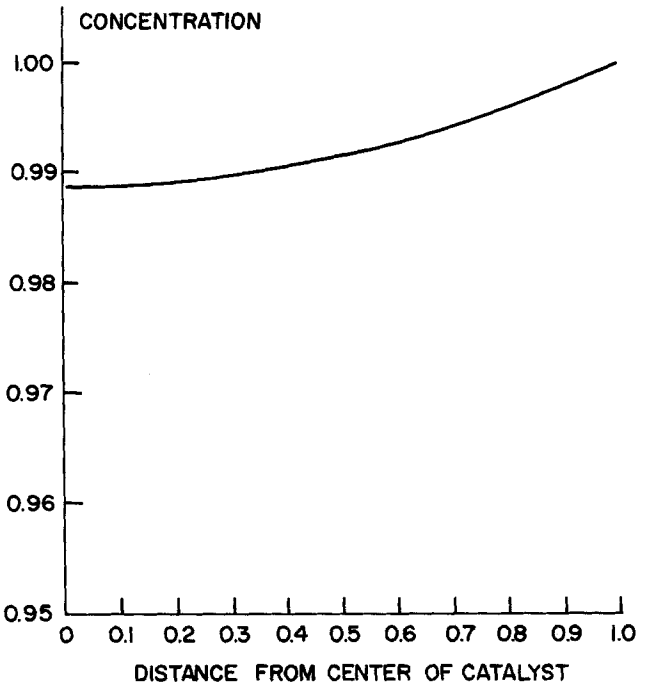

Fig. 4. Steady state concentration as a function of position case B.

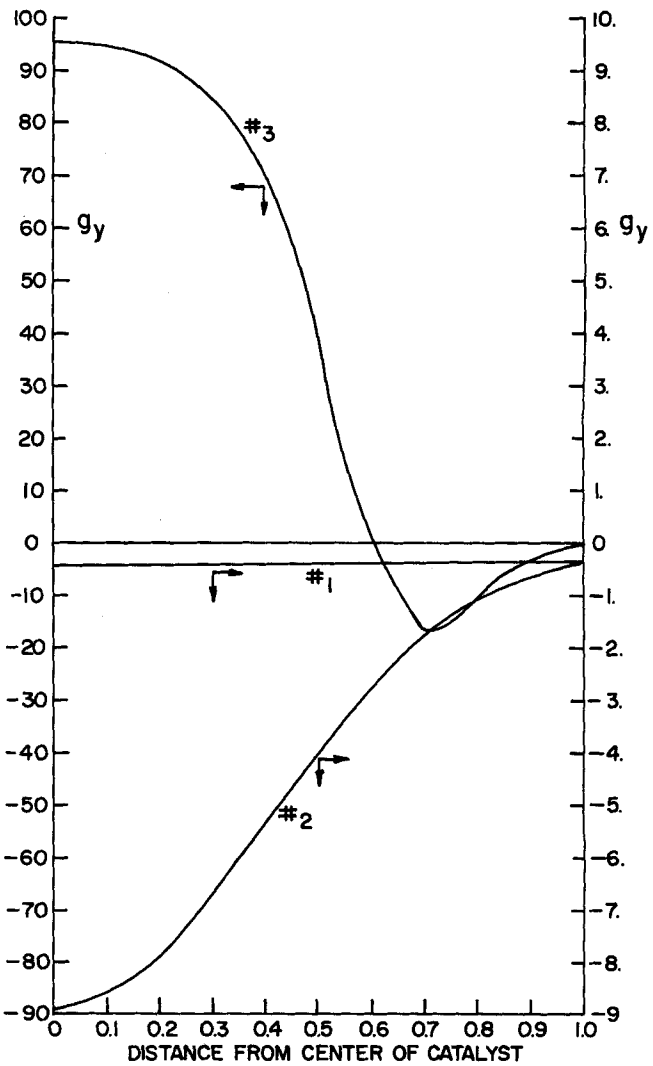

Fig. 5. g_y as a function of position case A.

For Case A, three steady states, the parameter values $\phi = 0.16$, $\beta = 0.7$ and $\gamma = 20$ are used. Figure 3 shows a plot of the steady state concentration vs. distance from

the center of the catalyst particle. The three steady state profiles were obtained by backwards integration of the steady state equation using a digital computer. Since this is a two point boundary value problem, the value of the dimensionless concentration at $x = 1$ is taken as unity and the steady state equation is integrated backwards until the boundary condition at the center of the particle is met. For Case B, one steady state, Figure 4 shows the equivalent concentration distance information. The parameter values are $\phi = 0.16$, $\beta = 0.1$ and $\gamma = 20$.

In Equation (12) g_y takes the form

$$g_y = \phi^2 y^* \exp\left\{\frac{\beta\gamma(1-y^*)}{1+\beta(1-y^*)}\right\} \left\{\frac{-\beta\gamma}{(1+\beta(1-y^*))^2} + \frac{1}{y^*}\right\}$$

Figure 5 shows a plot of g_y for Case A, and Figure 6 shows a plot of g_y for Case B.

Case A: For steady states 1 and 2 $g_y < 0$ over the entire interval and therefore $\alpha' = 0$ and $\beta' = 1$; for steady state 3 $g_y < 0$ only in the interval $0.605 \leqq x \leqq 1$. Computation of the stability criterion [Equation (27)] yields

Steady state no.	$\int_{\alpha'}^{\beta'} \lvert g_y \rvert (1-x)\,dx$	Comment
1	0.1878	stable
2	3.0101	no conclusion
3	0.8578	stable

Therefore two of the steady states, 1 and 3, are asymptotically stable, because we have met the sufficient condition for stability. The intermediate steady state furnishes no conclusion as to its stability, and it is known that this intermediate steady state is unstable [19]. The functional method has succeeded with the proper use of inequalities in showing the stability of the two steady state profiles. These are the same results as found by Wei, and while he arrived at his results by solution of an eigenvalue problem this was not necessary with the present functional method.

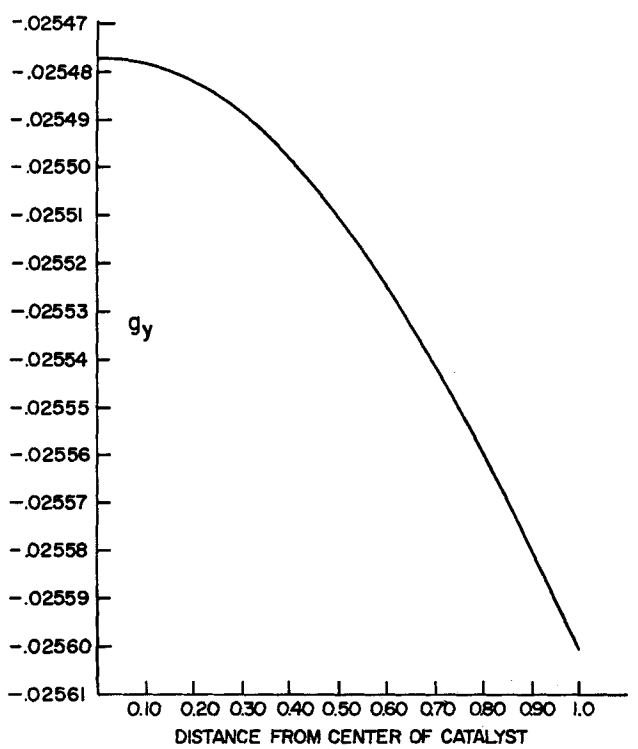

Fig. 6. g_y as a function of position case B.

Case B: For the single steady state profile, $g_y < 0$ over the entire interval and therefore, $\alpha' = 0$ and $\beta' = 1$; for this steady state there results

$$\int_{\alpha'}^{\beta'} |g_y|(1-x)\,dx = 0.01275 \qquad \text{Stable}$$

As would be expected a single steady state profile is asymptotically stable to infinitesimal perturbations. Once again this conclusion is easily drawn by the functional method using inequalities.

The Special Case of $N_{Le} = 1$ But With a Generalized Perturbation

The only restriction placed upon the present system is that the Lewis Number is still equal to one. As a result the transient equations of the temperature and concentration perturbations cannot easily be decoupled as was the situation in the previous case. It is also necessary to consider a more general Liapunov functional.

Using the balances of Equations (10) and (11), linearizing about the steady state profile with

$$f(y,z) = f(y^*,z^*) + \left.\frac{\partial f(y,z)}{\partial y}\right|_{\substack{y=y^*\\z=z^*}} u + \left.\frac{\partial f(y,z)}{\partial z}\right|_{\substack{y=y^*\\z=z^*}} v \qquad (28)$$

and using the steady state equations

$$\frac{\partial^2 y^*}{\partial x^2} = f(y^*,z^*) = f(y^*) \qquad (29)$$

$$\frac{\partial^2 z^*}{\partial x^2} = -\beta f(y^*,z^*) = -\beta f(y^*) \qquad (30)$$

yields

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - f_y u - f_z v \qquad (31)$$

$$\frac{\partial v}{\partial t} = \frac{\partial^2 v}{\partial x^2} + \beta f_y u + \beta f_z v \qquad (32)$$

It is possible to combine Equations (31) and (32) so as to obtain a single equation for the sum, $v + \beta u$. This sum can be shown to be stable, and in fact has a simple eigenfunction series expansion. Substitution of this series expansion for one of the variables does not lessen any of the mathematical difficulties encountered in trying to make $\dot{V}$ of definite sign.

Again f_y and f_z are only functions of position for a given steady state, and in this case are positive in the interval $0 \leqq x \leqq 1$. Specifically

$$f_y = \phi^2 \exp\left(\frac{\gamma\beta(1-y^*)}{1+\beta(1-y^*)}\right) \qquad (33)$$

$$f_z = \frac{\gamma\phi^2 y^*}{z^{*2}} \exp\left(\frac{\gamma(z^*-1)}{z^*}\right) = \frac{f_y \gamma y^*}{z^{*2}} \qquad (34)$$

The Liapunov functional for these two state variables is

$$V = \frac{1}{2}\int_0^1 (u^2 + v^2)\,dx \qquad (35)$$

The Liapunov functional is positive definite except when $u = v = 0$. The time derivative of this functional is

$$\dot{V} = \int_0^1 \left\{u\frac{\partial u}{\partial t} + v\frac{\partial v}{\partial t}\right\} dx \qquad (36)$$

and substituting Equations (31) and (32) into (36) yields

$$\dot{V} = \int_0^1 \left\{ u\frac{\partial^2 u}{\partial x^2} - f_y u^2 - f_z uv + v\frac{\partial^2 v}{\partial x^2} + \beta f_y uv + \beta f_z v^2 \right\} dx \quad (37)$$

Applying Green's first identity to this system we obtain

$$\dot{V} = -\int_0^1 \left\{ \left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial v}{\partial x}\right)^2 \right\} dx - \int_0^1 f_y u^2\, dx + \beta \int_0^1 f_z v^2\, dx - \int_0^1 uvf_z dx + \beta \int_0^1 f_y uv dx \quad (38)$$

Now using the following inequality

$$\pm uva \leqq |a|\ |uv| \leqq \frac{|a|}{2}(u^2 + v^2) \quad (39)$$

there results

$$\int_0^1 uv(-f_z + \beta f_y)dx \leqq \frac{1}{2}\int_0^1 (u^2 + v^2)\ |\beta f_y - f_z|\, dx \quad (40)$$

Inserting Equation (40) into (38) yields

$$\dot{V} \leqq -\int_0^1 \left\{ \left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial v}{\partial x}\right)^2 \right\} dx + \int_0^1 u^2 \left(-f_y + \left| \frac{\beta}{2} f_y - \frac{f_z}{2} \right| \right) dx + \int_0^1 v^2 \left(\beta f_z + \left| \frac{\beta}{2} f_y - \frac{f_z}{2} \right| \right) dx \quad (41)$$

Let

$$F_u = -f_y + \left| \frac{\beta}{2} f_y - \frac{f_z}{2} \right| \quad (42)$$

and using Equation (34)

$$F_u = f_y \left(-1 + \frac{1}{2} \left| \beta - \frac{\gamma y^*}{z^{*2}} \right| \right) \quad (43)$$

If $F_u > 0$, $\alpha'' \leqq x \leqq \beta''$, and $F_u < 0$, $\alpha'' \nleqq x \nleqq \beta''$ and

$$F_v = \beta f_z + \frac{1}{2}\ |\beta f_y - f_z| \quad (44)$$

then $F_v > 0$ for $0 \leqq x \leqq 1$
Again using Equation (34)

$$F_v = f_y \left(\frac{\beta\gamma y^*}{z^{*2}} + \frac{1}{2} \left| \beta - \frac{\gamma y^*}{z^{*2}} \right| \right) \quad (45)$$

we obtain

$$\dot{V} \leqq -\int_0^1 \left\{ \left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial v}{\partial x}\right)^2 \right\} dx + \int_0^1 |F_v| v^2 dx + \int_{\alpha''}^{\beta''} |F_u| u^2 dx - \int_{\alpha'' \nleqq x \nleqq \beta''} |F_u| u^2 dx \quad (46)$$

and

$$\dot{V} \leqq -\int_0^1 \left\{ \left(\frac{\partial u}{\partial x}\right)^2 + \left(\frac{\partial v}{\partial x}\right)^2 \right\} dx + \int_0^1 |F_v| v^2 dx + \int_{\alpha''}^{\beta''} |F_u| u^2 dx \quad (47)$$

But as derived previously we get

$$v^2 \leqq (1-x) \int_0^1 \left(\frac{\partial v}{\partial x}\right)^2 dx \quad (48)$$

$$u^2 \leqq (1-x) \int_0^1 \left(\frac{\partial u}{\partial x}\right)^2 dx \quad (49)$$

and putting these inequalities into Equation (47) finally yields

$$\dot{V} \leqq \int_0^1 \left(\frac{\partial v}{\partial x}\right)^2 dx \left\{ -1 + \int_0^1 (1-x)|F_v| dx \right\} + \int_0^1 \left(\frac{\partial u}{\partial x}\right)^2 dx \left\{ -1 + \int_{\alpha''}^{\beta''} (1-x)|F_u| dx \right\} \quad (50)$$

From Equation (50) we see that we have two stability criteria and both must be met to give a sufficient condition for asymptotic stability. These criteria are

Condition (*a*)

$$\int_{\alpha''}^{\beta''} (1-x)\ |F_u|\, dx < 1 \quad (51)$$

Condition (*b*)

$$\int_0^1 (1-x)\ |F_v|\, dx < 1 \quad (52)$$

Now we apply the two conditions, Equations (51) and (52), to Case *A* and Case *B* examples previously discussed.

Case A. For both steady states 1 and 2 F_u and F_v are both greater than zero over the entire interval and therefore $\alpha'' = 0$ and $\beta'' = 1$; for steady state 3 $F_v > 0$ over the entire interval, but $F_u > 0$ in the interval $0.685 \leqq x \leqq 1$. Computation of the stability conditions yields

Steady state no.	(*a*)	(*b*)	Comment
1	0.1247	0.3468	Stable
2	1.854	7.647	No conclusion
3	2.069	7.086	No conclusion

Therefore, in this case of three steady states, stability can be predicted for only one of the steady states. The above criteria do not provide sufficient conditions for the prediction of stability of the other stable steady state. For the intermediate steady state both conditions are not met as expected since it is unstable. It is evident that the stability criteria are not sharp enough for this general case.

Case B. For the single steady state F_u and F_v are both greater than zero over the entire interval and therefore $\alpha'' = 0$ and $\beta'' = 1$, for this steady state one obtains

$$(a) = \int_{\alpha''=0}^{\beta''=1} (1-x)\ |F_u|\, dx = 0.1153$$

$$(b) = \int_{\alpha''=0}^{\beta''=1} (1-x)\ |F_v|\, dx = 0.1542$$

Therefore this steady state profile is asymptotically stable. This result is expected for the case of a single steady state profile.

The Case $N_{Le} \neq 1$ and a Generalized Perturbation

Here the assumption that $N_{Le} = 1$ is removed and we assume only that the Lewis number is equal to some constant. The general system of linearized equations is

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial x^2} - f_y u - f_z v \quad (53)$$

$$\frac{\partial v}{\partial t} = \frac{1}{N_{Le}} \frac{\partial^2 v}{\partial x^2} + \frac{\beta f_y u}{N_{Le}} + \frac{\beta f_z v}{N_{Le}} \tag{54}$$

As before we define the Liapunov functional

$$V = \frac{1}{2} \int_0^1 (u^2 + v^2) dx \tag{55}$$

which is positive definite except when $u = v = 0$. It then follows that

$$\dot{V} = \int_0^1 \left(u \frac{\partial u}{\partial t} + v \frac{\partial v}{\partial t} \right) dx \tag{56}$$

and

$$\dot{V} = \int_0^1 \left(u \frac{\partial^2 u}{\partial x^2} - f_y u^2 - f_z uv + \frac{v}{N_{Le}} \frac{\partial^2 v}{\partial x^2} + \frac{\beta f_y uv}{N_{Le}} + \frac{\beta f_z v^2}{N_{Le}} \right) dx \tag{57}$$

Using the previous analysis we obtain

$$\dot{V} \leqq \int_0^1 \frac{1}{N_{Le}} \left(\frac{\partial v}{\partial x} \right)^2 dx \left(-1 + \int_0^1 (1-x) |F_v| \, dx \right) + \int_0^1 \left(\frac{\partial u}{\partial x} \right)^2 dx \left(-1 + \int_{\alpha''}^{\beta''} (1-x) |F_u| \, dx \right) \tag{58}$$

with

$$F_v = \beta f_z + \frac{1}{2} |\beta f_y - N_{Le} f_z| = f_y \left(\frac{\beta \gamma y^*}{z^{*2}} + \frac{1}{2} \left| \beta - \frac{N_{Le} \gamma y^*}{z^{*2}} \right| \right) \tag{59}$$

and

$$F_u = f_y \left(-1 + \frac{1}{2} \left| \frac{\beta}{N_{Le}} - \frac{\gamma y^*}{z^{*2}} \right| \right) \tag{60}$$

It should be noted that for various values of N_{Le} the stability characteristics of the system changed markedly. Computations with this system have not been carried further because of the lack of sharp stability bounds in the less general case of $N_{Le} = 1$.

THE ADIABATIC TUBULAR REACTOR PROBLEM

The system of equations is the same as that presented by Amundson and Raymond [1] and the reader is referred to their article for a definition of the terms. The only diffusion which is taking place is in the axial direction. The fluid is assumed to be in turbulent flow so radial effects can be neglected. The heat and mass balances are

$$\rho C_p \frac{\partial T}{\partial \theta} = \lambda \frac{\partial^2 T}{\partial x^2} - \rho v C_p \frac{\partial T}{\partial x} + (-\Delta H) k \, C \, \exp\left(-\frac{E}{RT} \right) \tag{61}$$

$$\frac{\partial C}{\partial \theta} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - k \, C \, \exp\left(-\frac{E}{RT} \right) \tag{62}$$

The boundary conditions are

$$\begin{aligned} \rho v C_p (T_o - T) &= -\lambda \frac{\partial T}{\partial x} && x = 0 \quad \theta > 0 \\ v(C_o - C) &= -D \frac{\partial C}{\partial x} && x = 0 \quad \theta > 0 \\ \frac{\partial C}{\partial x} &= \frac{\partial T}{\partial x} = 0 && x = l \quad \theta > 0 \end{aligned} \tag{63}$$

But for a tubular reactor in turbulent flow

$$\lambda = \rho C_p D$$

which is a consequence of the mechanism for heat transport and mass transport being the same.

We can rephrase these equations by defining

$$s = x/l; \quad z = T/T_o; \quad y = C/C_o$$

and

$$\alpha = \frac{l^2 k}{D}; \quad \beta = -\frac{\Delta H C_o}{T_o \rho C_p}; \quad v = \beta \alpha; \quad t = \frac{D\theta}{l^2}; \quad N_{Pe} = \frac{vl}{D}; \quad Q = \frac{E}{RT_o}$$

These changes convert Equations (61) to (63) to

$$\frac{\partial y}{\partial t} = \frac{\partial^2 y}{\partial s^2} - N_{Pe} \frac{\partial y}{\partial s} + \alpha y \exp(-Q/z) \tag{64}$$

$$\frac{\partial z}{\partial t} = \frac{\partial^2 z}{\partial s^2} - N_{Pe} \frac{\partial y}{\partial s} + \nu y \exp(-Q/z) \tag{65}$$

$$\begin{aligned} \text{at } s = 0 \qquad & N_{Pe}(1 - y(t,0)) = -\frac{\partial y(t,0)}{\partial s} \\ & N_{Pe}(1 - z(t,0)) = -\frac{\partial z(t,0)}{\partial s} \\ \text{at } s = 1 \qquad & \frac{\partial y(t,1)}{\partial s} = 0 \\ & \frac{\partial z(t,1)}{\partial s} = 0 \end{aligned} \tag{66}$$

As in the case of the catalyst particle we will first assume that the perturbation in the temperature is proportional to the perturbation in the concentration. If this procedure provides a sufficient criterion for the prediction of the stability of two steady states, then removal of this restriction may yield sufficient criteria for the prediction of stability in the general case.

For the adiabatic perturbation

$$z(t,s) = 1 + \beta(1 - y(t,s)) \tag{67}$$

substituting (67) into either Equation (64) or (65) yields a single equation

$$\frac{\partial y}{\partial t} = \frac{\partial^2 y}{\partial s^2} - N_{Pe} \frac{\partial y}{\partial s} - \alpha y \exp\left(\frac{-Q}{1 + \beta(1-y)} \right) \tag{68}$$

By letting Equation (68) equal zero the steady state profile may be generated. For the nonlinear reaction rate term

$$f = f(y) = y \exp\{-Q/[1 + \beta(1-y)]\} \tag{69}$$

linearizing about the steady state profile yields, with $u = y - y^*$,

$$f = f(y^*) + \left. \frac{\partial f}{\partial y} \right|_{y=y^*} u = f(y^*) + u f_y \tag{70}$$

Since we are dealing with infinitesimal perturbations we will assume that

$$u(t,0) = 0 \tag{71}$$

Applying the steady state equation and putting Equation (70) into (68) yields

$$\frac{\partial u}{\partial t} = \frac{\partial^2 u}{\partial s^2} - N_{Pe} \frac{\partial u}{\partial s} - \alpha u f_y \tag{72}$$

with boundary conditions

$$\begin{aligned} u(t,0) &= 0 \\ \frac{\partial u(t,1)}{\partial s} &= 0 \end{aligned} \tag{73}$$

In order to make the system more amenable to analysis the following change of variable is needed

$$u(t,s) = \xi(t,s) \exp(N_{Pe}s/2) \tag{74}$$

This converts Equations (72) and (73) to

$$\frac{\partial \xi}{\partial t} = \frac{\partial^2 \xi}{\partial s^2} - \xi\left(\frac{N_{Pe}^2}{4} + \alpha f_y\right) \tag{75}$$

$$\xi(t,0) = 0; \quad \frac{\partial \xi(t,1)}{\partial s} = -\xi(t,1)\frac{N_{Pe}}{2} \tag{76}$$

Since we now have one state variable, we can define the Liapunov functional as

$$V = \frac{1}{2}\int_0^1 \xi^2 ds \tag{77}$$

Differentiating (77) with respect to time and putting in (75) yields

$$\dot{V} = \int_0^1 \xi \frac{\partial \xi}{\partial t} ds = \int_0^1 \left\{ \xi \frac{\partial^2 \xi}{\partial s^2} - \xi^2\left(\frac{N_{Pe}^2}{4} + \alpha f_y\right)\right\} ds \tag{78}$$

If we apply Green's first identity to the first term under the integral sign, there results

$$\int_0^1 \xi \frac{\partial^2 \xi}{\partial s^2} ds = -\frac{N_{Pe}}{4}\xi^2(t,1) - \int_0^1 \left(\frac{\partial \xi}{\partial s}\right)^2 ds \tag{79}$$

and therefore

$$\dot{V} = -\frac{N_{Pe}}{4}\xi^2(t,1) - \int_0^1 \left(\frac{\partial \xi}{\partial s}\right)^2 ds + \int_0^1 \xi^2\left(-\frac{N_{Pe}^2}{4} - \alpha f_y\right) ds \tag{80}$$

The factor $\left(-\frac{N_{Pe}^2}{4} - \alpha f_y\right)$ in Equation (80) can be both positive and negative in the interval $0 \leqq s \leqq 1$. But in the example to be discussed $\left(-\frac{N_{Pe}^2}{4} - \alpha f_y\right)$ will be, at most, positive only in the interval $\alpha' \leqq s \leqq \beta'$. Therefore

$$\dot{V} \leqq -\frac{N_{Pe}}{4}\xi^2(t,1) - \int_0^1 \left(\frac{\partial \xi}{\partial s}\right)^2 ds + \int_{\alpha'}^{\beta'} \xi^2 \left|-\frac{N_{Pe}}{4} - \alpha f_y\right| ds \tag{81}$$

A derivation similar to that which led to Equation (22) can now be used. Thus

$$\xi = \int_0^s \left(\frac{\partial \xi}{\partial s}\right) ds \tag{82}$$

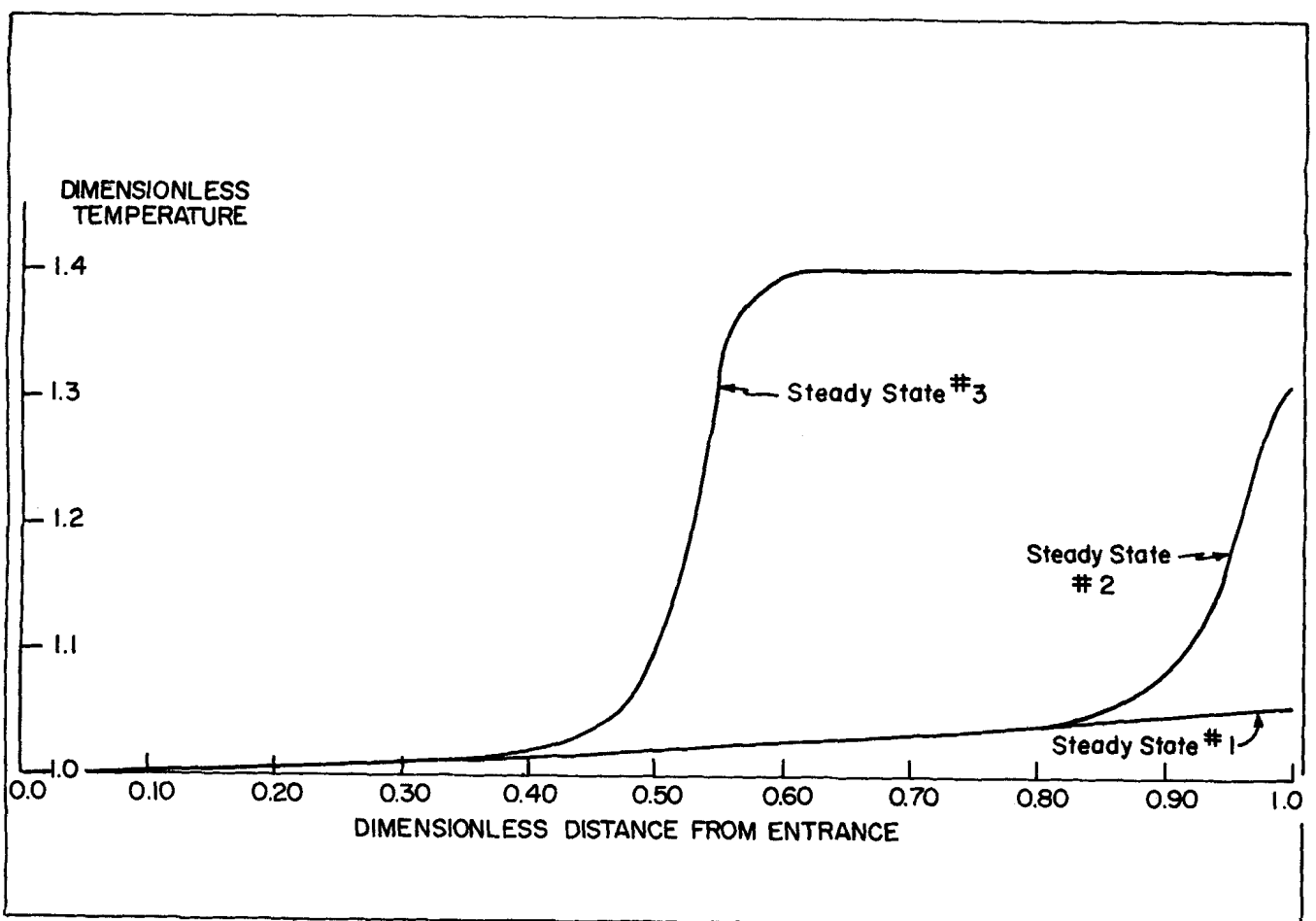

Fig. 7. Steady state temperature profiles for the adiabatic tubular reactor.

$$\xi^2 = \left\{ \int_0^s \left(\frac{\partial \xi}{\partial s} \right) ds \right\}^2 \tag{83}$$

and applying the Schwarz inequality

$$\xi^2 \leqq \int_0^s \left(\frac{\partial \xi}{\partial s} \right)^2 ds \int_0^s (1)^2 ds \leqq s \int_0^1 \left(\frac{\partial \xi}{\partial s} \right)^2 ds \tag{84}$$

Putting (84) into (81) yields

$$\dot{V} \leqq -\frac{N_{Pe}\xi^2(t,1)}{2} + \int_0^1 \left(\frac{\partial \xi}{\partial s} \right)^2 ds \left(-1 + \int_{\alpha'}^{\beta'} s \left| -\frac{N_{Pe}^2}{4} - \alpha f_y \right| ds \right) \tag{85}$$

Thus we see that for stability of a steady state $\dot{V} < 0$, and the stability criterion is now

$$\int_{\alpha'}^{\beta'} s \left| -\frac{N_{Pe}^2}{4} - \alpha f_y \right| ds < 1 \tag{86}$$

In order to determine if a steady state meets the stability criterion of Equation (86) it is necessary to generate the steady state profiles of either the temperature or the concentration in the reactor (the concentration and temperature are related by Equation (67). A method to determine these steady state profiles was proposed by Raymond and Amundson and consists of integrating the steady state equations backwards toward the inlet of the reactor, and then iterating until the Danckwert's boundary condition is met at the inlet. Using data generously provided by Amundson [3] steady states 1 and 2 were generated using a single precision Hamming predictor-corrector integrator routine on an IBM 7094 digital computer. The third steady state, which is almost discontinuous, could not be generated by this single precision routine or by a number of others tried. Instead it was necessary to use a double precision (96 bits) variable step Runge-Kutta method on a C.D.C. 1604 digital computer to generate this profile. The physical parameters for the specific system are

$$\alpha = \frac{l^2 k}{D} = 2.25 \times 10^{13} \qquad N_{Pe} = 30.$$

$$\beta = -\frac{\Delta H C_o}{T_o \rho C_p} = 0.40 \qquad Q = 30.$$

Figure 7 shows the steady state temperature profiles which were generated for these parameters. In order to document the profiles exactly the following results were obtained

Steady state no.	Temperature at the outlet
1	1.05705
2	1.30940
3	1.3999999999999999995

Using these steady state profiles with the stability criterion of Equation (86) yields the following results

Steady state no.	$\int_{\alpha'}^{\beta'} s \left\| -\frac{N^2_{Pe}}{4} - \alpha f_y \right\| ds$	Comment
1	0	Stable
2	64.032	No conclusion
3	20.788	No conclusion

Therefore, when the stability criterion is applied to these steady state profiles only one of them is definitely stable. The stable steady state is that one for which a low level of reaction is taking place in the reactor. Neither the intermediate or the upper steady states meet the criterion for stability. One of the reasons why this criterion is not sharp enough to show that the upper steady state is stable is because of the term $-\frac{N_{Pe}\xi^2(t,1)}{2}$ which occurs in Equation (85). An extra negative term as this one did not appear in the expression for $\dot{V}$ of the catalyst particle. Any further generalization of the perturbation will probably not yield any more satisfactory results. Thus we shall not pursue this problem further.

CONCLUSIONS

It has been shown that in certain situations the Liapunov functional method can be used to predict stability of distributed systems. Specifically, the approach which has been used is to employ mathematical inequalities in order to insure that the sign of V is negative definite. In the case of a catalyst particle, which is modeled as a slab exhibiting a Lewis number of unity and having an adiabatic perturbation form, the results from this approach are entirely satisfactory. When any further generalization of the catalyst particle model is made or the stability of an adiabatic tubular reactor investigated, the resulting stability criteria do not yield sharp results for some of the stable steady states. These poorer results are due to either the choice of the Liapunov functional form or the use of inequalities.

ACKNOWLEDGMENT

This work made use of the computer facilities supported in part by National Science Foundation Grant NSF-GP-579. In addition, the National Science Foundation supported part of this work under Grant NSF-CK-460, and an NSF Traineeship.

NOTATION

a = constant defined in Equation (39)
C = concentration
c_p = heat capacity
D = diffusivity
E = energy of activation
f = vector functions
$f(y, z)$ = see Equation (6)
F_u = see Equation (42)
$g(y)$ = see Equation (11)
ΔH = heat of reaction
$k(T_o)$ = reduced frequency factor
K = thermal conductivity
N_{Le} = Lewis number
N_{Pe} = Peclet number
P = positive definite symmetric matrix
R = gas constant
t = time
T = temperature
u = state vector for P.D.E.
u = dimensionless concentration perturbation
v = dimensionless temperature perturbation
V = Liapunov function or functional
x = state vector for O.D.E.
y = dimensionless concentration
z = dimensionless temperature

Greek Letters

$\alpha(\cdot), \beta(\cdot), \gamma(\cdot)$ = scalar constants
$\alpha', \beta', \alpha'', \beta''$ = limits of integration
α, β, ν = constants, see Equations (64) and (65)
β = heat of reaction coefficient
γ = reduced activation energy
δ, ϵ = scalar measure
ξ = reduced concentration variable

ρ = density
ϕ = solution vector for O.D.E.
ϕ^2 = Thiele modulus
Ω = spatial region

Subscripts

e = equilibrium state
o = initial state
y = derivative with respect to y
z = derivative with respect to z

Superscripts

$*$ = steady state condition

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Manuscript received June 22, 1967; revision received October 16, 1967; paper accepted October 18, 1967. Paper presented AIChE St. Louis Meeting.

Use of Molecular Shape Factors in Vapor-Liquid Equilibrium Calculations with the Corresponding States Principle

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Calculation of fugacities of components in a gaseous or liquid solution directly from the corresponding states principle requires an improvement in the pseudo-critical constants for the mixture. The derivation of the pseudo-criticals must take into account deviations from the simple two parameter corresponding states principle which require additional parameters incorporated into the definition of the pseudo-criticals. In this work parameters called molecular shape factors are introduced into the pseudo-criticals. A generalized correlation for these shape factors is presented.

Use of the shape factors greatly improves the calculation of vapor-liquid equilibrium ratios for nonpolar hydrocarbon mixtures with large differences in molecular size and shape. Excellent results are obtained both in the low pressure and in the retrograde region when the pseudo-reduced properties of the vapor and liquid lie within the range of accurately known properties of a reference fluid and the reduced temperatures for each component is greater than approximately 0.6.

Direct calculation of individual component fugacities in a mixture, and of equilibrium vapor-liquid distribution coefficients (K-values) from the corresponding states principle, offers some attractive possibilities in practical solution thermodynamics. In this procedure one defines pseudo-critical values for the mixture and determines the mixture properties from the known properties of a pure reference substance at the same pseudo-reduced conditions. In calculating individual fugacities and K-values one must differentiate the pseudo-critical constants with respect to composition. This requires a great deal more accuracy in the pseudo-critical definitions, than is necessary, to predict total solution properties. Inaccuracies in the definitions of pseudo-criticals arise from three sources:

1. Errors arising from the fact that the partition function and its thermodynamic derivatives for a pure reference cannot always exactly represent the corresponding functions for a mixture of dissimilar molecules, even when

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