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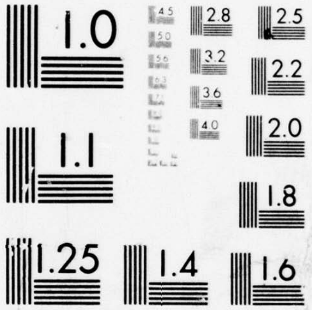
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THE INFLUENCE OF THE LEWIS NUMBER ON THE DYNAMICS OF CHEMICALLY REACTING SYSTEMS

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W. Harmon Ray[†] and Stuart P. Hastings[‡]

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ABSTRACT

The influence of Lewis number on stability and oscillations for stirred tanks, catalytic wires and gauzes, and catalyst particles is determined quantitatively. The mathematical structure is discussed and illustrated by example. Relaxation oscillations are found to be the natural asymptote to the bifurcating limit cycles as the Lewis number vanishes.

AMS (MOS) Subject Classifications - 80.34

Key Words - Chemical systems, stability, relaxation oscillations, limit cycles, Hopf bifurcation

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SIGNIFICANCE AND EXPLANATION

This paper shows explicitly the effect of the Lewis number (a measure of the relative importance of the thermal and material time scales) on the dynamic behaviour of a wide variety of chemically reacting systems. The mathematical structure, which is the same for all the diverse physical systems treated (which include stirred tanks, and porous and nonporous catalysts), shows that the dynamic state tends to one of relaxation oscillations as the Lewis number vanishes. The results will aid the understanding of experimental observations in many chemical systems.

The responsibility for the wording and views expressed in this descriptive summary lies with MRC, and not with the authors of this report.

THE INFLUENCE OF THE LEWIS NUMBER ON THE DYNAMICS OF CHEMICALLY REACTING SYSTEMS

W. Harmon Ray[†] and Stuart P. Hastings[‡]

INTRODUCTION

Chemically reacting systems show very interesting dynamics for a wide range of applications [1-4]. The influence of various parameters on this behavior has been studied for catalyst particles, continuous stirred tank reactors (CSTR's), etc. A particularly important parameter is the ratio of intrinsic thermal time constant to intrinsic material time constant (generically referred to as the "Lewis" number) for these reacting systems. It is well known that this parameter has a very striking effect on the system dynamics, but the quantitative effects have not been completely understood. Previous numerical results by Hlaváček et al. [5-7], Luss and Lee [8,9], and others [10-16], showed that catalyst particles and their lumped models demonstrate oscillations for sufficiently small values of the Lewis number in some cases. Although these results have been particularly well treated in the fine surveys by Aris [15] and Sheintuch and Schmitz [4], the form of the bifurcation phenomena, the asymptotic behavior as $Le \to 0$, and the quantitative dependence on parameters have not yet been dealt with.

In this paper we endeavor to demonstrate rather explicitly the influence of the Lewis number for several major classes of reacting systems and attempt to show the underlying mathematical structure which transcends a wide range of specific problems. First we develop the key results for CSTR's and then extend these to porous and nonporous catalytic surfaces. One particularly interesting result is the natural appearance of relaxation oscillations in all of these systems as the Lewis number vanishes.

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THE CONTINUOUS STIRRED TANK REACTOR

The dynamic behavior of the CSTR has been analyzed earlier by bifurcation theory [17,18] and the influence of reactor parameters explicitly determined when the Lewis number was unity. Here we wish to be more general and pose the CSTR modelling equations for a first order, irreversible exothermic reaction as

$$V_M \frac{dc_A}{dt'} = F(c_{Af} - c_A) - Vk_0\exp\{-E/RT\}c_A \tag{1}$$

$$V_T(\rho C_p)_T \frac{dT}{dt'} = \rho C_p F(T_f - T) + V(-\Delta H)k_0\exp\{-E/RT\}c_A$$

$$-hA(T - T_c) \tag{2}$$

The quantity $V_T(\rho C_p)_T$ corresponds to the total thermal capacitance of the reactor (perhaps including solid packing, reactor wall, etc.) while $V\rho C_p$ represents the thermal capacity of the reacting fluid alone. Similarly V_M is the total material capacitance of the reactor while V is the material capacitance of the reactive part of the reactor. As an example, volume V might be influenced by a catalyst while $V_M - V$ is not. A recent experimental study [19] illustrates the necessity of this more general formulation.

By defining the dimensionless quantities

$$x_1 = \frac{c_{Af} - c_A}{c_{Af}}, \quad x_2 = \frac{T - T_f}{T_f}\left(\frac{E}{RT_f}\right), \quad \tau = \frac{V}{F}$$

$$Da = k_0\, e^{-\gamma}\tau, \quad t = t'\frac{F}{V_m}, \quad \gamma = E/RT_f \tag{3}$$

$$B = \frac{(-\Delta H)c_{Af}}{\rho C_p T_f}\left(\frac{E}{RT_f}\right) \qquad x_{2c} = \frac{T_c - T_f}{T_f}\left(\frac{E}{RT_f}\right)$$

$$\beta = \frac{hA}{F\rho C_p}, \quad Le = \frac{V_T}{V_M}\frac{(\rho C_p)_T}{\rho C_p}$$

one obtains

$$\frac{dx_1}{dt} = -x_1 + Da(1 - x_1)\exp\left\{\frac{x_2}{1 + x_2/\gamma}\right\} = f_1(x_1,x_2) \tag{4}$$

$$Le\,\frac{dx_2}{dt} = -x_2 + BDa(1 - x_1)\exp\left\{\frac{x_2}{1 + x_2/\gamma}\right\} -\beta(x_2 - x_{2c}) \tag{5}$$

When one assumes $Le = 1$, these model equations reduce to those treated in [17,18].

To begin our discussion we should provide a general definition of the Lewis number. Earlier definitions (e.g.; [20]) are limited in scope and the physical interpretation has not always been made clear. Here we define the Lewis number as the ratio of the physical transport thermal time constant to the physical transport material time constant. As we shall show, this allows an appropriate Lewis number for each reacting system with all playing the same role and having the same physical interpretation.

For the CSTR, the Lewis number can be written

$$Le = \frac{V_T}{V_M}\,\frac{(\rho C_p)_T}{\rho C_p} = \frac{\dfrac{V_T(\rho C_p)_T\Delta T}{F\rho C_p\Delta T}}{\dfrac{V_M\Delta c}{F\Delta c}} = \frac{\left\{\begin{array}{l}\text{time required to raise the tempera-}\\ \text{ture of the entire system by an}\\ \text{amount } \Delta T \text{ through inflow and out-}\\ \text{flow of fluid at flow rate } F\end{array}\right\}}{\left\{\begin{array}{l}\text{time required to raise the concen-}\\ \text{tration of the entire material}\\ \text{volume an amount } \Delta c \text{ through in-}\\ \text{flow and outflow of fluid at flow}\\ \text{rate } F\end{array}\right\}} \tag{6}$$

which is, of course, the ratio of the physical transport thermal and material time constants.

By carrying through the bifurcation analysis with respect to Le, just as was done earlier with respect to Da and τ [17,18] and augmenting this with an analysis of relaxation phenomena, one can see the entire structure of the dynamic behavior. Obviously steady state multiplicity is not influenced by Le, so that we shall only consider stability and oscillatory behavior here. Let us divide Eq. (5) through by Le to yield

$$\frac{dx_2}{dt} = -\frac{(1+\beta)}{Le} x_2 + \frac{B}{Le} Da(1 - x_1) \exp\left\{\frac{x_2}{1 + x_2/\gamma}\right\} + \frac{\beta x_{2c}}{Le} = f_2(x_1, x_2) \tag{7}$$

This puts Eqs. (4,7) in the same form as the equations treated in [17,18] if one defines

$$\alpha = \left(\frac{1+\beta}{Le}\right) \quad , \hat{B} = \frac{B}{Le} \quad , \hat{x}_{2c} = \frac{x_{2c}}{Le} \tag{8}$$

Thus all of the graphs, calculations, etc. found in [17,18] can be used directly.

To illustrate these results, let us take the case when $x_{2c} = 0$, and look at Figure 1 which is adapted from [17]. Some very interesting features may be noted:

(i) Along any straight line through the origin, the steady state behavior x_{1s}, x_{2s} as a function of Da is invariant. For straight lines below the multiplicity line (M) (curve 1), the steady state behavior is in the form of Figure 2, while for straight lines above line M (curve 2), the steady state behavior takes the form of Figure 3.

(ii) The range of dynamic instability behavior of the steady states depends on $\hat{B}$, α as shown in Figure 1. By reducing Le while keeping all other parameters fixed, the parameters $\hat{B}$, α move to the right along these straight lines. Curve 1 type lines would begin

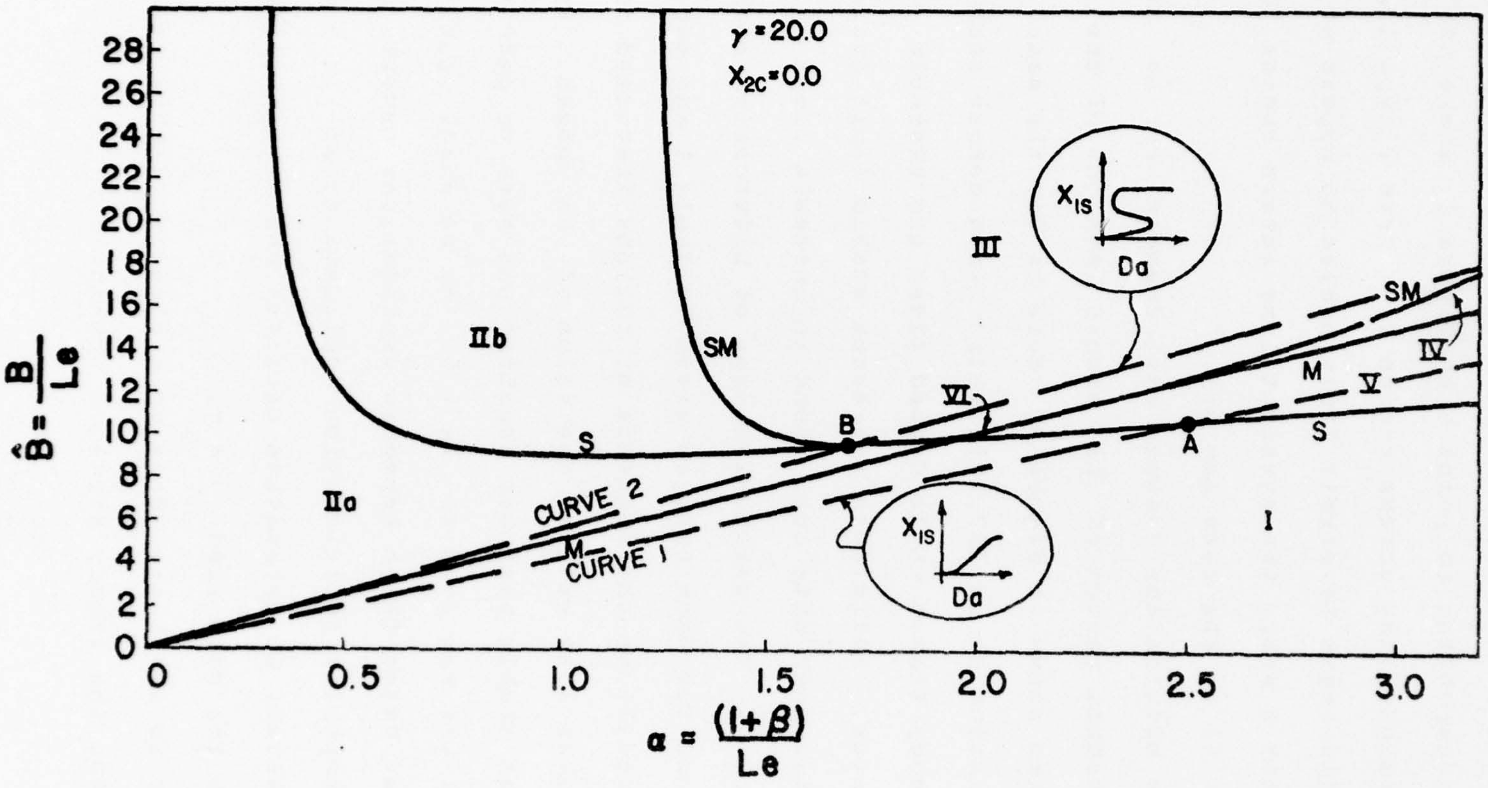

Figure 1 Influence of Lewis Number on dynamic behavior

to allow limit cycle behavior for Le values corresponding to point A on Figure 1, where the straight line enters region V. Curve 2 type lines would begin to permit limit cycles to appear at point B where the straight line enters region III (or VI as the case may be).

(iii) The bifurcation diagram with respect to Le at constant values of Da should have one of the forms shown in Figure 4. Here we use the same notation as in [17,18]; solid lines denote stable steady states while dashed lines are unstable steady states. Solid dots represent stable limit cycles while open dots correspond to unstable limit cycles. The particular type of bifurcation curve found for each case is given in Table 1 and depends strongly on the sequence of regions traversed in Figure 1 as well as the value of Da chosen. Note that stable periodic oscillations seem to persist all the way down to Le = 0. As we shall show, in some cases these harmonic oscillations become asymptotic to relaxation oscillations as $Le \to 0$. However, no relaxation oscillations are possible for the case when $\gamma \to \infty$.

In order to see these ideas more clearly, let us linearize Eqs. (4,7) about the steady state to obtain

$$\frac{d\underset{\sim}{y}}{dt} = \underset{\sim}{A}\,\underset{\sim}{y} \qquad (9)$$

where
$$y = \begin{bmatrix} x_1 - x_{1s} \\ x_2 - x_{2s} \end{bmatrix}$$

$$\underset{\sim}{A} = \begin{bmatrix} \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} \\ \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} \end{bmatrix}_{x_{1s}, x_{2s}}$$

As noted in [17,18], the bifurcation points to periodic solutions are the real roots of $\mathrm{tr}\ \underset{\sim}{A} = 0$ which also satisfy $\mathrm{Det}\ \underset{\sim}{A} > 0$ and we can examine the locus of these points as Le varies by solving the cubic

$$\mathrm{tr}\ \underset{\sim}{A} = \frac{C}{Le}\,[s^3 + a_2 s^2 + a_1 s + a_0] = 0 \tag{10}$$

Here
$$\left.\begin{aligned} r &= \frac{B}{1+\beta} \\ C &= \frac{r^2(1+\beta)}{\gamma^2(1-x_{1s})(1+x_{2s}/\gamma)^2} \\ a_0 &= -\left\{1 + \frac{Le}{1+\beta}\right\}\frac{\gamma^2}{r^2} \\ a_1 &= \frac{\gamma^2}{r} + \frac{\gamma^2}{r^2} - \frac{2\gamma}{r}\left(1 + \frac{Le}{1+\beta}\right) \\ a_2 &= -\left[\frac{\gamma^2}{r} + \frac{Le}{1+\beta} + 1 - \frac{2\gamma}{r}\right] \end{aligned}\right\} \tag{11}$$

The cubic in (10) may be solved numerically to determine the bifurcation points, s_1, s_2. The critical value of Lewis number, Le_c, above which there are no oscillations, is the solution to

$$\frac{(2a_2^3 - 9a_2a_1 + 27a_0)^2}{4} + [3a_1 - (a_2)^2]^3 = 0 \tag{12}$$

For the case where $\gamma \to \infty$, Eq. (10) reduces to a quadratic

$$\operatorname{tr} \underset{\sim}{A} = \frac{-r(1+\beta)}{(1-x_{1s})\mathrm{Le}} \left\{ s^2 - \frac{(r+1)s}{r} + \frac{1}{r}\left[1 + \frac{\mathrm{Le}}{1+\beta}\right]\right\} = 0 \qquad (13)$$

which has the solution

$$s = \frac{1}{2}\left[\frac{r+1}{r} \pm D^{1/2}\right] \qquad (14)$$

where

$$D = \left(\frac{r+1}{r}\right)^2 - \frac{4}{r}\left[1 + \frac{\mathrm{Le}}{1+\beta}\right] > 0 \qquad (15)$$

is required for real roots. Thus Le_c in this case is given by

$$\mathrm{Le}_c = \left[\frac{(r+1)^2}{4r} - 1\right](1+\beta) \qquad (16)$$

In general for values of $\mathrm{Le} < \mathrm{Le}_c$, there is a range of Da over which periodic solutions will exist provided $\operatorname{Det} \underset{\sim}{A} > 0$. The actual bifurcation value of Le depends on the value of Da selected.

The locus of the bifurcation points s_1, s_2 are explicitly calculated for two cases in Figures 2 and 3 and these serve to illustrate the essential points. Note that for parameters yielding a unique steady state always, i.e. $r < \frac{4\gamma}{\gamma-4}$ as in Figure 2 and for parameters allowing multiple steady states (i.e. $r > \frac{4\gamma}{\gamma-4}$ as in Figure 3), the range of transient instability $s_1 < x_{1s} < s_2$ expands as $\mathrm{Le} \to 0$. This may be seen explicitly for the case $\gamma \to \infty$, where $s_1 \to 1/r$ and $s_2 \to 1$ as $\mathrm{Le} \to 0$.

Thus for a fixed value of Da, limit cycles are expected to persist down to very low values of

Le as shown in Figure 4. In fact for the case of finite γ, these limit cycles become asymptotic to relaxation oscillations as Le vanishes. This may happen both for the case of a unique unstable steady state (Figure 5) or for the case of three unstable steady states (Figure 6). The relaxation trajectory begins at point A (Figures 5,6), follows the quasi-steady-state defined by $\dot{x}_2 = 0, \dot{x}_1 > 0$ to point B where it must jump quickly to C, follows $\dot{x}_2 = 0, \dot{x}_1 < 0$ again to point D where it jumps quickly to A again. Clearly this process repeats, giving a periodic solution of the limiting or reduced problem

$$\frac{dx_1}{dt} = f_1(x_1,x_2)$$

$$0 = f_2(x_1,x_2)$$

It is useful to discuss the properties of these relaxation oscillations (cf. Stoker [21] for a more general treatment). Firstly, it is easy to show that relaxation oscillations do not exist for the case $\gamma \to \infty$ because the isocline $\dot{x}_2 = 0$ does not have the proper form (i.e. three branches do not exist). Secondly, for relaxation oscillations, it is necessary that the steady states of the system (corresponding to intersections of $\dot{x}_1 = 0, \dot{x}_2 = 0$) fall on the middle branch of $\dot{x}_2 = 0$. It is easy to show as well that for steady states on either the upper or lower branch of $\dot{x}_2 = 0$, tr $\underset{\sim}{A} < 0$ always and no bifurcating periodic solutions are possible. Thus whenever there are limit cycle oscillations around a unique steady state or around three unstable steady states, these may become asymptotic to relaxation oscillations of the same type.

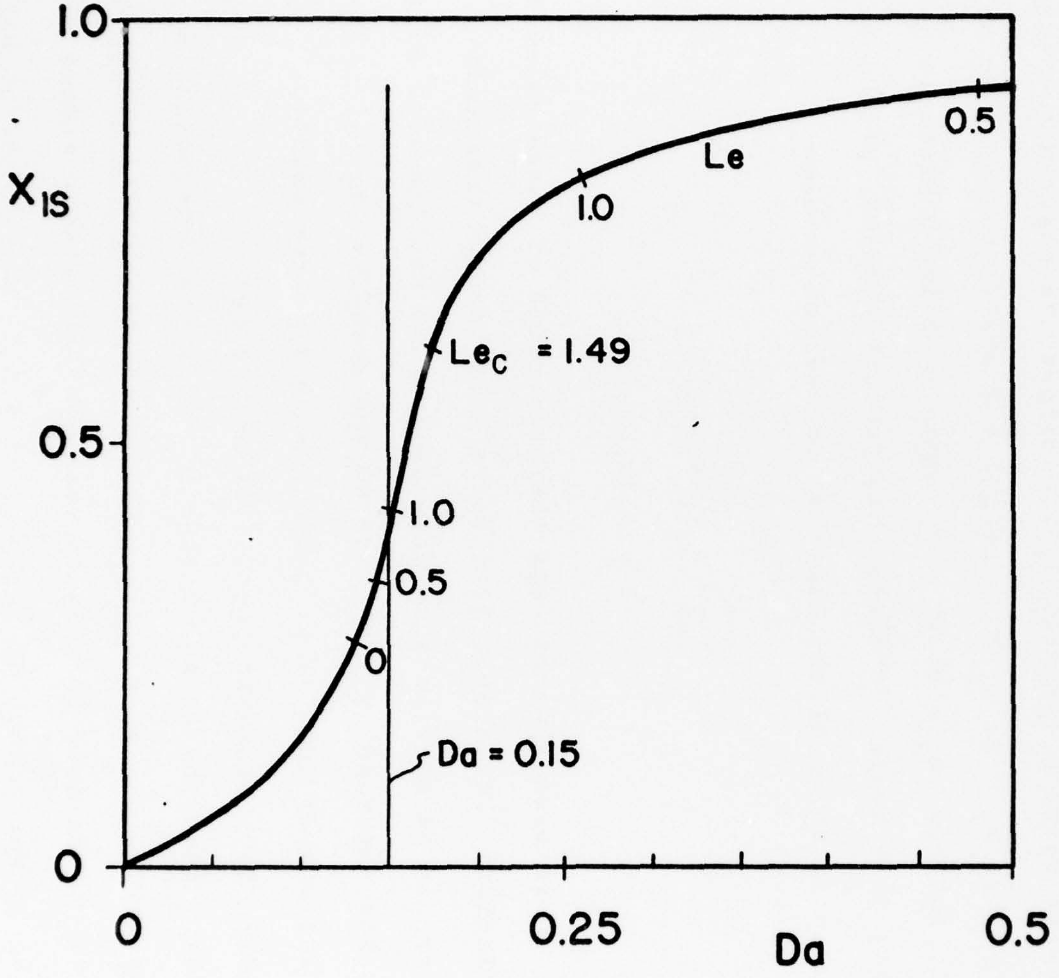

Figure 2 Steady state behavior and locus of bifurcation points as Le changes; $\gamma = 20$, $r = 4.05$, $\beta = 3.0$, $x_{2c} = 0$, $Le_c = 1.49$

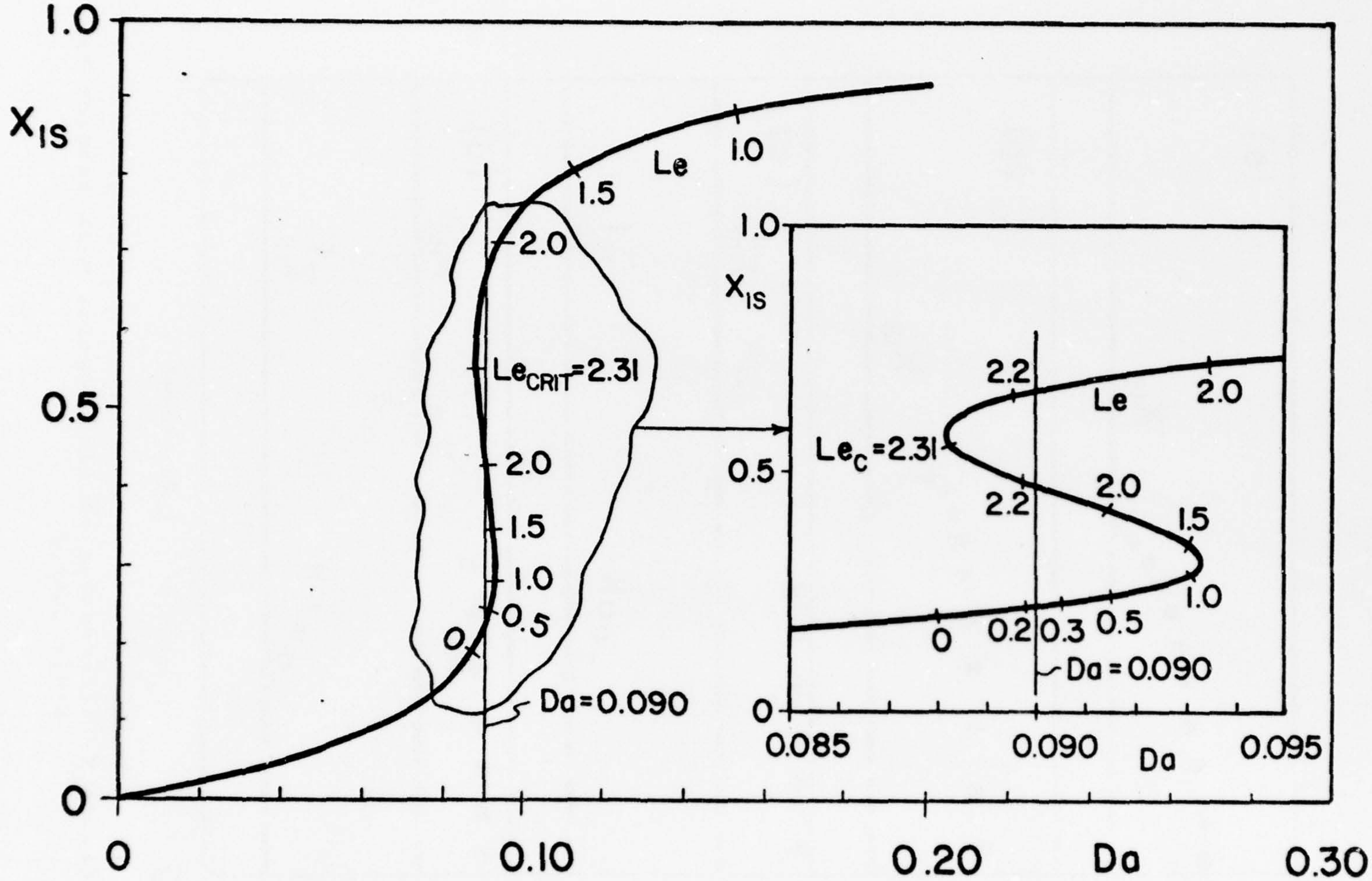

Figure 3 Steady state behavior and locus of bifurcation points as Le changes; $\gamma = 20$, $r = 5.5$, $\beta = 3.0$, $x_{2c} = 0$, $Le_c = 2.31$

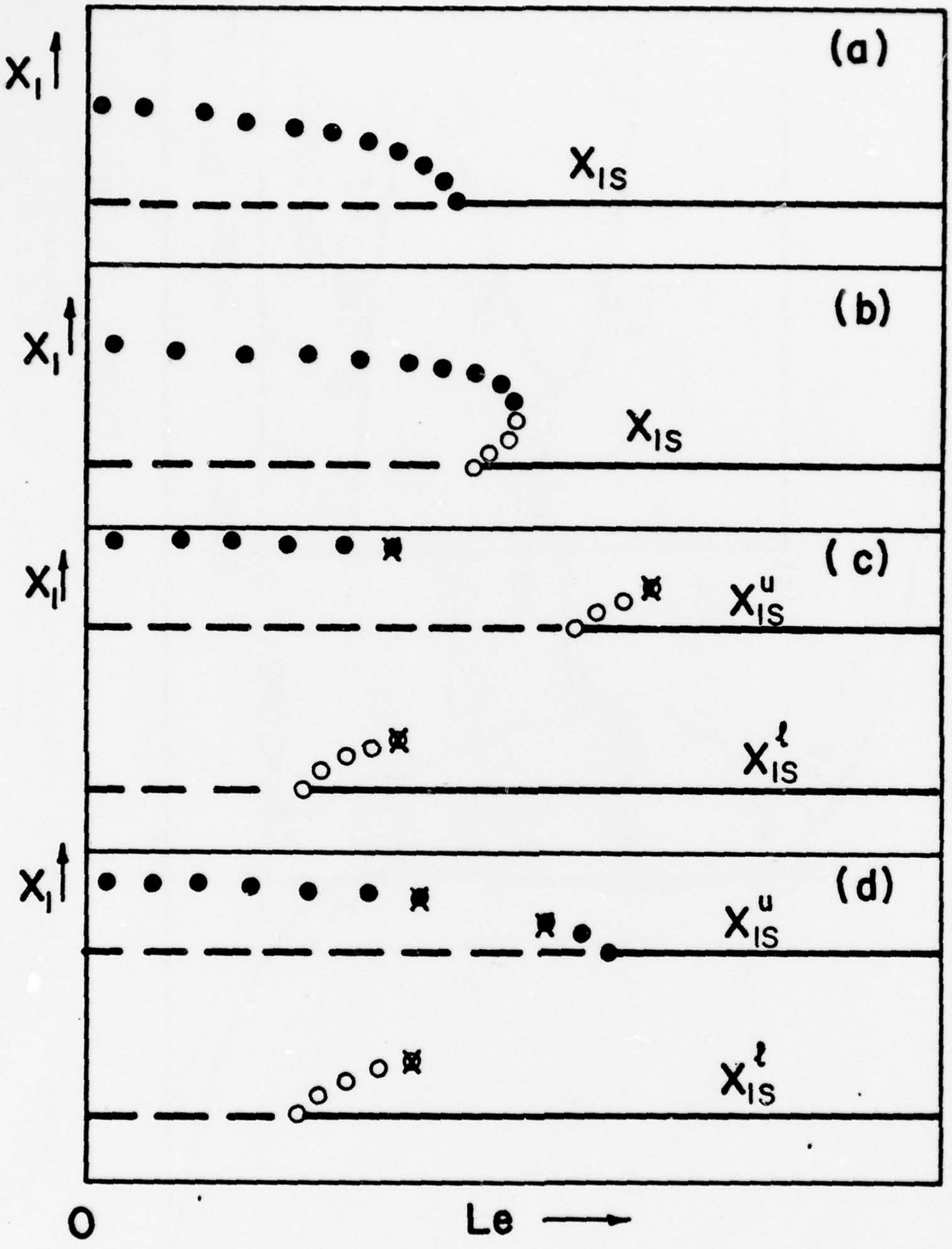

Figure 4 Bifurcation of limit cycles with respect to Lewis number

Table 1 Types of Bifurcation Behavior for Le

Sequence of Regions (Fig. 1) as Le → 0	Types of Bifurcation (Figure 4)
1. I → V	(i) Type (b) for left hand bifurcation point in region Va
	(ii) Type (a) otherwise
2. I → VI → IIIb → IV	(i) Type (d) for bifurcation in the region of multiplicity
	(ii) Type (a) for the upper branch in region of uniqueness
	(iii) Type (b) for the lower branch in region of uniqueness
3. I → IIIa → IIIb → IV	(i) Type (c) or type (d) for bifurcation in the region of multiplicity (depending on the particular value of Da)
	(ii) Type (a) for the upper branch in the region of uniqueness
	(iii) Type (b) for the lower branch in the region of uniqueness.

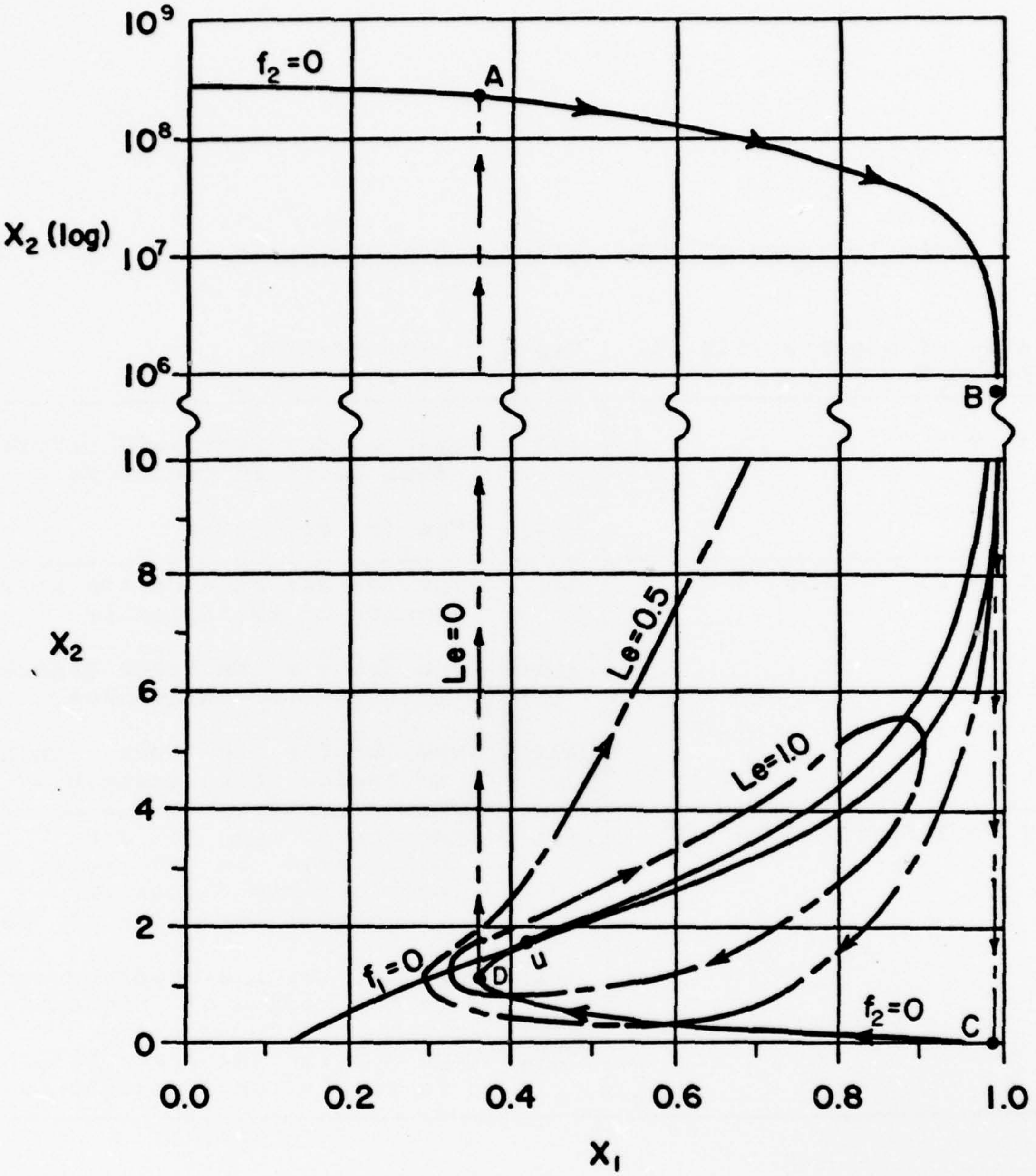

Figure 5 Sustained oscillations for the case of a unique steady state; $\gamma = 20$, $r = 4.05$, $\beta = 3.0$, $x_{2c} = 0$, $Da = 0.15$

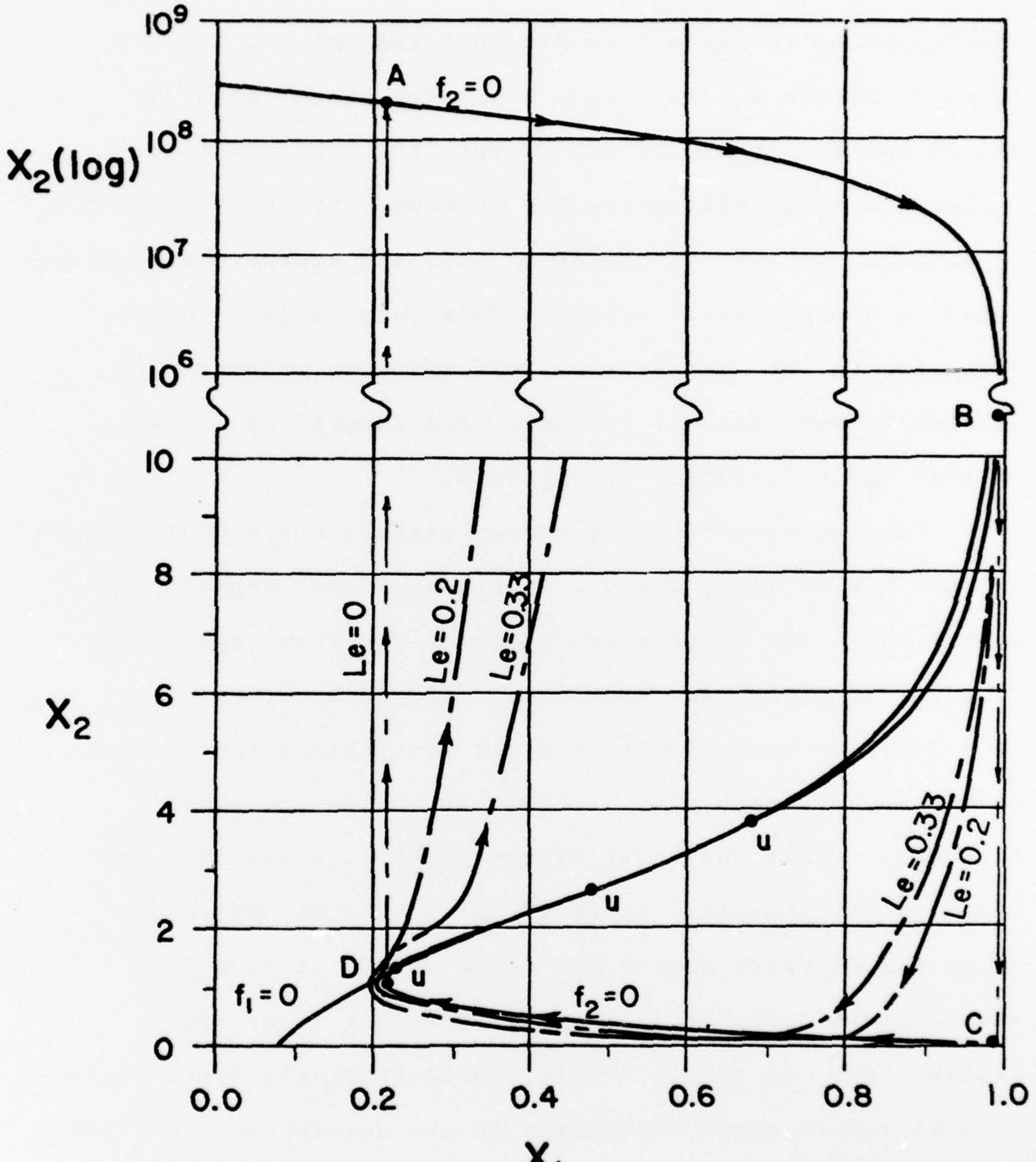

Figure 6 Sustained oscillations for the case of three steady states; $\gamma = 20$, $r = 5.5$, $\beta = 3.0$, $x_{2c} = 0$, $Da = 0.090$

As an illustration of these points, consider Figures 5 and 6 where computed stable limit cycles are shown as a function of Lewis number. The case of a unique steady state corresponding to curve 1 in Figure 1 and $Da = 0.15$, is shown in Figure 5. For $Le = 1.0$, the steady state is stable and surrounded by both stable and unstable limit cycles (to avoid cluttering the drawing, only the stable one is shown). As Le decreases to 0.5, the steady state becomes unstable and the limit cycle becomes very large. Further reduction in Le causes the limit cycle to approach the relaxation oscillation. Clearly this example is a case of type (b) bifurcation in Figure 4.

For the case of three steady states, the dynamic behavior as Le varies along curve 2 in Figure 1 was computed for $Da = 0.090$. The bifurcation behavior for this case is of type (c) in Figure 4. From about $Le = 2.25$ down to $Le = 2.16$, an unstable limit cycle was found surrounding a stable upper steady state. From $Le = 2.16$ to about $Le = 0.33$, only the lower steady state is stable with no limit cycles present. At about $Le = 0.33$ an unstable limit cycle appears around the lower steady state and a stable limit cycle appears, encircling all three steady states. For $Le < 0.21$, only the large stable limit cycle remains and it grows asymptotic to the relaxation oscillation as $Le \to 0$.

NONPOROUS CATALYTIC SURFACES

For nonporous catalytic materials such as catalytic wires or gauzes, the dynamic equations can take the general form of Eqs. (4,7) where depending on the specific model assumptions, the parameters Da, B, γ, β, Le can have several meanings [22]. To illustrate a specific case, consider the model of Ervin and Luss [23] for an infinite length, cylindrical, catalytic wire upon which oxidation reactions are carried out. This model assumes that mass transport to the wire surface is controlled by irreversible adsorption of reactant, and that the reaction products have negligible surface coverage. In primitive form, the model equations are

$$\frac{d\theta_A}{dt'} = k_1 c_g(\theta_T - \theta_A) - k_0 e^{-E/RT_s} \theta_A \tag{17}$$

$$\frac{\pi(d_w)^2}{4} \rho_s C_{ps} \frac{dT_s}{dt'} = \pi d_w h(T_g - T_s) + (-\Delta H)\pi d_w k_0 e^{-E/RT_s} \theta_A \tag{18}$$

where θ_A and θ_T represent the surface coverages of reactant and total surface respectively, T_g, c_g are the gas phase temperature and reactant concentration, and k_1 represents a temperature independent adsorption rate constant. Further, h is a heat transfer coefficient, T_s the wire temperature, and d_w the wire diameter. By defining the dimensionless quantities:

$$x_1 = \frac{\theta_T - \theta_A}{\theta_T} \ , \ x_2 = \frac{T_s - T_g}{T_g}(E/RT_g) \ , \ Da = \frac{k_0 e^{-\gamma}}{k_1 c_g} \ ,$$

$$t = t' k_1 c_g \ , \ \gamma = E/RT_g \ , \ B = \frac{(-\Delta H) k_1 c_g \theta_T \gamma}{hT_g} \ , \ Le = \frac{d_w \rho_s C_{ps} k_1 c_g}{4h} \ , \tag{19}$$

$$x_{2c} = \beta = 0$$

then Eqs. (17,18) take the form of Eqs. (4,7). Here our definition of the Lewis number for the catalytic wire is totally consistent with our general definition presented above, for

$$Le \equiv \frac{d_w \rho_s C_{ps} k_1 c_g}{4h} \equiv \frac{\left[\frac{\pi (d_w)^2}{4} \rho_s C_{ps} \Delta T / \pi d_w h \Delta T\right]}{(\theta_T / k_1 c_g \theta_T)} \tag{20}$$

or

$$Le \equiv \frac{\left\{\begin{array}{l}\text{time required to raise the wire temperature}\\ \text{an amount } \Delta T \text{ through heat}\\ \text{transfer from the gas}\end{array}\right\}}{\left\{\begin{array}{l}\text{time required to increase the surface concentration}\\ \text{by an amount } \theta_T \text{ due to adsorption on the surface}\end{array}\right\}}$$

which is, of course, the proper ratio of physical transport time constants.

Having put (17,18) into the equivalent CSTR form (4,7), all of the analysis of the previous section immediately applies. Thus one may readily determine the influence of the Lewis number (as well as other parameters) on the dynamic behavior. From a practical point of view one may calculate the critical Lewis number, Le_c and compare with the actual value to determine whether or not periodic solutions or relaxation type oscillations are to be expected. As noted in [22], for the most common models of catalytic wires, such oscillations are not predicted by the equations. However, there are models for which Le is in the proper range to allow oscillations for nonporous catalytic surfaces [24].

POROUS CATALYTIC MATERIALS

Porous catalytic materials such as catalyst particles, catalyst impregnated gels, etc. are known to have exotic dynamics which are influenced by the Lewis number. To illustrate, let us consider the case of a single irreversible first order reaction, for which the basic equations take the form [15]

$$\frac{\partial c}{\partial t'} = \frac{\mathcal{D}}{z^a}\frac{\partial}{\partial z}\left[z^a \frac{\partial c}{\partial z}\right] - k_0\, e^{-E/RT}\, c \tag{21}$$

$$\rho C_p \frac{\partial T}{\partial t'} = \frac{k}{z^a}\frac{\partial}{\partial z}\left[z^a \frac{\partial T}{\partial z}\right] + (-\Delta H) k_0\, e^{-E/RT}\, c \tag{22}$$

$$\left.\begin{aligned} \mathcal{D}\frac{\partial c}{\partial z} &= k_m(c_g - c) \\ k\frac{\partial T}{\partial z} &= h(T_g - T) \end{aligned}\right\} \quad z = \ell \tag{23}$$

and

$$\frac{\partial c}{\partial z} = \frac{\partial T}{\partial z} = 0 \quad \text{at} \quad z = 0 \tag{24}$$

where c is the reactant concentration, T the temperature, $\mathcal{D}$ the mass diffusivity, k the thermal conductivity, k_m and h external heat and mass transfer coefficients, and a is geometric parameter having the following values: $a = 0$ (slab), $a = 1$ (cylinder), $a = 2$ (sphere). By defining the dimensionless quantities

$$\begin{aligned} &x_1 = \frac{c_g - c}{c_g}, \quad x_2 = \frac{T - T_g}{T_g}\left[\frac{E}{RT_g}\right], \quad \phi^2 = \frac{k_0\, e^{-\gamma}\ell^2}{\mathcal{D}}, \quad r = z/\ell \\ &\tau = \frac{t'\mathcal{D}}{\ell^2}, \quad B = \frac{(-\Delta H)\mathcal{D} c_g}{kT_g}, \quad Le = \frac{\mathcal{D}\rho C_p}{k}, \quad \gamma = E/RT_g \\ &Sh = \frac{k_m \ell}{\mathcal{D}}, \quad Nu = \frac{h\ell}{k} \end{aligned} \tag{25}$$

one obtains the dimensionless equations

$$\frac{\partial x_1}{\partial \tau} = \frac{1}{r^a}\frac{\partial\left(r^a \frac{\partial x_1}{\partial r}\right)}{\partial r} + \phi^2(1 - x_1)\exp\left\{\frac{x_2}{1 + x_2/\gamma}\right\} = g_1(x_1,x_2) \tag{26}$$

$$\mathrm{Le}\frac{\partial x_2}{\partial \tau} = \frac{1}{r^a}\frac{\partial\left(r^a \frac{\partial x_2}{\partial r}\right)}{\partial r} + B\phi^2(1 - x_1)\exp\left\{\frac{x_2}{1 + x_2/\gamma}\right\} = g_2(x_1,x_2) \tag{27}$$

$$\left.\begin{aligned} &\frac{\partial x_1}{\partial r} + \mathrm{Sh}x_1 = 0 \qquad (28)\\ &\frac{\partial x_2}{\partial r} + \mathrm{Nu}x_2 = 0 \qquad (29)\end{aligned}\right\} \quad r = 1$$

$$\frac{\partial x_1}{\partial r} = \frac{\partial x_2}{\partial r} = 0 \qquad r = 0 \tag{30}$$

Notice that (28,29) are <u>Robin</u> type boundary conditions; however as Nu, Sh → ∞, they reduce to <u>Dirichlet</u> conditions of the form

$$x_1 = x_2 = 0\ ; \quad r = 1\ . \tag{31}$$

Consistent with the earlier definition, the Lewis number for this catalyst particle is the ratio of appropriate transport time constants; i.e.,

$$\mathrm{Le} \equiv \frac{\mathcal{D}\rho C_p}{k} \equiv \frac{\left(\frac{V_p\rho C_p\Delta T}{A_p k\Delta T/\ell}\right)}{\left(\frac{V_p\Delta c}{A_p\mathcal{D}\Delta c/\ell}\right)} \equiv \frac{\left\{\begin{array}{l}\text{time required to raise the catalyst}\\ \text{particle temperature an amount } \Delta T \text{ due to}\\ \text{heat conduction across the external surface}\end{array}\right\}}{\left\{\begin{array}{l}\text{time required to raise the catalyst parti-}\\ \text{cle concentration an amount } \Delta c \text{ due to}\\ \text{diffusive mass transport across the}\\ \text{external surface}\end{array}\right\}} \tag{32}$$

By the use of any number of lumping procedures [15], Eqs. (26-30) may be reduced to an equivalent set of CSTR equations of the form of Eqs. (4,7). Thus the effect of Lewis number may be seen by using the CSTR results developed above together with one of these lumping procedures.

To provide an example, consider the lumping procedure of Hlavaček and coworkers [5-7] for the case of a slab geometry ($a = 0$ in (26,27)). Their equivalent stirred tank equations take the form

$$\frac{dx_1}{d\tau} = -(\lambda_1)^2 x_1 + \phi^2 (1 - x_1) \exp\left\{\frac{x_2}{1 + x_2/\gamma}\right\} \tag{33}$$

$$Le \frac{dx_2}{d\tau} = -(\mu_1)^2 x_2 + B\phi^2 (1 - x_1) \exp\left\{\frac{x_2}{1 + x_2/\gamma}\right\} \tag{34}$$

where λ_1, μ_1 are first positive roots of the transcendental equations

$$\tan \lambda = - \lambda/Nu \tag{35}$$

$$\tan \mu = -\mu/Sh \tag{36}$$

Note that as $Nu, Sh \to \infty$, and the Dirichlet boundary conditions apply, $\lambda_1 = \mu_1 = \pi$. By defining

$$t = (\lambda_1)^2 \tau \quad , \; Da = \frac{\phi^2}{(\lambda_1)^2} \quad , \; 1 + \beta = (\mu_1)^2/(\lambda_1)^2 \quad , \; x_{2c} = 0$$

Equations (33,34) are exactly in the form of the CSTR equation (4,7). Thus all of the earlier CSTR analysis and resulting structure also applies to the catalyst particle problem.

In spite of numerical calculations showing reasonable agreement between the behavior of the distributed and approximate lumped systems, the formal, nonrigorous nature of these lumping approximations to distributed reacting systems may cause concern. Thus it is useful to consider more direct evidence that suggests we have the correct structure. Firstly, a number of detailed numerical case studies of the distributed catalyst particle

[6,8-14,16] with varying Lewis number show the type of behavior predicted from the lumping analysis. In particular, the oscillations observed become stiffer with decreasing Le so that distributed relaxation oscillations seem to be the plausible asymptote. The general nature of these distributed relaxation oscillations can be seen with the aid of Figure 5 and Eqs. (26-30). When Le → 0, then $g_2(x_1,x_2) = 0$ and (26) together with appropriate boundary conditions define the behavior of the system. For a given composition profile, $x_1(r)$, the equation $g_2(x_1,x_2) = 0$ and associated boundary conditions could have three quasi-steady-state solutions $x_2^{\ell}(r)$, $x_2^{m}(r)$, $x_2^{u}(r)$ as shown in Figure 7. This is similar to the situation for the lumped system shown in Figures 5 or 6 where for any value of x_1 between points A and B, there are three quasi-steady-state solutions x_2. It is conjectured that by analogy with the lumped case, $\frac{\partial x_1(r,t)}{\partial t} < 0$ on the lower branch $x_{2\ell}(r)$, and $\frac{\partial x_1(r,t)}{\partial t} > 0$ on the upper branch $x_2^{u}(r)$, so that a distributed relaxation oscillation jumping between a sequence of lower solutions $x_2^{\ell}(r)$ and a sequence of upper solutions $x_2^{u}(r)$ should occur.

Further evidence of this behavior may be seen if we let the composition profile $x_1(r)$ be the steady state solution corresponding to a steady state value of $x_{2ss}(r)$ on the middle branch such as in Figures 5 and 6. Recalling that $x_2^{\ell}(r) < x_2^{m}(r) = x_{2ss}(r) < x_2^{u}(r)$, we can see that $\frac{\partial x_1(r,t)}{\partial t}$ in Eqn. (26) will have the signs noted above if $x_{2ss}(r)$ is replaced by $x_2^{\ell}(r)$ (lower branch) or $x_2^{u}(r)$ (upper branch). This is due to the monotone increasing nature of the term $\exp\left\{\frac{x_2}{1 + x_2/\gamma}\right\}$ in Eqn. (26).

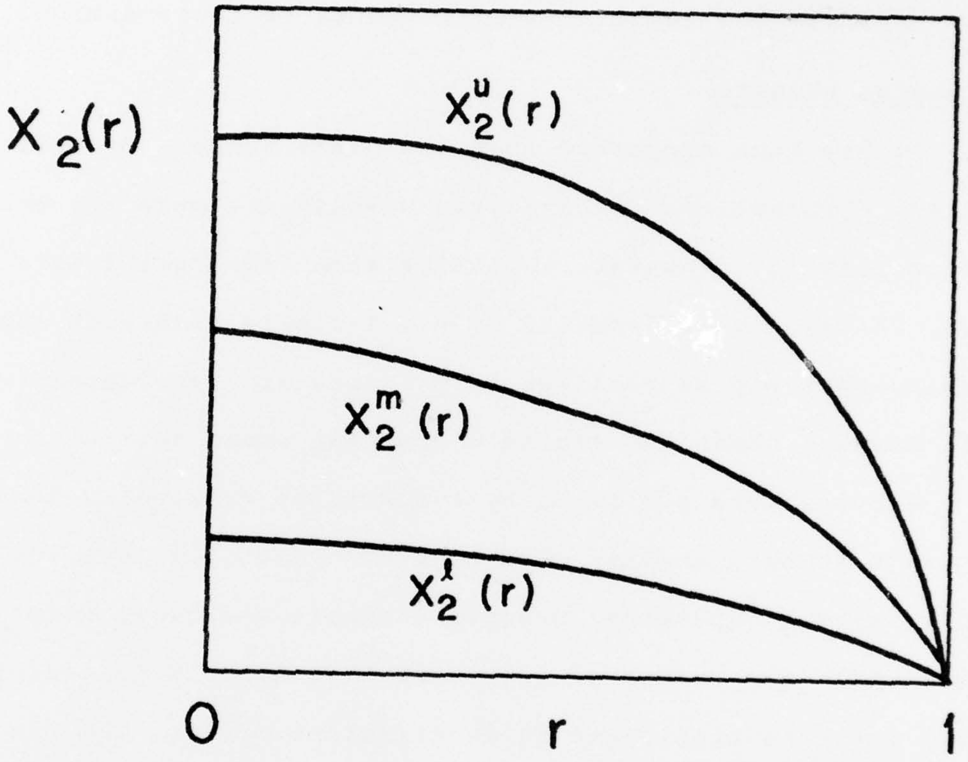

Figure 7 Quasi-steady-state catalyst particle temperature profiles

One should note that the observed oscillations of Lee and Luss [8] for Le = 0.1 are rather stiff; however, their spatial character, showing a transient hot spot close to the external surface, cannot be due to purely relaxation phenomena. This illustrates the point that relaxation oscillations must be considered no more than an asymptote to the bifurcating limit cycle oscillations found at finite values of Lewis number.

CONCLUDING REMARKS

It has been suggested that the Lewis numbers necessary to allow oscillations in catalytic systems are much too small to be realistic. However, as can be seen from recent work (e.g., [4,24]), more detailed models indicate that such small Lewis numbers may be realized in practice and consideration of Lewis numbers close to zero is a fruitful exercise.

A conjecture put forth by a number of workers is that for Lewis numbers smaller than some bifurcation value, the steady state in question becomes unstable and oscillations arise, while for values greater than this bifurcation value the steady state is stable and no oscillations arise. The present analysis shows that this conjecture is, in principle, correct; however as seen in Figure 4, things are a little more complicated. For a unique steady state, bifurcation can be to the right as in Figure 4(b) and stable oscillations observed even when the steady state is stable. Furthermore, for the case of multiple steady states as in Figure 4(c),(d), there are different bifurcation values of the Lewis number for the upper and the lower branches.

Although a rather wide range of reacting systems have been considered here, it has been possible to put them all within a unified mathematical structure. This has the advantage that in analyzing new problems of stability and oscillations, these results may serve as an aid to physical intuition in order to evaluate the dynamic phenomena to be expected.

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The influence of Lewis number on stability and oscillations for stirred tanks, catalytic wires and gauzes, and catalyst particles is determined quantitatively. The mathematical structure is discussed and illustrated by example. Relaxation oscillations are found to be the natural asymptote to the bifurcating limit cycles as the Lewis number vanishes.

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