A Justification of the Internal Isothermal Model for Gas-Solid Catalytic Reactions

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The commonly employed internal isothermal model for gas-solid catalytic reactions, wherein the pellet is assumed internally isothermal but with internal concentration gradient, is justified by analyzing the full non-isothermal diffusion-reaction equations as an appropriate perturbation problem (β small, and Bi_h/β finite). The internal isothermal model is shown to be the zeroth order solution of the perturbation problem. Analytic expressions for the first order corrections are given for a first order reaction.

SCOPE

It has been stressed in various analyses (Carberry 1975) and experimental observations (Kehoe and Butt 1972, Butt et al. 1977) that since the Biot number for external mass transfer, Bi_m, is much larger than that for heat transfer, Bi_h, the predominant temperature gradient in gas-solid catalytic reactions occurs in the external film. The catalyst pellet itself may therefore be taken as internally isothermal, but with internal gradients of concentration. The assumption of pellet internal isothermality is rigorously examined here, in general, and in some detail for the irreversible first order reaction.

CONCLUSIONS AND SIGNIFICANCE

The assumption of pellet internal isothermality is rigorously justified for gas-solid catalytic reactions by regular perturbation theory. It is shown that if the general non-isothermal conservation equations for diffusion-reaction in a catalyst pellet are cast in the form of a regular perturbation problem with β—the Prater temperature—as the small parameter and Bi_h/β finite, the general equations yield the commonly employed internal isothermal model as the zeroth order solution. Higher order solutions are obtained analytically for a first order reaction, which provide corrections to the internal pellet temperature, and thus superior estimates of the catalytic effectiveness. Both compare rather well with exact numerical solutions of the general conservation equations. In the case of multiple steady states, the analysis also provides a tighter upper bound on the region of multiplicity than that obtained from the assumption of pellet isothermality.

THE BASIC EQUATIONS

For a non-isothermal irreversible reaction occurring in the steady state in a catalyst pellet of symmetric shape, the fundamental mass and heat balances yield the diffusion-reaction equations (Aris 1975)

$$\frac{1}{x^n}\frac{d}{dx}\left[D_e x^n \frac{dC}{dx}\right] = r(C,T); \quad x\epsilon(0,R) \qquad (1a)$$

$$\frac{1}{x^n}\frac{d}{dx}\left[\lambda_e x^n \frac{dT}{dx}\right] = -(-\Delta H)r(C,T); \quad x\epsilon(0,R) \qquad (1b)$$

where $n = 0$, 1 and 2 represent the pellet geometries infinite slab, infinite cylinder and sphere, respectively. The associated general boundary conditions are

$$\frac{dC}{dx} = 0; \quad x = 0; \quad \frac{dT}{dx} = 0 \qquad (2a)$$

$$D_e \frac{dC}{dx} = k_g(C_f - C); \quad x = R; \quad \lambda_e \frac{dT}{dx} = h(T_f - T) \qquad (2b)$$

Assuming constant properties, and introducing the dimensionless variables

$$u = C/C_f, \quad v = T/T_f, \quad s = x/R, \quad Bi_m = k_g R/D_e,$$
$$Bi_h = hR/\lambda_e, \quad f(u,v) = r(C,T)/r(C_f,T_f),$$
$$\phi^2 = r(C_f,T_f)R^2/D_e C_f, \quad \beta = (-\Delta H)D_e C_f/\lambda_e T_f \qquad (3)$$

Equations (1-2) reduce to the dimensionless form

$$L[u] = \phi^2 f(u,v); \quad s\epsilon(0,1) \qquad (4a)$$

$$L[v] = -\beta\phi^2 f(u,v); \quad s\epsilon(0,1) \qquad (4b)$$

$$\frac{du}{ds} = 0; \quad s = 0; \quad \frac{dv}{ds} = 0 \qquad (5a)$$

$$\frac{du}{ds} = Bi_m(1-u); \quad s = 1; \quad \frac{dv}{ds} = Bi_h(1-v) \qquad (5b)$$

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where

$$L[\,] \equiv \frac{1}{s^n}\frac{d}{ds}\left(s^n\frac{d}{ds}[\,]\right)$$

The catalyst effectiveness factor, η, is as usual, defined as the ratio of the actual reaction rate to that which would have prevailed if the entire catalyst pellet interior were at bulk fluid conditions

$$\eta = (n+1)\int_0^1 s^n f(u, v)\,ds \tag{6}$$

and can be expressed variously, utilizing Equations (4-5)

$$\eta = \frac{(n+1)}{\phi^2}u'(1) = \frac{(n+1)Bi_m}{\phi^2}[1 - u(1)] \tag{7a}$$

$$= -\frac{(n+1)}{\beta\phi^2}v'(1) = \frac{(n+1)Bi_h}{\beta\phi^2}[v(1) - 1] \tag{7b}$$

As noted earlier, for most gas-solid catalytic reactions, β is a relatively small number ($\sim$0.05), while Bi_m/Bi_h is relatively large ($\gtrsim 50$). Physically, the reason this occurs is that the effective diffusion coefficient for gas within the pellet, D_e is smaller than the bulk gas value, while the effective pellet thermal conductivity λ_e is higher. Also note that the ratio $Bi_h/\beta \equiv hRT_f/(-\Delta H)D_eC_f$ is independent of solid thermal properties.

THE PERTURBATION PROBLEM

As discussed, since β—the Prater temperature—is generally relatively small due to the high pellet thermal conductivity, we may call it ϵ, a small parameter. Let us further let Bi_h/β to be finite, since it is independent of solid thermal properties. With this, Equations (4-5) take the form of a *regular perturbation* problem (Bellman 1966, Cole 1968)

$$L[u] = \phi^2 f(u, v); \quad s\epsilon(0, 1) \tag{8a}$$

$$L[v] = -\epsilon\phi^2 f(u, v); \quad s\epsilon(0, 1) \tag{8b}$$

$$u' = 0; \quad s = 0; \quad v' = 0 \tag{9a}$$

$$u' = Bi_m(1 - u); \quad s = 1; \quad v' = \left(\frac{Bi_h}{\beta}\right)\epsilon(1 - v) \tag{9b}$$

since the reduced (i.e., $\epsilon \equiv 0$) problem is of the same order as the full (i.e., $\epsilon \neq 0$) problem. Equations (8-9) may thus be solved by the regular perturbation method, in which u and v are taken to have the asymptotic form

$$u(x) \sim \sum_{j=0}^{\infty} \epsilon^j u_j(s), \quad v(s) \sim \sum_{j=0}^{\infty} \epsilon^j v_j(s) \tag{10}$$

For u and v of the form (10), $f(u, v)$ takes the asymptotic form

$$f(u, v) \sim \sum_{j=0}^{\infty} \epsilon^j f_j(u_0, v_0, u_1, v_1, \ldots, u_j, v_j) \tag{11}$$

where

$$f_0 = f(u_0, v_0)$$

$$f_1 = f_u(u_0, v_0)u_1 + f_v(u_0, v_0)v_1$$

$$f_2 = f_u(u_0, v_0)u_2 + f_v(u_0, v_0)v_2 + f_{uv}(u_0, v_0)u_1v_1 + [\{f_{uu}(u_0, v_0)u_1^2 + f_{vv}(u_0, v_0)v_1^2\}/2]$$

and $f_u(u_0, v_0)$ means $\partial f/\partial u$ evaluated at (u_0, v_0), etc.

Substituting the asymptotic forms suggested by Equations (10-11) in Equations (8-9), and comparing terms of equal order in ϵ gives for the ϵ^0 terms

$$L[u_0] = \phi^2 f(u_0, v_0); \quad s\epsilon(0, 1) \tag{12a}$$

$$L[v_0] = 0; \quad s\epsilon(0, 1) \tag{12b}$$

$$u_0' = 0; \quad s = 0; \quad v_0' = 0 \tag{13a}$$

$$u_0' = Bi_m(1 - u_0); \quad s = 1; \quad v_0' = 0 \tag{13b}$$

which imply that

$$v_0(s) \equiv K, \quad \text{a constant} \tag{14}$$

and u_0 satisfies

$$L[u_0] = \phi^2 f(u_0, K); \quad s\epsilon(0, 1) \tag{15}$$

$$u_0' = 0; \quad s = 0 \tag{16a}$$

$$u_0' = Bi_m(1 - u_0); \quad s = 1 \tag{16b}$$

Note that the zeroth order solution for temperature, v_0 is as yet an undetermined constant. The zeroth order solution for reactant concentration, u_0 can be found in terms of K by solving Equations (15-16).

Comparing terms of order ϵ^1 in Equations (8-9) gives that the first order corrections, u_1 and v_1, satisfy

$$L[u_1] = \phi^2 f_1(u_0, K, u_1, v_1); \quad s\epsilon(0, 1) \tag{17a}$$

$$L[v_1] = -\phi^2 f(u_0, K); \quad s\epsilon(0, 1) \tag{17b}$$

along with the boundary conditions

$$u_1' = 0; \quad s = 0; \quad v_1' = 0 \tag{18a}$$

$$u_1' = -Bi_m u_1; \quad s = 1; \quad v_1' = \frac{Bi_h}{\beta}(1 - K) \tag{18b}$$

From Equation (17*b*),

$$\int_0^1 s^n L[v_1]\,ds \equiv \int_0^1 \frac{d}{ds}\left[s^n\frac{dv_1}{ds}\right]ds = -\phi^2\int_0^1 s^n f(u_0, K)\,ds$$

On integrating the *lhs*, and applying the boundary conditions of Equation (18), this yields

$$\frac{Bi_h}{\beta}(K - 1) = \phi^2\int_0^1 s^n f(u_0, K)\,ds \tag{19}$$

which is an equation for the unknown constant K, since u_0 is "known" in terms of K from Equations (15-16). It is important to note here that Equations (15-16, 19) are *precisely* a statement of the internal isothermal model for the catalyst pellet (Luss 1977).

Thus summarizing so far, we have shown that if the full non-isothermal equations for diffusion-reaction in a catalyst pellet are considered as a perturbation problem with β the small parameter *and* Bi_h/β finite, the zeroth order solution of the full problem is precisely the commonly-employed model where the pellet is assumed internally isothermal, but with an internal concentration gradient. Also note that if the boundary condition for v at $s = 1$ is not transformed as $Bi_h(1 - v) = (Bi_h/\beta)\epsilon(1 - v)$, then the internal isothermal model does *not* result. In that case, the zeroth order solution yields $v_0(s) \equiv 1$, which implies that the pellet temperature is identical to that of the bulk gas.

Also observe that Equation (19), which gives the unknown constant K, may well have multiple solutions;

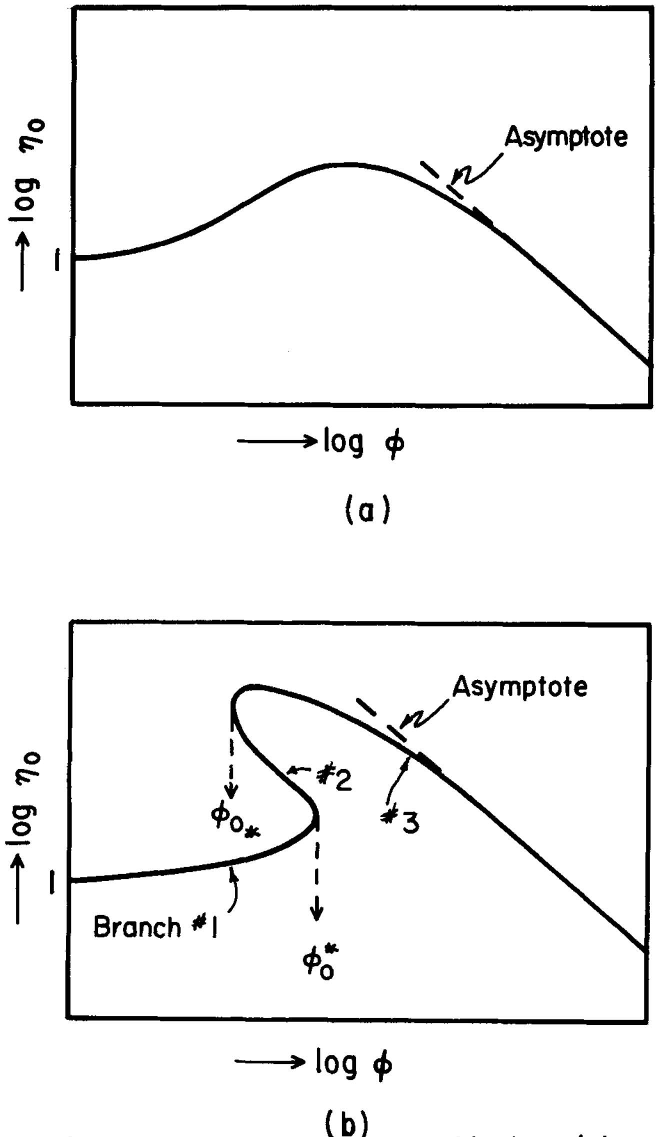

Figure 1. The general shape of the η_0-ϕ curve (a) unique solutions for all ϕ, (b) multiple solutions for a range of ϕ.

this point is further elaborated in the next section.

There are three other remarks that are worth making at this juncture. The first is that, as is usual in perturbation problems, the equations which first and higher order corrections satisfy are *linear*, although those for the zeroth order solution are *nonlinear*. This is already apparent in the context of the first order correction Equations (17-18); the higher order corrections ($j \geq 2$) satisfy

$$L[u_j] = \phi^2 f_j(u_0, K, u_1, v_1, \ldots, u_j, v_j); \quad s\epsilon(0, 1) \tag{20a}$$

$$L[v_j] = -\phi^2 f_{j-1}(u_0, K, u_1, v_1, \ldots, u_{j-1}, v_{j-1}); \quad s\epsilon(0, 1) \tag{20b}$$

$$u_j' = 0; \quad s = 0; \quad v_j' = 0 \tag{21a}$$

$$u_j' = -Bi_m u_j; \quad s = 1; \quad v_j' = -\frac{Bi_h}{\beta} v_{j-1} \tag{21b}$$

which are linear in u_j, v_j. The explicit calculation of u_j and v_j requires prior evaluation of u_k, v_k; $k = 0 \to j - 1$.

Secondly, just as the full evaluation of $v_0(s) \equiv K$ required going to the first order correction Equations (17-18) and deriving therefrom Equation (19) as a consistency condition, the full evaluation of $v_1(s)$ is made from the second order correction equations, and so on.

Finally, utilizing the expansion, Equation (11), for f, an asymptotic form for the effectiveness factor η can be written as

$$\eta \sim \sum_{j=0}^{\infty} \epsilon^j \eta_j \tag{22}$$

where

$$\eta_j = (n + 1) \int_0^1 s^n f_j(u_0, K, u_1, v_1, \ldots, u_j, v_j) ds \tag{23}$$

For $j = 0$, this gives, using Equation (19)

$$\eta_0 = \frac{(n + 1)Bi_h}{\beta\phi^2} [K - 1] \tag{24}$$

which is precisely the catalytic effectiveness predicted by the internal isothermal model. Higher order corrections to η_0 are simply

$$\eta_j = \frac{(n + 1)Bi_h}{\beta\phi^2} v_j(1) \tag{25}$$

utilizing Equation (20b) and its associated boundary conditions.

Although all of the above has been general, to obtain numerical results and to evaluate contributions of higher order corrections, it becomes necessary to specify the kinetic expression $f(u, v)$. Since only the first order irreversible reaction permits analytic evaluation for the isothermal case, this is now considered.

THE IRREVERSIBLE FIRST ORDER REACTION

For the irreversible first order reaction,

$$f(u, v) = u\rho^2(v) \tag{26}$$

where

$$\rho(v) = \exp\left\{\frac{\gamma}{2}\left(1 - \frac{1}{v}\right)\right\} \tag{27}$$

and $\gamma = E/R_g T_f$ is the dimensionless activation energy.

From Equations (15-16), u_0 for the slab ($n = 0$) and the sphere ($n = 2$) is given by (Pereira et al. 1979)

$$u_0(s) = \frac{\cosh(Xs)}{\cosh X + (X/Bi_m)\sinh X}; \quad n = 0 \tag{28a}$$

$$= \frac{\sinh(Xs)}{s[\sinh X + (1/Bi_m)(X \cosh X - \sinh X)]}; \quad n = 2 \tag{28b}$$

where $X = \phi\rho(K)$. Substituting these in Equation (19), and carrying out the indicated integration, gives that K satisfies the transcendental equation:

$$\frac{Bi_h}{\beta}(K - 1) = F(X) \tag{29}$$

where

$$F(X) = \frac{X \tanh X}{1 + (X/Bi_m)\tanh X}; \quad n = 0 \tag{29a}$$

$$= \frac{X \coth X - 1}{1 + (1/Bi_m)(X \coth X - 1)}; \quad n = 2 \tag{29b}$$

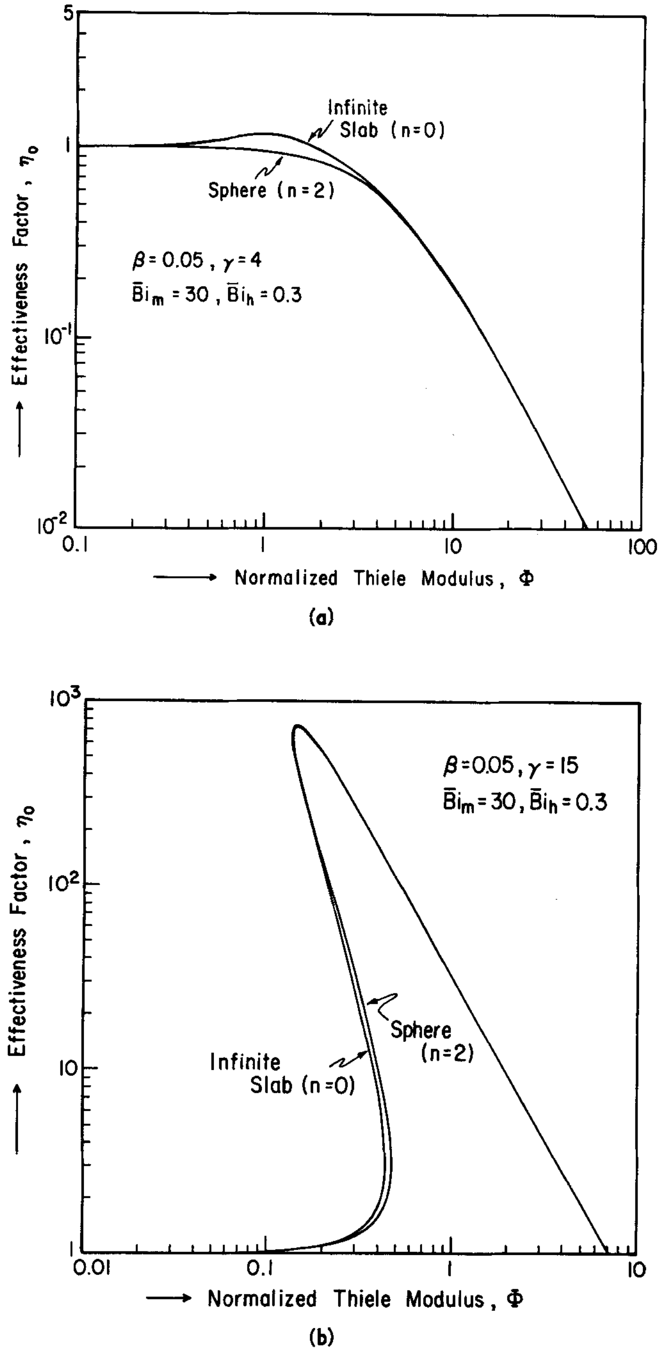

Figure 2. The η_0-Φ curves for the infinite slab ($n = 0$) and sphere ($n = 2$), (a) unique solutions for all Φ, (b) multiple solutions for a range of Φ.

and from Equation (24), either sides of Equation (29) are precisely $\phi^2\eta_0/(n + 1)$.

It is readily shown from Equations (29) that if ϕ is small, $K \to 1$ and $\eta_0 \to 1$ as $\phi \to 0$. For large ϕ, in the exothermic ($\beta > 0$) case, two cases arise depending on whether Bi_m is finite or infinite; as $\phi \to \infty$,

I. $Bi_m = \infty$:

$$K \to \infty \equiv K_u, \eta_0 \to (n + 1)\exp(\gamma/2)/\phi \tag{30}$$

II. Bi_m finite:

$$K \to 1 + (\beta Bi_m/Bi_h) \equiv K_u, \eta_0 \to (n + 1)Bi_m/\phi^2$$

Numerical calculations (Cresswell 1970) and analytic results (Pereira et al. 1979) indicate that Equations (29) may possess multiple solutions (i.e., multiple K values). It has been recently shown (Pereira et al. 1979) that

a. For $\gamma \leq 4$, unique solutions result for all ϕ, β, Bi_m and Bi_h.

b. For fixed values of $\gamma \epsilon (4, 8)$ and Bi_m, there exists a critical value of ϕ, termed ϕ_c, such that unique solutions result for all Bi_h and β values if $\phi > \phi_c$, while three solutions result for a range of Bi_h/β values if $\phi < \phi_c$.

c. For a fixed $\gamma \geq 8$ and $Bi_m = \infty$, there is always a range of Bi_h/β values, regardless of ϕ, wherein three solutions result. However, if Bi_m is finite, then there exists a critical value of ϕ, ϕ_c such that the solution pattern is exactly the same as described above in *b*.

There is an η_0, given by Equation (24), corresponding to each K. Whenever multiple solutions exist, the region of multiplicity can equivalently be represented as a range of ϕ, for fixed values of the other physico-chemical parameters. On a log-log plot, the curve of η_0 versus ϕ will have the general shape shown in Figure 1a for the case where unique solutions exist for all ϕ, and in Figure 1b when multiple solutions exist for a range of ϕ values. From Equation (30), the asymptotic slope for large ϕ is -1 for $Bi_m = \infty$, and -2 for finite Bi_m. In the case of multiple solutions, the region of multiplicity is bounded by $\phi \epsilon [\phi_{0*}, \phi_0^*]$, where the bounds are obtained by evaluating the transcendental Equation (29) numerically (Pereira et al. 1979). From the qualitative behavior analyzed in the same paper it follows that K rises monotonically as the $\eta_0 - \phi$ curve is traversed, from $K \to 1$ as $\phi \to 0$ to K_u as $\phi \to \infty$. Thus $dK/d\phi > 0$, if unique solutions exist for all ϕ (Figure 1*a*) *or* on branches 1 and 3 in the case of multiple solutions (Figure 1*b*), and $dK/d\phi < 0$ on branch 2 (Figure 1*b*).

If the length dimension used in defining ϕ and Bi is changed from R to V_p/S_x, where V_p is the pellet volume and S_x the external pellet surface area; thus

$$\Phi = \phi/(n + 1), \quad \overline{Bi} = Bi/(n + 1)$$

then the various catalyst pellet shapes have the *same* asymptotic behavior for small or large Φ, and then $\eta_0 - \Phi$ curves for various shapes follow one another rather closely over the entire Φ range as shown in Figures 2a and 2b, just as they do in the isothermal case (Aris 1957). What is most interesting and useful is that the region of multiplicity for the various shapes is also thereby virtually normalized. For the parameters of Figure 2b, this region is $\Phi \epsilon [0.1349, 0.4404]$ for the slab, and $\Phi \epsilon [0.1370, 0.4779]$ for the sphere. Thus although asymptotically they are the same, the $\eta_0 - \Phi$ curve for the sphere is always somewhat lower and to the right of the curve for the slab.

In the case of the first order reaction, analytic solutions for u_1, v_1 and hence η_1 can be obtained following the procedure outlined in the previous section, where for the *infinite slab* ($n = 0$)

$$u_1(s) = \frac{\gamma A^2}{2K^2} + \psi \cosh Xs + \frac{\gamma X A \Delta}{2K^2} s \sinh Xs - \frac{\gamma A^2}{6K^2} \cosh 2Xs \tag{31a}$$

$$v_1(s) = \Delta - A \cosh Xs \tag{31b}$$

$$\eta_1 = \frac{Bi_h}{\beta\phi^2} [\Delta - A \cosh X] \tag{32}$$

where

$$A = 1/[\cosh X + (X/Bi_m)\sinh X] \tag{33a}$$

$$\psi = -\frac{\gamma X \Delta A^2}{2K^2} [\sinh X + (1/Bi_m)(\sinh X + X \cosh X)]$$

$$+\frac{\gamma A^3}{6K^2}[\cosh 2X + (2X/Bi_m)\sinh 2X - 3] \quad (33b)$$

$$\Delta = \frac{(Bi_h/\beta)A\cosh X - (\gamma XA^3/3K^2)(2+\cosh^2 X)\sinh X}{(Bi_h/\beta) - (\gamma XA^2/2K^2)(X + \sinh X\cosh X)} \quad (33c)$$

and $X = \phi\rho(k)$ as before.

For small ϵ, it is sufficient to calculate only the first order corrections since successive terms progressively contribute negligibly. The asymptotic forms of Equations (10) and (22) are thus approximated as

$$u(s) \sim u_0(s) + \epsilon u_1(s) + 0(\epsilon^2) \quad (34a)$$

$$v(s) \sim K + \epsilon v_1(s) + 0(\epsilon^2) \quad (34b)$$

$$\eta \sim \eta_0 + \epsilon\eta_1 + 0(\epsilon^2) \quad (34c)$$

For the *sphere* ($n = 2$)

$$u_1(s) = \frac{\Omega \sinh Xs}{s} + \frac{\gamma XB\Lambda}{2K^2}\left\{\cosh Xs - \frac{\sinh Xs}{2Xs}\right\} - \frac{\gamma XB^2}{4K^2}\left[\{\mathrm{Chi}(3Xs) - \mathrm{Chi}(Xs)\}\frac{\sinh Xs}{s} - \{\mathrm{Shi}(3Xs) - 3\,\mathrm{Shi}(Xs)\}\frac{\cosh Xs}{s}\right] \quad (35a)$$

$$v_1(s) = \Lambda - (B/s)\sinh Xs \quad (35b)$$

$$\eta_1 = \frac{3Bi_h}{\beta\phi^2}[\Lambda - B\sinh X] \quad (36)$$

where

$$B = 1/[\sinh X + (1/Bi_m)(X\cosh X - \sinh X)] \quad (37a)$$

$$\Omega = -\frac{\gamma X\Lambda B^2}{2K^2}\left[\cosh X - \frac{\sinh X}{2X} + (1/Bi_m)\left(X\sinh X - \frac{\cosh X}{2} + \frac{\sinh X}{2X}\right)\right] + \frac{\gamma XB^2}{4K^2}[\mathrm{Chi}(3X) - \mathrm{Chi}(X)] - \frac{\gamma XB^3}{4K^2}[\mathrm{Shi}(3X) - 3\,\mathrm{Shi}(X)][\cosh X + (1/Bi_m)(X\sinh X - \cosh X)] \quad (37b)$$

$$\Lambda = \frac{(Bi_h/\beta)B\sinh X - (\gamma X^2B^3/4K^2)[\mathrm{Shi}(3X) - 3\,\mathrm{Shi}(X)]}{(Bi_h/\beta) + (\gamma XB^2/2K^2)[X - \sinh X\cosh X]} \quad (37c)$$

and $X = \phi\rho(K)$ as before.

Shi(x) and Chi(x) are integrals related to the exponential integral, defined as (Abramowitz and Stegun 1965)

$$\mathrm{Shi}(x) = \int_0^x \frac{\sinh t}{t}\,dt,$$

$$\mathrm{Chi}(x) = \bar{\gamma} + \ln x + \int_0^x \frac{\cosh t - 1}{t}\,dt \quad (38)$$

where $\bar{\gamma} = 0.57721\ldots$ is Euler's constant. The functions Shi(x) and Chi(x) have series expansions

$$\mathrm{Shi}(x) = \sum_{n=0}^{\infty} \frac{x^{2n+1}}{(2n+1)(2n+1)!} \quad (39a)$$

$$\mathrm{Chi}(x) = \bar{\gamma} + \ln x + \sum_{n=1}^{\infty} \frac{x^{2n}}{2n(2n)!} \quad (39b)$$

which prove useful in their numerical evaluation. These functions have not been commonly employed in chemical engineering, but were utilized recently in the context of a different diffusion-reaction problem in the spherical catalyst (Pereira and Varma 1978).

As discussed earlier, there may be multiple K values for a fixed set of physico-chemical parameters, and criteria for the existence of unique and multiple solutions were summarized above. With the nature of the $\eta_0 - \phi$ curves (Figures 1a, b) also discussed above, some interesting results concerning the first order corrections can now be deduced. These are presented below as Remarks 1-3.

Remark 1. If $dK/d\phi > 0$ (<0) for a branch of the $\eta_0 - \phi$ curve, then η_1 is positive (negative) for that branch.

The proof follows directly from Equations (29), (32) and (36). To show this, differentiating both sides of Equation (29) with respect to ϕ, we obtain

$$\frac{dK}{d\phi} = \frac{X}{\phi}\,\frac{F'(X)}{(Bi_h/\beta) - (\gamma X/2K^2)F'(X)} \quad (40)$$

where

$$F'(X) \equiv \frac{dF}{dX} \quad (41)$$

It can be readily shown that the numerators of η_1 in Equations (32) and (36), and of $dK/d\phi$ in Equation (40) are always positive. The algebraic signs of η_1 and $dK/d\phi$ are thus determined by their respective denominators. The latter, however, are *identical.* So if $dK/d\phi > 0$ (<0), then $\eta_1 > 0$ (<0).

Remark 2. At the bifurcation points of the zeroth order solution (i.e., ϕ_{0*} and ϕ_0^*), $\eta_1 \to +\infty$ for branches 1 and 3, and $\eta_1 \to -\infty$ for branch 2.

Along branch 1, $d\eta_0/d\phi \to +\infty$ as $\phi \to \phi_0^*$ by definition. From Equation (24), this means $dK/d\phi \to +\infty$ as $\phi \to \phi_0^*$. Since as stated under the previous remark, the numerator of $dK/d\phi > 0$, thus the denominator of $dK/d\phi \to 0_+$ as $\phi \to \phi_0^*$. Also as stated under the previous remark, the denominators of η_1 and $dK/d\phi$ are identical, while the numerators of both are positive. Thus $\eta_1 \to +\infty$ as $\phi \to \phi_0^*$ along branch 1. Similarly, $\eta_1 \to +\infty$ as $\phi \to \phi_{0*}$ along branch 3, and $\eta_1 \to -\infty$ as $\phi \to \phi_{0*}$ *or* $\phi \to \phi_0^*$ along branch 2.

Remark 3. For fixed values of β, γ, Bi_m and Bi_h, $\eta_1 \to 0$ and the zeroth order effectiveness factor η_0 approaches the exact η as $X \to \infty$.

For large X, by replacing the hyperbolic functions in Equations (32) and (36) by exponential forms suitable for large X, using Equations (30) for η_0, and utilizing the series in Equations (39) for the functions Shi and Chi, it is readily seen that $\eta_1/\eta_0 \to 0$ as $X \to \infty$. Note that in this limit, η_0 itself also approaches zero following the expressions indicated in Equation (30). These asymptotic limits for η_0 are the *same* as for the exact η (Aris 1975, p. 272).

Note that slightly better estimates of η can be obtained in the limit $\phi \to \infty$ directly from Equation (29):

$$\frac{(n+1)}{\eta} \sim \frac{\phi^2}{Bi_m} + \frac{\phi}{\rho(K)} \quad (42)$$

which aid in representing η in the ϕ range, where low values of the centerline concentration lead to computational difficulty.

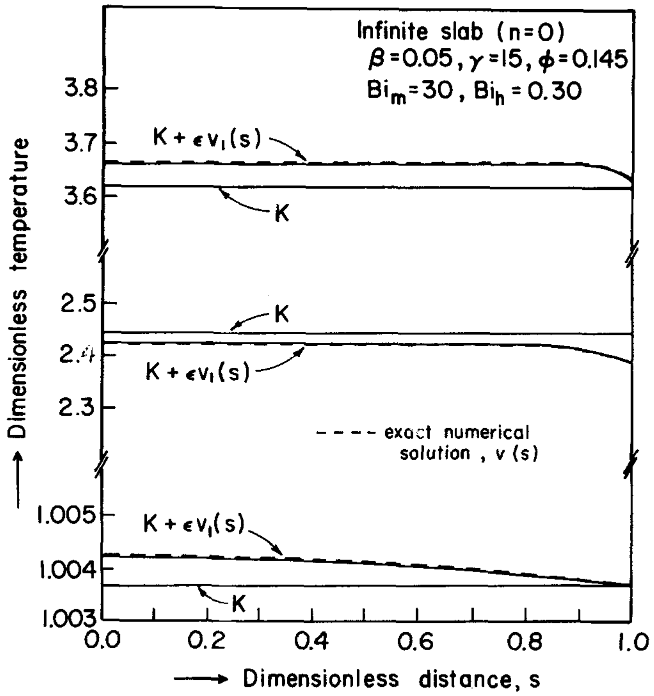

Figure 3. A comparison of the zeroth order [K], first order corrected [$K + \epsilon v_1(s)$] and exact [$v(s)$] temperature profiles for a case of multiple steady states.

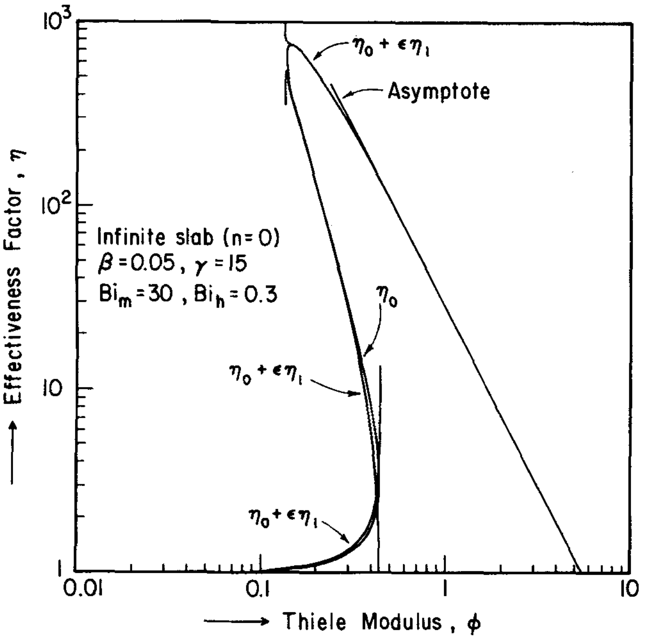

Figure 5. A comparison of the effectiveness factor-Thiele modulus curves for the zeroth order (η_0) and first order corrected ($\eta_0 + \epsilon\eta_1$) solutions.

NUMERICAL RESULTS AND DISCUSSION

A comparison of temperature profiles for the zeroth order [K], including the first order correction [$K + \epsilon v_1(s)$], and the exact numerical solution of Equations (4-5), for a first order reaction and a case where multiple solutions exist is shown in Figure 3. The exact numerical solution was computed using the shooting method (McGinnis 1965). The figure shows that while the first order corrected profile virtually matches with the exact numerical solution, the zeroth order profile is in the same temperature range. Due to its simplicity, the zeroth order solution may be conveniently used in modeling gas-solid catalytic systems. But, as stressed before, the validity of the internal isothermal model is justified only by analyzing the complete conservation equations as a regular perturbation problem.

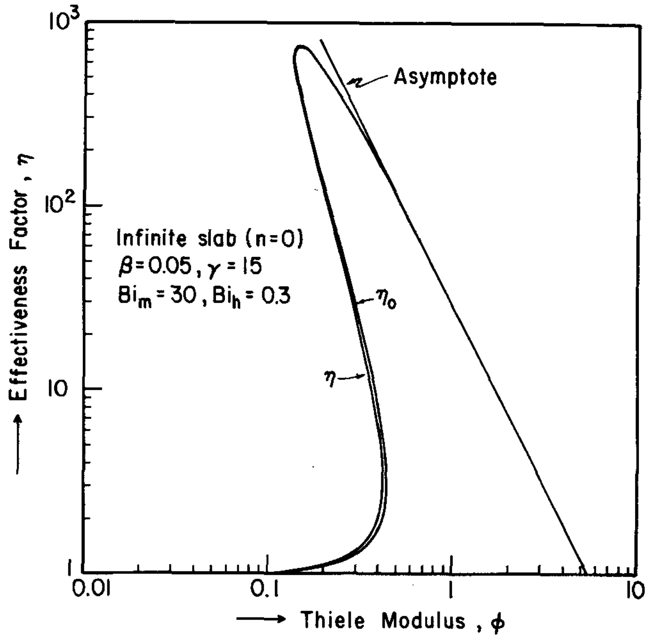

Figure 4. A comparison of the effectiveness factor-Thiele modulus curves for the zeroth order (η_0) and exact (η) solutions.

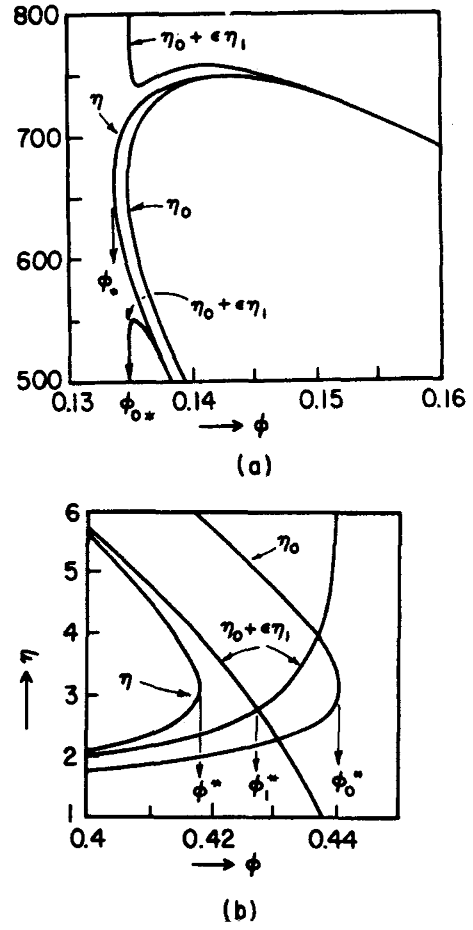

Figure 6. Enlarged versions of Figure 5 near the bifurcation points (a) lower, (b) upper.

The $\eta_0 - \phi$ and the exact $\eta - \phi$ curves are compared in Figure 4 for a specific set of parameters; the latter curve is

TABLE 1. BOUNDS ON THE REGION OF MULTIPLE STEADY STATES†

γ	β	Bi_m	Bi_h	Bi_m/Bi_h	ϕ_*	ϕ_{0*}	ϕ^*	ϕ_1^*	ϕ_0^*	Reference
					A. Infinite slab ($n = 0$)					
27.0	0.01	30	0.3	100	0.268	0.270	0.946	0.963	0.980	Pereira et al. (1979)
15.0	0.05	30	0.3	100	0.134	0.135	0.418	0.428	0.441	Pereira et al. (1979)
27.0	0.333	30	10.0	3	0.168	0.270	0.328	0.655	0.980	Hatfield and Aris (1979)
					B. Sphere ($n = 2$)					
10.0	0.01	250	0.1	2500	0.806	0.807	1.294	1.302	1.304	Pereira et al. (1979)
10.0	0.05	250	0.5	500	0.802	0.807	1.250	1.290	1.304	Pereira et al. (1979)
10.0	0.10	250	5.0	50	5.08	5.210	5.20	5.282	5.453	Cresswell (1970)
20.0	0.01	250	0.5	500	0.19	0.198	2.40	2.451	2.460	Cresswell (1970)

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† The exact values ϕ_* and ϕ^* are obtained by numerical integration of Eqs (4-5), and are from references noted in the last column.

obtained by numerically solving Equations (4-5). The $\eta_0 - \phi$ curve is *always* quite close to the exact $\eta - \phi$ curve, although somewhat to the southeast direction of it. At large K and ϕ (i.e., large X), the two curves virtually coincide. The effect of ϵ is examined in Figure 5 by comparing the $\eta_0 - \phi$ and the first order corrected $\eta_0 + \epsilon\eta_1 - \phi$ curves. Since ϵ is relatively small ($\epsilon \equiv \beta = 0.05$), the correction is relatively minor and the curves are in agreement with Remarks 1-3 made above. At the zeroth order bifurcation points ϕ_{0*} and ϕ_0^*, $|\eta_1| \to \infty$ following Remark 2. Expanded versions of the curves near the bifurcation points are shown in Figures 6a, b. Note that except for near the true bifurcation points ϕ_* and ϕ^*, the first order corrected effectiveness factor $\eta_0 + \epsilon\eta_1$ is everywhere *very* close to the exact η.

Remarks 1-2 guarantee the existence of two distinct K values at ϕ_1^*, to the left of the zeroth order bifurcation point ϕ_0^*, which give the same first order corrected effectivness. ϕ_1^* thus provides a corrected upper bound on ϕ^*, which is an improvement over ϕ_0^*. On the other hand, at the lower bifurcation point ϕ_{0*}, since $\eta_1 \to -\infty$ ($+\infty$) along branch 2(3), no improvement in the ϕ_* prediction is made. But as shown in Table 1, where a comparison of ϕ_0^*, ϕ_1^* with ϕ^* and of ϕ_{0*} with ϕ_* is made, ϕ_{0*} is always quite close to, and always somewhat higher than, ϕ_* (see also Figures 4-6). The improvement in predicting the region of multiplicity over the zeroth order values is thus made where it is most needed.

CONCLUDING REMARKS

It is important to make some general comments in conclusion. First, rather good a priori criteria for uniqueness and multiplicity of solutions can be obtained whenever the general diffusion-reaction Equations (4-5) can be reduced to a single equation (Luss 1971). This occurs when either there is no external transport limitation ($Bi_m = Bi_h = \infty$), or when $Bi_m = Bi_h$. For $Bi_m \neq Bi_h$, this reduction cannot be made, and the criteria derived by directly analyzing Equations (4-5) as in Jackson (1972), or in Pereira and Varma (1978), are quite conservative.

As shown recently (Pereira et al. 1979) and here (Table 1), in the practically important case where β is relatively small and Bi_m/Bi_h relatively large, the *a priori* criteria for uniqueness and multiplicity using the internal isothermal model approximate the exact region of multiplicity rather well. It should be noted, however, that if relatively larger β and relatively smaller Bi_m/Bi_h are considered, multiplicity patterns other than only the 1-3-1 pattern possible by the internal isothermal model, can arise. Indeed, Hatfield and Aris (1969) show numerically the existence of 1-3-1-3-1 and 1-3-5-3-1 patterns. Thus the full non-isothermal Equations (4-5) are capable of giving patterns of multiplicity more exotic than those possible from the internal isothermal model. But, for most practical cases, and in particular for the design of fixed bed reactors, the assumption of pellet isothermality at most improved by first order corrections should prove quite adequate.

NOTATION

A = constant defined by Equation (33*a*)
B = constant defined by Equation (37*a*)
Bi = Biot number; $Bi_m = k_g R/D_e$, $Bi_h = hR/\lambda_e$
C = reactant concentration
D_e = effective diffusivity
E = activation energy
f = $r(C, T)/r(C_f, T_f)$
F = function defined by Equation (29)
h = heat transfer coefficient
ΔH = heat of reaction
k_g = mass transfer coefficient
K = zeroth order temperature
$L[\,]$ = differential operator
n = integer characteristic of pellet geometry; = 0 for infinite slab, = 2 for sphere
r = intrinsic reaction rate
R = characteristic pellet dimension; half-thickness ($n = 0$), radius ($n = 2$)
R_g = gas constant
s = x/R
S_x = pellet external surface area
T = temperature
u = C/C_f
v = T/T_f
V_p = pellet volume
x = distance from center of pellet
X = $\phi\rho(K)$

Greek Letters

β = Prater temperature, $(-\Delta H)D_eC_f/\lambda_eT_f$
γ = E/R_gT_f
$\overline{\gamma}$ = Euler's constant
ϵ = small parameter
ϕ = Thiele modulus, $R\sqrt{r(C_f, T_f)/D_eC_f}$
Φ = normalized Thiele modulus, $(V_p/S_x)\sqrt{r(C_f, T_f)/D_eC_f}$
λ_e = effective pellet thermal conductivity
η = effectiveness factor

$\rho(v) = \exp\left\{\frac{\gamma}{2}\left(1 - \frac{1}{v}\right)\right\}$

ψ, Δ = constants defined by Equation (33)

Ω, Λ = constants defined by Equation (37)

Subscripts

c = critical value

f = bulk value

h = heat transfer

m = mass transfer

n = n-th term in series

$*$ = lower bifurcation value

Superscripts

$*$ = upper bifurcation value

LITERATURE CITED

Abramowitz, M. and I. A. Stegun, *Handbook of Mathematical Functions*, Dover, New York (1965).

Aris, R., "On Shape Factors for Irregular Particles—I. The Steady State Problem—Diffusion and Reaction," *Chem. Eng. Sci.*, **6**, 262 (1957).

Aris, R., *The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts*, Vol. 1, Clarendon Press, Oxford (1975).

Bellman, R., *Perturbation Techniques in Mathematics, Engineering and Physics*, Holt, Rinehart and Winston, New York (1966).

Butt, J. B., D. M. Downing and J. W. Lee, "Inter-Intraphase Temperature Gradients in Fresh and Deactivated Catalyst Particles," *Ind. Eng. Chem. Fundam.*, **16**, 270 (1977).

Carberry, J. J., "On the Relative Importance of External-Internal Temperature Gradients in Heterogeneous Catalysis," *Ind. Eng. Chem. Fundam.*, **14**, 129 (1975).

Cole, J. D., *Perturbation Methods in Applied Mathematics*, Blaisdell, Waltham, Mass. (1968).

Cresswell, D. L., "On the Uniqueness of the Steady State of a Catalyst Pellet Involving Both Intraphase and Interphase Transport," *Chem. Eng. Sci.*, **25**, 267 (1970).

Hatfield, B. and R. Aris, "Communications on the Theory of Diffusion and Reaction—IV. Combined Effects of Internal and External Diffusion in the Non-isothermal Case," *Chem. Eng. Sci.*, **24**, 1213 (1969).

Jackson, R., "Some Uniqueness Conditions for the Symmetric Steady State of a Catalyst Particle with Surface Resistance," *Chem. Eng. Sci.*, **27**, 2205 (1972).

Kehoe, J. P. G. and J. B. Butt, "Interactions of Inter-and Intra-phase Gradients in Diffusion Limited Catalytic Reaction," *AIChE J.*, **18**, 347 (1972).

Luss, D., "Uniqueness Criteria for Lumped and Distributed Parameter Chemically Reacting Systems," *Chem. Eng. Sci.*, **26**, 1713 (1971).

Luss, D., "Steady State and Dynamic Behavior of a Single Catalytic Pellet," Chapter 4 in *Chemical Reactor Theory—A Review*, L. Lapidus and N. R. Amundson (Editors), Prentice-Hall, Englewood Cliffs, N.J. (1977).

McGinnis, P. H., Jr., "Numerical Solutions of Boundary Value Nonlinear Ordinary Differential Equations," *Chem. Eng. Prog.*, Symp. Series, **61** (55), 2 (1965).

Pereira, C. J. and A. Varma, "Effectiveness Factors for the Case of Mildly Concentration-dependent Diffusion Coefficients," *Chem. Eng. Sci.*, **33**, 396 (1978).

Pereira, C. J. and A. Varma, "Uniqueness Criteria of the Steady State in Automotive Catalysis," *Chem. Eng. Sci.*, **33**, 1645 (1978).

Pereira, C. J., J. J. Carberry and A. Varma, "Uniqueness Criteria for First Order Catalytic Reactions with External Transport Limitations," *Chem. Eng. Sci.*, **34**, 249 (1979).

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Multivariable Controller Design for Linear Systems Having Multiple Time Delays

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A multivariable, multidelay compensator, capable of handling general, linear time delay problems is derived in a form applicable both in continuous and discrete time. The controller developed is shown to have the same structure as the linear-quadratic optimal feedback controller for input delays and reduces to the Smith predictor (and the analytical predictor) for the special case of a single time delay. Some examples representative of engineering practice are used to demonstrate the effectiveness of the controller.

SCOPE

Time delays in feedback control loops often are a serious obstacle to good process operation. Such delays prevent high controller gains from being used, leading to offset and sluggish system response. Smith (1957, 59) suggested a compensator design which effectively removes a single delay from the feedback loop. This result has been extended to discrete time operation and multivariable systems having a single delay (e.g., Moore et al. 1970, Alevisakis and Seborg 1973, 1974), but the common situation of multiple time delays has remained a problem. In the present work, a new multivariable, multidelay compensator is developed to allow mitigation of the effects of multiple delays in multivariable control problems.

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