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Dead zones in porous catalysts: Concentration profiles and efficiency factors☆

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ABSTRACT

This paper examines the conditions under which a dead zone, or a portion of the catalyst devoid of reactant, can form in a porous catalyst in which simultaneous reaction and diffusion are occurring. The condition that allows for the existence of a dead zone is defined by a critical Thiele modulus. When the Thiele modulus – the ratio of chemical reaction to diffusion – is greater than the critical Thiele modulus, a dead zone exists. This dead zone can be mathematically defined by a change of boundary conditions. We examine *n*th order reactions in isothermal infinite slabs, infinite cylinders, and spheres. In addition, we provide analytical concentration profiles and efficiency factors for zero-order reactions in non-isothermal infinite slabs (in the so-called low beta approximation). We also discuss some common errors and misconceptions associated with this phenomenon.

1. Introduction

Heterogeneous catalysis is a vital part of industrial chemistry [1]. Recent advances in surface science and nanoscience may have a profound impact on how we think about and design heterogeneous catalysts [2]. We may soon be designing catalysts on an atomic basis [3]. Despite these breakthroughs, it is vital to remember that the overall rate of a chemical process involves both diffusion of the reactants to the catalysts, diffusion of the products away from the catalyst, and the reaction rate itself. Reaction and diffusion can also be of upmost importance in biological systems [4], in addition to other processes [5].

Steady-state reaction and diffusion in porous catalysts is a system that was first modeled in the 1930s. Today, it is a subject discussed in nearly all chemical reaction engineering textbooks [6–9]. The basic ideas were originally worked out by such pioneers as Thiele [10] and Zeldowitsch [11]. Later, Wheeler [12] provided a critical review of the field and Aris wrote a book that summarized the field up to 1973 [9].

This article deals with the conditions under which a “dead zone” develops in a porous catalyst—defined as a region totally devoid of reactant. Mathematically, this means that at some “critical” Thiele modulus the boundary conditions that define the physical situation change. In other words, at this critical Thiele modulus, the concentration reaches zero at the very center of the pellet. This idea was first proposed by Wheeler in 1951 [12], and later studied more extensively by Aris in 1971 [9,13]. In 1975, Temkin coined the term “dead zone”, which he defined as a zone where reaction does not take place [14]. In this paper, Temkin looked at the case of arbitrary kinetics as a power series of the granule radius continued to the series member proportional to the fourth power of the radius in an isothermal sphere. Later, Temkin examined the conditions under which a dead zone forms in an isothermal sphere for *n*th order reactions [15]. Fedotov et al. explored the case of slightly non-monotonic kinetics in 1985 [16]. In 1988, Garcia-Ochoa and Romero examined the conditions under which a dead zone forms in isothermal particles and the critical efficiency factors associated with these conditions [17]. The following year, Koltsov and Alekseev published a paper discussing reaction and diffusion in non-isothermal slab catalysts [18]. More recently, Koltsov and Andreev [19] and Andreev [20] have examined the conditions under which a dead zone forms for consecutive parallel reactions in porous medium. This paper builds upon many of the papers listed above by explicitly stating the concentration profiles for many different geometries and conditions in the porous catalyst. The concentration profile provides all the relevant data for the catalytic particle, including the efficiency factor, a parameter of interest to many engineers.

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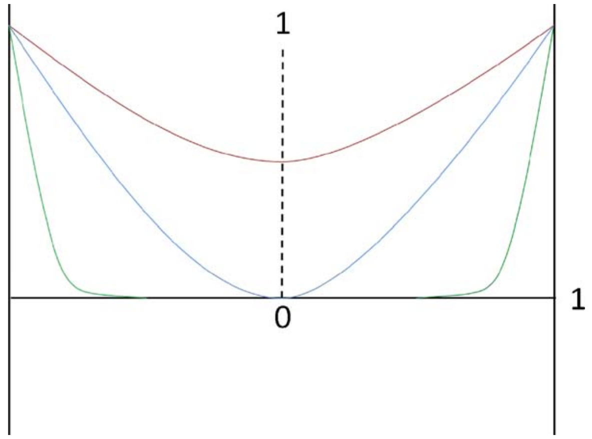

Fig. 1. A sketch of a several concentration profiles in a porous catalyst. The red curve shows a concentration profile arising from "normal" boundary conditions (i.e. $\phi < \phi_c$), and the green curve shows a concentration profile arising from "dead zone" boundary conditions (i.e. $\phi > \phi_c$, $0 < z_c < 1$). The blue curve represents the onset of the dead zone (i.e. $\phi = \phi_c$, $z_c = 0$). For the blue curve, either set of boundary conditions can be used. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

In our earlier publication [21], we pointed out how several textbooks [6–8] have mishandled this change of boundary conditions leading to incorrect concentration profiles and efficiency factors. A schematic of concentration profiles under regular boundary conditions, dead zone boundary conditions, and the transition between the two regimes is given in Fig. 1.

Here, we begin with the case of an *n*th order reaction in an isothermal infinite slab, and show that by assuming a critical value of the Thiele modulus one can determine the values of *n* where a dead zone exists. This arises from the restriction that the critical Thiele modulus must be a positive real number, in addition to the fact the assumed concentration profile must satisfy the original differential equation and associated boundary conditions. Our results are in agreement with the general solution first presented by Mehta and Aris [13,22]. However, our strategy of assuming a dead zone and later showing this assumption is self-consistent is different than the work of Aris in two important ways. First, with the exception of the isothermal slab, a complete analytic solution is not generally available for all values of *n*. Therefore, the only way one can surmise if a dead zone exists is by assuming a critical Thiele modulus and showing this is self-consistent (i.e. the critical Thiele modulus is positive and real, in addition to the concentration profile satisfying the differential equation and associated boundary conditions). Secondly, the general solution for the isothermal slab – which is in terms of hypergeometric functions – is a difficult function to work.

We then discuss in more detail how this method can be applied to isothermal pellets of different shape. The correct analytical concentration profile for a zero-order reaction in a spherical pellet is presented here for the first time. We discuss how failing to change boundary conditions can lead to incorrect and unphysical concentration profiles and efficiency factors. Lastly, we examine a zero-order non-isothermal reaction in an infinite slab, and determine under which conditions a dead zone forms, the concentration profiles under both sets of boundary conditions, and the efficiency factors for both sets of boundary conditions. To the best of our knowledge, this is the first time the concentration profiles for a zero-order non-isothermal reaction have been elucidated. Table 1 summarizes the findings of this paper for the various conditions studied herein.

2. Analysis

As reactant diffuses into the catalyst pellet, it is consumed by reaction. A material balance over a slice of thickness Δx under steady-state conditions gives:

$$JS|_{x+\Delta x} - JS|_x = (S\Delta x)r \tag{1}$$

where *J* is the flux of reactant across the surface area *S* of the slice, *r* is the reaction rate per unit volume, and *x* is the distance out from the center. For rectangular infinite slab geometry, *S* is the same at all positions *x*, so shrinking Δx to zero gives, for an irreversible *n*th order reaction with rate constant *k* per unit volume and concentration *c* of reactant at position x:

$$\frac{dJ}{dx} = kc^n \tag{2}$$

The diffusive flux can be described by Fick's law, where *D* is the effective diffusivity of the porous slab:

$$J = D\frac{dc}{dx} \tag{3}$$

Combining Eqs. (2) and (3) when *D* is independent of position yields:

$$D\frac{d^2c}{dx^2} = kc^n \tag{4}$$

Table 1
A summary of equations presented in this paper.

Isothermal	Slab	$-1 < n < 1$	ϕ_c	Eq. (10)
			$f(z)$, $\phi > \phi_c$	Eq. (19)
			η, $\phi > \phi_c$	Eq. (21)
			z_c	Eq. (18)
	Cylinder	$-1 < n < 1$	ϕ_c	Eq. (13)
			$f(z)$, $\phi = \phi_c$	Eq. (11)
	Sphere	$-1 < n < 1$	ϕ_c	Eq. (15)
			$f(z)$, $\phi = \phi_c$	Eq. (11)
		$n = 0$	ϕ_c	Eq. (27)
			$f(z)$, $\phi < \phi_c$	Eq. (25)
			$f(z)$, $\phi > \phi_c$	Eq. (32)
			η, $\phi > \phi_c$	Eq. (42)
			z_c	Eq. (31)
Non-isothermal	Slab	$n = 0$, low Beta Approx.	$\phi_{0,c}$	Eq. (62)
			$f(z)$, $\phi_0 < \phi_{0,c}$	Eqs. (57) and (58)
			$f(z)$, $\phi_0 = \phi_{0,c}$	Eq. (69)
			$f(z)$, $\phi_0 > \phi_{0,c}$	Eq. (67)
			η, $\phi_0 < \phi_{0,c}$	Eqs. (57) and (59)
			η, $\phi_0 > \phi_{0,c}$	Eq. (68)
			z_c	Eq. (66)

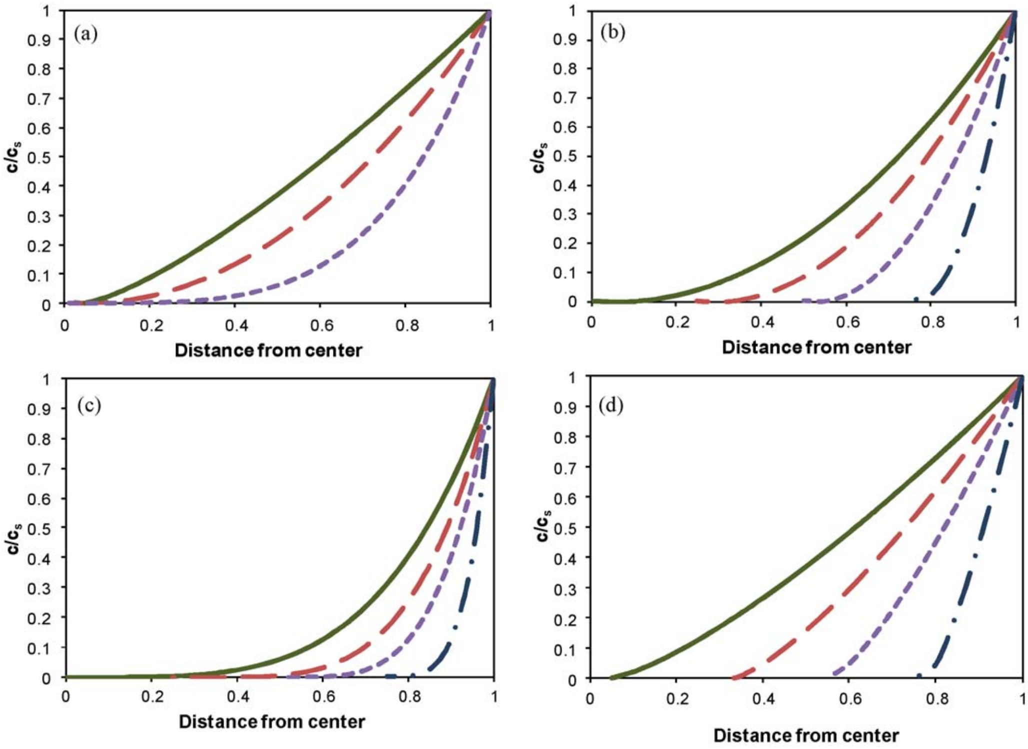

Fig. 2. (a) Concentration profile for an isothermal slab at the critical Thiele modulus, φ_c, for zero-order (— —), negative half-order (—), and half-order (- - -). (b) A zero-order reaction in an isothermal slab for $\varphi = 1.5$ (—), 2 (— —), 3 (- - -), and 6 (— · —). (c) A half-order reaction in an isothermal slab for $\varphi = 3.5$ (—), 5 (— —), 7 (- - -), and 14 (— · —). (d) A negative half-order reaction in an isothermal slab for $\varphi = 0.7$ (—), 1 (— —), 1.5 (- - -), and 3 (— · —).

which can be rewritten in terms of the Thiele modulus as:

$$\frac{d^2f}{dz^2} = \phi^2 f^n \tag{5}$$

with the following definitions for dimensionless variables:

$z = \frac{x}{L}$ = fractional distance from the center of the slab with half-width L

$f = \frac{c}{c_s}$ = ratio of the concentration at position × relative to that at the surface c_s

$\phi = L\sqrt{\frac{kc_s^{n-1}}{D}}$ = Thiele modulus.

The typical boundary conditions employed are $f(1) = 1$ and $f'(0) = 0$. In his seminal work, Thiele [10] found f as a function of z for first and second order isothermal reactions whereas the zero-order reaction was considered by Wheeler [12].

2.1. General nth order case

Denoting the concentration gradient as $p = df/dz$ and recognizing from the chain rule that

$$\frac{dp}{dz} = \frac{df}{dz}\frac{dp}{df} = p\frac{dp}{df} = \frac{d^2f}{dz^2} \tag{6}$$

allows for the elimination of z in Eq. (5) and the variables p and f can be separated and the equation integrated for the case where ϕ is constant (i.e. uniform temperature throughout the slab results in constant rates of reaction and diffusion), yielding for $n \neq -1$

$$p^2 = \frac{2}{n+1}\phi^2 f^{n+1} + C. \tag{7}$$

where C is an integration constant. Letting f_0 represent the concentration where the gradient becomes zero, i.e. $p = 0$ where $f = f_0$, leads to

$$p = \frac{df}{dz} = \phi\sqrt{\frac{2}{n+1}}\sqrt{f^{n+1} - f_o^{n+1}} \tag{8}$$

It is possible to separate variables f and z and integrate Eq. (8) to find the complete concentration profile as discussed by Bischoff [23] and Mehta and Aris [13]. However, except for the simple first or zero-order case, the general solutions of these authors yield cumbersome elliptic or hypergeometric integrals.

2.2. Mathematical definition of dead zone

Mehta and Aris [13] have noted, "in some cases the concentration at the center of the slab drops to zero." To examine specific circumstances leading to that condition, let us find the critical value of ϕ that makes $f_0 = 0$ at $z = 0$. Separating the variables and integrating from the center to the surface, Eq. (8) yields

$$\int_0^1 \frac{df}{f^{(n+1)/2}} = \int_0^1 \phi\sqrt{\frac{2}{n+1}}\,dz \tag{9}$$

Thus the critical value of ϕ such that the concentration becomes zero at the center is

$$\phi_c = \sqrt{\frac{2}{n+1}}\left(\frac{n+1}{1-n}\right)\text{(rectangular slab pellet)} \quad -1 < n < 1 \tag{10}$$

The constraint on the order n arises from the requirement that ϕ_c must be a positive real number. Integrating Eq. (9) from the center to z at this critical value of ϕ_c gives the concentration profile

$$f = z^{2/(1-n)} \quad \text{for} \quad \phi = \phi_c \tag{11}$$

The dimensionless concentration profile at the critical ϕ_c value for zero, half, and negative half reaction orders are shown in

Fig. 2(a). In addition to the slab geometry, the reaction/diffusion equations for cylindrical and spherical pellets are also satisfied by Eq. (11). For a cylinder the surface area S is proportional to x, so the reaction/diffusion equation becomes

$$\frac{d^2f}{dz^2}+\frac{1}{z}\frac{df}{dz}=\phi^2f^n. \tag{12}$$

Solving for the condition in which the concentration initially becomes zero at the center of the pellet ($f=0$ at $z=0$) via substitution of Eq. (11) into Eq. (12) yields a critical ϕ value:

$$\phi_c=\frac{2}{1-n}\quad \text{(cylindrical pellet)}\quad -1<n<1 \tag{13}$$

In the case of a sphere, the surface area S is proportional to x^2 resulting in the following reaction/diffusion equation:

$$\frac{d^2f}{dz^2}+\frac{2}{z}\frac{df}{dz}=\phi^2f^n \tag{14}$$

The critical ϕ value where concentration at the center of the pellet initially becomes zero in the case of the spherical pellet can then be solved in the same manner as the cylindrical pellet through substitution of Eq. (11) into Eq. (14)

$$\phi_c=\frac{\sqrt{6-2n}}{1-n}\quad \text{(spherical pellet)}\quad -1<n<1 \tag{15}$$

It is important to note that the reactant will be depleted at the core of a cylindrical or spherical pellet *only* for reaction orders less than +1 arising from the constraint that ϕ_c be both real and positive (i.e. both diffusion and reaction must be positive real values). Additionally, the constraint that the reaction order be greater than -1 arises from the fact that the boundary conditions can only be satisfied for $n>-1$. This is clear from inspection of Eq. (11). This approach and these results shed light on the equations shown in a footnote on page 147 of volume 1 of Aris' book, and describe how the presence or absence of a dead zone can be surmised.

2.3. *Concentration profile in a slab for $\phi>\phi_c$*

As the reaction rate increases, the reactant concentration decreases in the center of the pellet. Internal diffusion limits the overall rate of reaction when $\phi>\phi_c$, thus creating a "dead zone" in the center of the pellet. Mathematically, this would present as *negative* concentrations. Since that has no physical meaning, a *new* boundary condition is required:

$$f=0\quad\text{and}\quad p=0\quad\text{at}\quad z=z_c \tag{16}$$

where z_c is the critical position at which *both* the concentration and its gradient become zero. Integrating Eq. (9) between z_c and z, where f varies from 0 to f, gives

$$f=\left[\frac{\phi}{\phi_c}(z-z_c)\right]^{2/(1-n)} \tag{17}$$

Using the boundary condition $f=1$ at $z=1$ the critical position, z_c, can be obtained from Eq. (17).

$$z_c=1-\frac{\phi_c}{\phi} \tag{18}$$

The complete concentration profile for any reaction order ranging from -1 and +1 for $\phi\geq\phi_c$ stems from Eqs. (17) and (18):

$$f=\left[1-\frac{\phi}{\phi_c}(1-z)\right]^{2/(1-n)} \tag{19}$$

Dimensionless concentration profiles for zero, half, and negative half-order reactions generated from Eq. (19) are shown in Fig. 2(b)–(d) for various values of $\phi\geq\phi_c$.

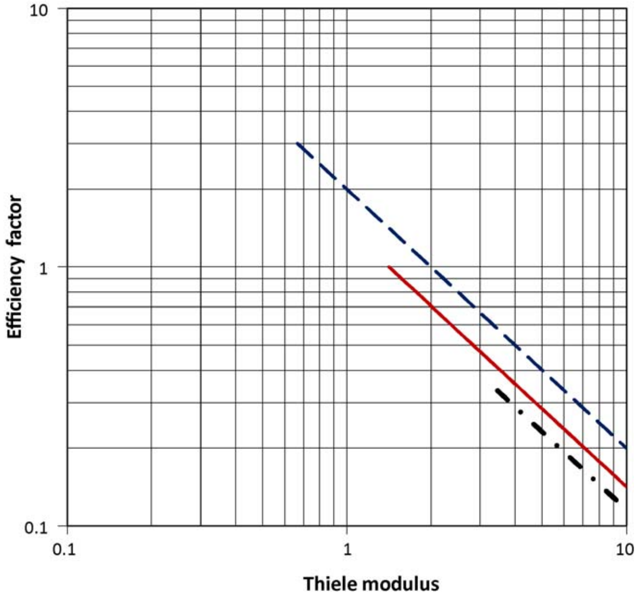

Fig. 3. Efficiency factor vs. Thiele modulus for zero-order (━━), half-order (▬ ▪ ▬), and negative half-order (▬ ▬ ▬) for $\phi\geq\phi_c$ for an isothermal slab.

The physical interpretation of zero-order behavior in heterogeneous catalysis is when the adsorbate almost completely covers the surface (*cf.* [21,24]). Fractional order kinetics arise from dissociative adsorption of reactants on surfaces. Additionally, Langmuir–Hinshelwood kinetics can approximate fractional order kinetics under certain conditions. Look and Smith [25] numerically integrated the reaction/diffusion equation for half-order kinetics and were surprised to discover that reactant concentrations fall to zero in the core of the catalyst under certain conditions. Negative reaction orders represent inhibitory effects. Several authors [26,27] have analyzed negative order reactions and found solutions displaying multiplicity patterns. All these observations are simply explained by the analysis presented here.

2.4. *Efficiency factor for isothermal slabs*

Defining the efficiency factor η as the ratio of the actual diffusion rate entering the slab to the "ideal" reaction rate (when the concentration throughout the slab is the same as at its surface), Eq. (8), which is valid for *any* reaction order $n\neq-1$, gives

$$\eta=\frac{2SD(dc/dx)\big|_{z=L}}{S2Lkc_s^n}=\left(\frac{1}{\phi^2}\right)\frac{df}{dz}\bigg|_{z=1}=\sqrt{\frac{2(1-f_o^{n+1})}{n+1}}\frac{1}{\phi} \tag{20}$$

This simple derivation shows that the efficiency factor varies inversely with the Thiele modulus. This is also true under conditions where the concentration in the interior of the pellet is much smaller than at the surface, i.e. where $f_o\ll1$ and consequently for $\phi\gg1$ in agreement with the asymptotic expansion results of Peterson [28] for $n=1$ and 2.

From Eq. (20) with $f_o=0$ occurring when $\phi\geq\phi_c$, the efficiency factor for reaction orders between -1 and +1 is *exactly*

$$\eta=\sqrt{\frac{2}{n+1}}\frac{1}{\phi}\qquad\text{for}\quad\phi\geq\sqrt{\frac{2}{n+1}}\left(\frac{n+1}{1-n}\right) \tag{21}$$

Fig. 3 shows the efficiency factor as a function of Thiele modulus for zero, half, and negative half-order reactions under conditions where a dead zone occurs in a slab pellet.

2.5. Literature errors for the zero-order case

Several recent texts [6–8] analyze the zero-order reaction; this is solved easily by integrating Eq. (5) twice to yield

$$f=\frac{\phi^2}{2}z^2+C_1z+C_2 \quad \text{(slab)} \tag{22}$$

or from Eq. (14)

$$f=\frac{\phi^2}{6}z^2-\frac{C_3}{z}+C_4 \quad \text{(sphere)} \tag{23}$$

Using the boundary conditions that z and f are 1 at the surface while z and $\partial f/\partial z$ are 0 at the center yields:

$$f=\frac{\phi^2}{2}(z^2-1)+1 \quad \text{(slab)} \tag{24}$$

$$f=\frac{\phi^2}{6}(z^2-1)+1 \quad \text{(sphere)} \tag{25}$$

Note that there is a critical value of ϕ such that $f=0$ at the center, namely

$$\phi_c=\sqrt{2} \quad \text{(slab)} \tag{26}$$

$$\phi_c=\sqrt{6} \quad \text{(sphere)} \tag{27}$$

which are special cases of Eqs. (10) and (15) for $n=0$.

These texts then assume the same boundary conditions continue to apply for $\phi>\phi_c$ and solve for the location z_c at which f is zero, which incorrectly yields

$$z_c=\sqrt{1-\left(\frac{\phi_c}{\phi}\right)^2} \quad \text{for both slab and sphere} \quad \text{(incorrect)} \tag{28}$$

Note Eqs. (24) and (25) predict that f becomes negative for $z>z_c$. These authors then stipulate that $f=0$ for $0\le z\le z_c$ where Eq. (28) is taken to locate z_c. This leads to a prediction of a non-zero concentration gradient at z_c. This implies that reactant is diffusing into the core of the pellet, but is not being consumed there—an impossible situation at steady state. We see from the results found previously that Eqs. (24) and (25) are in fact incorrect for $\phi>\phi_c$. For a slab, the correct results are Eqs. (18) and (19), which for the zero-order reaction give

$$f=\left[1-\frac{\phi}{\phi_c}(1-z)\right]^2 \quad \text{for slab when } \phi\ge\phi_c \tag{29}$$

and the correct distance from the center to the start of the "dead zone" where the concentration becomes zero is

$$z_c=1-\frac{\phi_c}{\phi}=1-\frac{\sqrt{2}}{\phi} \quad \text{for slab when } \phi\ge\phi_c \tag{30}$$

For example, with $\phi^2=8$, the onset of the dead zone in a slab actually occurs halfway from the center of the slab ($z_c=0.500$), whereas Eq. (28) incorrectly predicts $z_c=0.866$.

By using the correct boundary conditions for Thiele moduli larger than the critical Thiele modulus (i.e. $f(1)=1, f(z_c)=0), f'(z_c)=0$ into Eq. (23)) it can be shown that the correct start of the dead zone in a spherical pellet occurs at

$$z_c=\cos\left\{\frac{2\pi-\arccos(12/\phi^2-1)}{3}\right\}+\frac{1}{2} \quad \text{for sphere when } \phi\ge\phi_c \tag{31}$$

With concentration profile

$$f=\frac{\phi^2z^2}{6}+\frac{\phi^2z_C^3}{3z}-\frac{\phi^2z_C^2}{2} \quad \text{for sphere when } \phi\ge\phi_c \tag{32}$$

For example, with $\phi^2=12$, the location of the onset of the dead zone in a sphere actually occurs halfway from the center of the sphere ($z_c=0.500$), whereas Eq. (28) incorrectly predicts $z_c=0.707$. Fig. 4 shows concentration profiles for zero-order reactions in isothermal spheres for various values of the Thiele modulus.

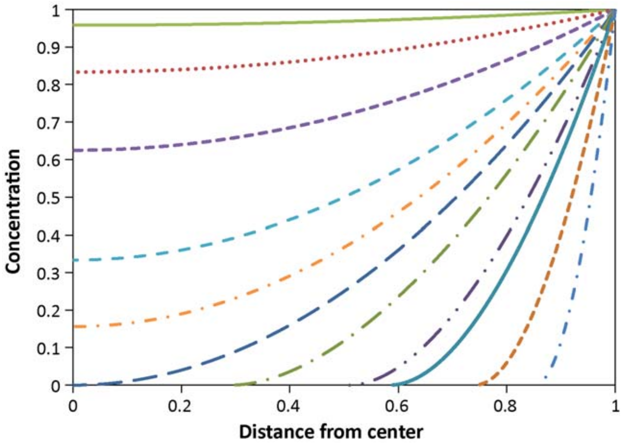

Fig. 4. Concentration profiles for a zero-order reaction in an isothermal sphere for a Thiele modulus, φ, of 0.5 (—), 1 (⋯), 1.5 (⋯), 2 (– –), 2.25 (– · –), $\sqrt{6}$ (– –), 3 (– · –), 3.5 (– · ·), 4 (—), 6 (– –), and 10 (– · –).

Note that differentiating Eq. (24) and evaluating at $z=1$ incorrectly predicts that the slope of the concentration gradient at the surface of the slab is ϕ^2. Using Eq. (20) to find the efficiency factor η incorrectly leads to the prediction $\eta=1$ for all values of ϕ. The same conclusion is reached in the case of a spherical pellet. However, that is impossible since there is an inactive dead zone when $\phi>\phi_c$. These text authors instead use the alternate definition for the efficiency factor as the ratio of the actual reaction rate in the pellet to that occurring at the surface

$$\eta=\int_{z_c}^{1}f^n\,dz \quad \text{for a slab} \tag{33}$$

$$\eta=3\int_{z_c}^{1}f^nz^2\,dz \quad \text{for a sphere} \tag{34}$$

Substituting the incorrect prediction of z_c from Eq. (28) for the lower limit of these integrals gives

$$\eta=1-\sqrt{1-\frac{2}{\phi^2}} \quad \text{for a slab with } \phi\ge\sqrt{2} \quad \text{(incorrect)} \tag{35}$$

$$\eta=1-\left[1-\frac{6}{\phi^2}\right]^{3/2} \quad \text{for a sphere with } \phi\ge\sqrt{6} \quad \text{(incorrect)} \tag{36}$$

Note for large values of $\phi\gg\phi_c$ a binomial expansion of the above predicts

$$\eta=1-\left(1-\frac{1}{2}\cdot\frac{2}{\phi^2}+\ldots\right)\to\frac{1}{\phi^2} \quad \text{for a slab} \tag{37}$$

which contradicts Eq. (21) and

$$\eta=1-\left(1-\frac{3}{2}\cdot\frac{6}{\phi^2}+\ldots\right)\to\frac{9}{\phi^2} \quad \text{for a sphere} \tag{38}$$

Instead of η decreasing as $1/\phi$, these incorrectly predict η decreases as $1/\phi^2$ for large ϕ. Also note that since

$$r=\eta r_{ideal}=\eta kc_s^n \tag{39}$$

this incorrectly predicts that for large ϕ with a zero-order reaction in a slab

$$r\to\frac{k}{\phi^2}=\frac{Dc_s}{L^2} \tag{40}$$

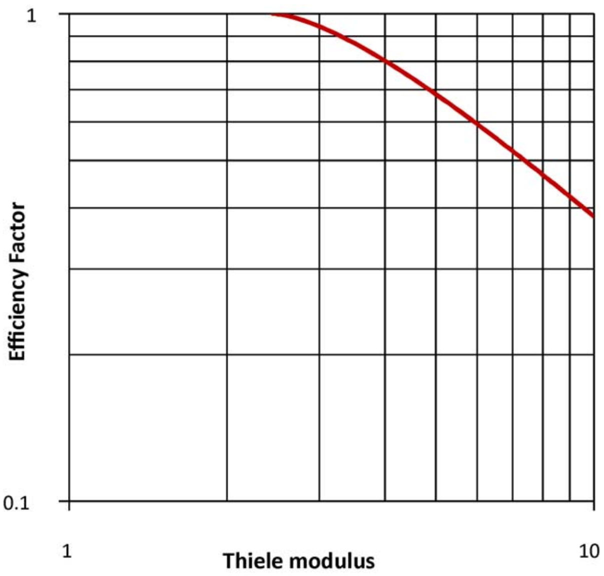

Fig. 5. Efficiency factor vs. Thiele modulus for zero-order isothermal sphere when $\phi \geq \phi_c$.

Thus according to this incorrect analysis, the zero-order reaction under extreme diffusion limitation would appear to be first order with no temperature dependence.

Using the correct result of Eq. (18) as the lower limit of the integral in Eq. (33) gives for a slab

$$\eta = \frac{\sqrt{2}}{\phi} \quad \text{for a slab with} \quad \phi \geq \sqrt{2} \tag{41}$$

in agreement with Wheeler's [12] result. This correctly predicts that for a reaction which is intrinsically zero-order, the reaction appears to be one-half-order with an observed activation energy half the true value when $\phi \geq \sqrt{2}$. For this slab pellet, when $\phi^2 = 8$, Eq. (35) incorrectly predicts an efficiency factor of 0.134 whereas the correct value is 0.500.

For the spherical pellet, the correct efficiency factor for the zero-order reaction is obtained from Eq. (34) yielding

$$\eta = 1 - z_c^3 \quad \text{for a sphere with} \quad \phi \geq \sqrt{6} \tag{42}$$

where z_c is given by Eq. (31). For example, with $\phi^2 = 12$, the correct efficiency factor for the sphere is 0.875, while Eq. (36) incorrectly predicts $\eta = 0.646$. The correct efficiency factor for a zero-order sphere is shown in Fig. 5.

Jang et al. [21] discuss these published errors in the zero-order analysis more completely through graphical comparisons of the incorrect and correct results for slab, cylindrical, and spherical geometries.

3. The non-isothermal case

In this section, we demonstrate the existence of a dead zone in a non-isothermal slab-shaped pellet. Non-isothermal pellets were first examined by Carberry [29], Tinkler and Metzner [30], and later by Peterson [28] and Weisz and Hicks [31]. The mathematical derivation of this problem is well described in the work of Tavera [32]. We follow his derivation, using the same symbols as this work. We begin by using normal boundary conditions (i.e. no presence of a dead zone) to show a dead zone exists.

Consider a catalyst pellet with the shape of a slab of thickness $2L$. Under steady-state conditions, the mole balance is:

$$-D\frac{d^2c}{dx^2} = r \tag{43}$$

where r is the volumetric reaction rate in the pellet. The energy balance is:

$$-k_{eff}\frac{d^2T}{dx^2} = (-\Delta H_R)r \tag{44}$$

where k_{eff} is the effective thermal conductivity, T is the temperature, and ΔH_R is the reaction enthalpy. The boundary conditions for this system of differential equations are:

$$T(x = \pm L) = T_S, \qquad c(x = \pm L) = c_S \tag{I}$$

$$\frac{dT}{dx}(x = 0) = 0, \qquad \frac{dc}{dx}(x = 0) = 0 \tag{II}$$

From the two boundary conditions and the mass and energy balances, it is possible to eliminate the reaction rate. After integration:

$$\frac{\Delta H_R D}{k_{eff}}(c - c_S) + T - T_S = 0 \tag{45}$$

After the definition of the non-dimensional variables:

$$z = \frac{x}{L}, \qquad f = \frac{c}{c_S}, \qquad \theta = \frac{T}{T_S}, \qquad \beta = \frac{\Delta H_R D c_S}{k_{eff} T_S},$$

We have the dimensionless equation:

$$\theta = 1 - \beta(f - 1) \tag{46}$$

The non-dimensional group β has been referred in the literature as the thermicity or heat generation function (note that for exothermic reactions $\beta > 0$). It represents the ratio between the rates of heat generation due to chemical reaction and transportion by thermal conduction mechanisms. The thermicity is a direct measure of non-isothermal effects.

Assuming an nth order reaction rate:

$$r = k_S \exp\left(-\frac{E}{R_g}\left(\frac{1}{T} - \frac{1}{T_S}\right)\right) f^n \tag{47}$$

where k_S is the pre-exponential factor at the surface temperature, E is the activation energy, and R_g is the gas constant, we can rewrite the mass balance:

$$\frac{d^2f}{dz^2} = \frac{2\phi_0^2}{n+1}\exp\left(-\gamma\left(\frac{1}{\theta} - 1\right)\right) f^n \tag{48}$$

where

$$\phi_0 = L\sqrt{\frac{(n+1)k_S c_S^{n-1}}{2D}}$$

This defines the generalized Thiele modulus. The dimensionless number, $\gamma = E/R_g T_S$ is called the Arrhenius group and represents a dimensionless activation energy for the reaction. Substituting Eq. (46) for θ, we have:

$$\frac{d^2f}{dz^2} = \frac{2\phi_0^2}{n+1}\exp\left(-\frac{\gamma\beta(f-1)}{1-\beta(f-1)}\right) f^n \tag{49}$$

This equation correlates concentration with position. Using the same method as in the previous section, let $p = df/dz$. Then

$$\int p\,dp = \int \frac{2\phi_0^2}{n+1}\exp\left(-\frac{\gamma\beta(f-1)}{1-\beta(f-1)}\right) f^n\,df \tag{50}$$

To the best of our knowledge, there is no closed form solution of the integral on the right. However, if we examine the zero-order case:

$$\frac{df}{dz} = \left[\int 4\phi_0^2 \exp\left(-\frac{\gamma\beta(f-1)}{1-\beta(f-1)}\,df\right)\right]^{1/2} \tag{51}$$

Again, we know of no method by which to solve the above integral. However, we can apply the low beta approximation, as discussed by Tavera [32]. The low beta approximation is defined as:

$$-\frac{\gamma\beta(f-1)}{1-\beta(f-1)} \approx \gamma - \frac{\gamma}{1+\beta}\left[1+\frac{\beta}{1+\beta}f\right] \tag{52}$$

After substitution and integration, we have:

$$\frac{df}{dz} = 2\phi_0\left[\frac{\exp(-\gamma+(\gamma/(1+\beta))+(\gamma\beta/(1+\beta)^2)f}{(\gamma\beta/(1+\beta)^2)}+C_5\right]^{1/2} \tag{53}$$

where C_5 is an integration constant. Integrating for a second time yields:

$$2\phi_0 z = \frac{-2(1+\beta)^2}{\gamma\beta\sqrt{C_5}}\tanh^{-1}\left[\left(\frac{C_5+(\exp(-\gamma+(\gamma/(1+\beta))+(\gamma\beta/(1+\beta)^2)f)/(\gamma\beta/(1+\beta)^2))}{C_5}\right)^{1/2}\right] + C_6 \tag{54}$$

where C_6 is another integration constant. Solving for f:

$$f = \frac{\ln[((\gamma\beta C_5/(1+\beta)^2)(\tanh^2-1))]+\gamma-(\gamma/(1+\beta))}{(\gamma\beta/(1+\beta)^2)} \tag{55}$$

This is the general solution (before the application of any boundary conditions). For "normal" boundary conditions:

BC 1: at the center $z=0$ $df/dz=0$ leads to

$$C_6 = 0 \tag{56}$$

BC 2: at the surface $z=1$ $f=1$

$$\frac{\exp((\gamma\beta/(1+\beta)^2)-\gamma+(\gamma/(1+\beta)))}{(\gamma\beta/(1+\beta)^2)} = C_5\left(\tanh^2\left(\frac{\gamma\beta\sqrt{C_5}\phi_0}{(1+\beta)^2}\right)-1\right) \tag{57}$$

This cannot be solved for C_5; nonetheless, it defines C_5 (and C_5 can be calculated numerically). Therefore, the solution is:

$$f = \frac{\ln[(\gamma\beta C_5/(1+\beta)^2)(\tanh^2(-(\gamma\beta\sqrt{C_5}/(1+\beta)^2)(\phi_0 z))-1)]+\gamma-(\gamma/(1+\beta))}{(\gamma\beta/(1+\beta)^2)} \tag{58}$$

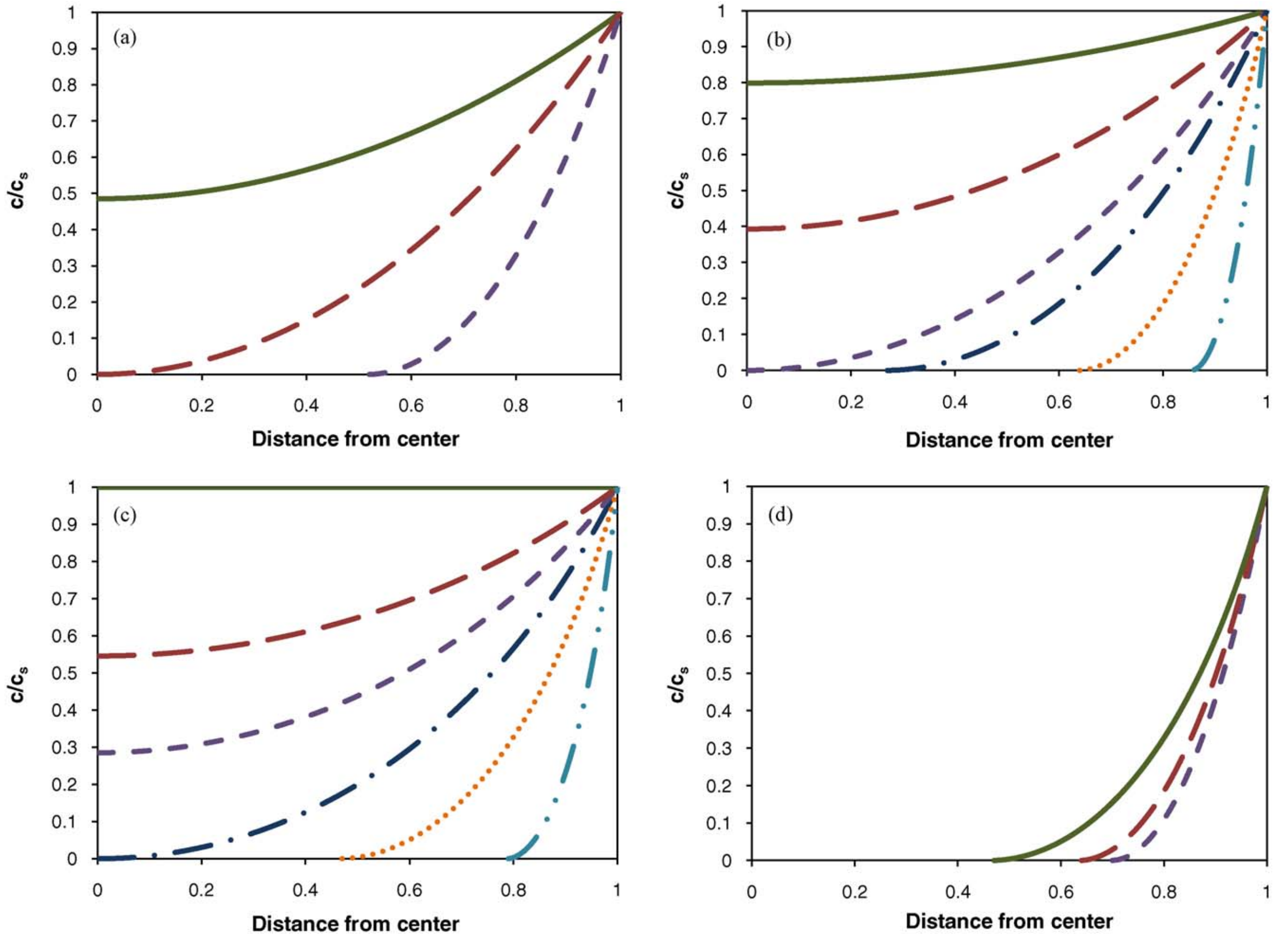

Fig. 6. (a) Concentration profile for a non-isothermal zero-order slab for various Thiele moduli, φ, of 0.8 (▬▬), the critical Thiele modulus of 1.21243 (▬ ▬), and 2.5 (▬ ▬ ▬). The Arrhenius group, γ, and the thermicity, β, were held constant at 5 and 0.1, respectively. (b) Concentration profile for a non-isothermal zero-order slab for various Thiele moduli, φ, of 0.5 (▬▬), 1 (▬ ▬) the critical Thiele modulus of 1.46952 (▬ ▬ ▬), 2 (▬ · ▬), 4 (••••••••), and 10 (▬ · ·). The Arrhenius group, γ, and the thermicity, β, were held constant at 10 and 0.1, respectively. (c) Concentration profile for a non-isothermal zero-order slab for various Thiele moduli, φ, of 0 (▬▬), 1 (▬ ▬),1.5 (▬ ▬ ▬), the critical Thiele modulus of 2.15815 (▬ · ▬), 4 (••••••••), and 10 (▬ · ·). The Arrhenius group, γ, and the thermicity, β, were held constant at 20 and 0.1, respectively. (d) Concentration profile for a non-isothermal slab for an Arrhenius group of 5 (▬▬), 10 (▬ ▬), and 20 (▬ ▬ ▬). The Thiele modulus and thermicity are held constant at 4 and 0.1, respectively.

where C_5 is given by Eq. (57). The efficiency factor can be calculated to be:

$$\eta = \frac{1}{2}\left(\frac{1}{\phi_0}\right)^2 \left.\frac{df}{dz}\right|_{z=1} = -\frac{\sqrt{C_5}}{\phi_0}\tanh\left(\frac{\gamma\beta\sqrt{C_5}\phi_0}{(1+\beta)^2}\right) \tag{59}$$

where C_5 is again defined by Eq. (57). Next, we calculate the "critical Thiele modulus" (i.e., the Thiele modulus at which the concentration reaches zero ($f=0$) at the center ($z=0$) of the pellet):

$$0 = \frac{\ln[(\gamma\beta C_5/(1+\beta)^2)([\tanh(0)]^2-1)] + \gamma - (\gamma/(1+\beta))}{(\gamma\beta/(1+\beta)^2)} \tag{60}$$

$$C_5 = -\frac{\exp(-(\gamma\beta/(1+\beta)))}{(\gamma\beta/(1+\beta)^2)} \tag{61}$$

Substituting Eq. (61) into Eq. (57) and solving for the critical Thiele modulus:

$$\phi_{0,c} = \left(-\frac{\gamma\beta}{(1+\beta)^2}\exp\left(-\frac{\gamma\beta}{1+\beta}\right)\right)^{-(1/2)} \times \tanh^{-1}\left(\sqrt{1-\exp\left(\frac{\gamma\beta}{(1+\beta)^2}\right)}\right) \tag{62}$$

When the above quantity is real and positive, a dead zone exists in the catalyst. When a dead zone does exist under this critical condition, the concentration profile can be obtained by letting $\phi_0 = \phi_{0,c}$, which will be shown below.

We now examine what the concentration profile looks like after the onset of this dead zone. We begin with the same mass and energy balances given above (Eqs. (43) and (44)), subject now to the new boundary conditions:

$$T(x=\pm L) = T_S, \qquad c(x=\pm L) = c_S, \qquad \frac{dT}{dx}(x=x_c) = 0,$$
$$\frac{dc}{dx}(x=x_c) = 0, \qquad c(x=x_c) = 0$$

We can then eliminate the reaction rate in the same way we did before, integrate and arrive at Eq. (45). After substitution and integration of Eq. (47), we arrive at the general solution, Eq. (55). This equation is now subjected to the following dimensionless boundary conditions:B.C. 1: $df/dz = 0$ at $z = z_c$

$$C_6 = -2\phi_0 z_c \tag{63}$$

B.C. 2: $f = 0$ at $z = z_c$

$$C_5 = -\frac{\exp(-(\gamma\beta/(1+\beta)))}{(\gamma\beta/(1+\beta)^2)} \tag{64}$$

B.C. 3: $f = 1$ at $z = 1$

$$C_6 = \frac{2\tanh^{-1}(\sqrt{1+(\exp((\gamma\beta/(1+\beta)^2)-\gamma+(\gamma/(1+\beta)))/(\gamma\beta C_5/(1+\beta)^2)})}{(\gamma\beta\sqrt{C_5}/(1+\beta)^2)} - 2\phi_0 \tag{65}$$

Substituting Eqs. (64) and (65) into (63) we deduce z_c:

$$Z_c = \frac{-\tanh^{-1}(\sqrt{1-\exp(\gamma\beta/(1+\beta)^2)})}{(\phi\gamma\beta\sqrt{-(\exp(-(\gamma\beta/(1+\beta))/(\gamma\beta/(1+\beta)^2))}/(1+\beta)^2)} + 1 \tag{66}$$

Substituting C_5 and C_6 into the Eq. (55), we obtain:

$$f(z) = \frac{(1+\beta)^2}{\gamma\beta}\ln\left[1-\left(\tanh^2\left(\sqrt{-\frac{\gamma\beta\exp(-(\gamma\beta/(1+\beta)))}{(1+\beta)^2}}\left(\phi_0 z - \phi_0 + \frac{\tanh^{-1}(\sqrt{1-\exp(\gamma\beta/(1+\beta)^2)})}{\sqrt{-(\gamma\beta\exp(-(\gamma\beta/(1+\beta)))/(1+\beta)^2)}}\right)\right)\right)\right] \tag{67}$$

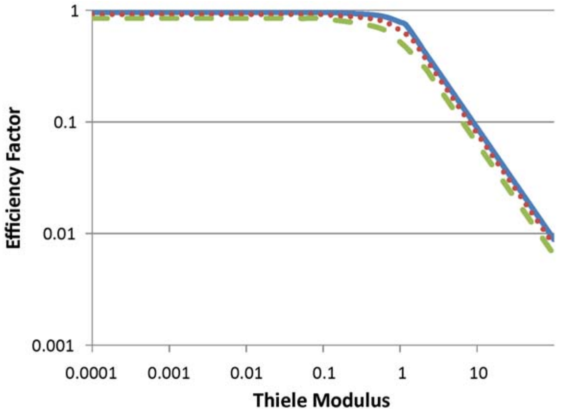

Fig. 7. Change in the efficiency factor as a function of Thiele modulus for a zero-order reaction in a non-isothermal slab for an Arrhenius group, $\gamma = E/R_gT_S$, of 5 (━━━), 10 (••••••••••), and 20 (▬ ▬ ▬). The Arrhenius group is the dimensionless activation energy for the reaction. The thermicity, β, is 0.1.

With efficiency factor:

$$\eta = \frac{1}{2}\left(\frac{1}{\phi_0}\right)^2 \left.\frac{df}{dz}\right|_{z=1} = -\frac{\sqrt{\left(-\left(\frac{\gamma\beta}{(1+\beta)^2}\right)\right)\exp\left(-\left(\frac{\gamma\beta}{(1+\beta)}\right)\right)\left(1-\exp\left(\frac{\gamma\beta}{(1+\beta)^2}\right)\right)}}{\left(\frac{\gamma\beta\phi_0}{(1+\beta)^2}\right)} \tag{68}$$

In a similar manner to what was done with the "normal" boundary conditions, we can ask the question, "at what value of the Thiele modulus does the concentration reach zero at the center of the pellet (i.e. $f(0) = 0$)?"

$$\phi_{0,c} = \tanh^{-1}\left(\sqrt{1-\exp\left(\frac{\gamma\beta}{(1+\beta)^2}\right)}\right) \times \left(-\frac{1}{(\gamma\beta/(1+\beta)^2)\exp(-(\gamma\beta/(1+\beta)))}\right)^{1/2}$$

For both the "normal" and "dead zone" boundary conditions, it can be shown that the concentration profile at the critical modulus is:

$$f = \frac{(1+\beta)^2}{\gamma\beta}\ln\left[1-\tanh^2\left(z\tanh^{-1}\left(\sqrt{1-\exp\left(\frac{\gamma\beta}{(1+\beta)^2}\right)}\right)\right)\right] \tag{69}$$

Concentration profiles for various values of β and γ are given in Fig. 6; efficiency factors as a function of the Thiele modulus is shown in Fig. 7.

4. Discussion and conclusion

The purpose of this paper is to point out to engineers the existence and consequences of dead zones in porous catalysts. We have discussed in depth nth order reactions in isothermal slabs and, to a lesser extent, cylinders and spheres. Possible mistakes that can be made without considering the possibility of a dead zone (or, more specifically, the necessity of changing boundary conditions after the onset of a dead zone) were also discussed. The correct concentration profile and efficiency factors for isothermal zero-order reactions in spheres and (using the low beta approximation) non-isothermal zero-order reactions in slabs (this is the first time, to the best of our knowledge) was also shown. Future work on this subject will entail studies of determining the concentration profiles and efficiency factors for *n*th order reactions in isothermal cylinders, *n*th order reactions in non-isothermal slabs, and both zero and *n*th order reactions in non-isothermal cylinders and spheres.

We would like to finish by making a comment about the kind of analytical solutions presented here. Although non-linear differential equations like the ones presented here in very little time can be computed numerically, we found numerical approaches to be of limited use in the analysis presented here. This is, presumably, due to the fact that finding the precise critical Thiele modulus proved difficult (likely due to round off error). Even with the existence of a dead zone known, it is difficult to work with the uncommon boundary conditions presented by this physical situation. However, future work in this area may require use of more complex numerical analysis in order to make progress.

Symbols

$J\,(\mathrm{mol/s\,m^2})$	flux
$S\,(\mathrm{m^2})$	surface area
$x\,(\mathrm{m})$	position
$r\,(\mathrm{mol/s\,m^3})$	reaction rate per unit volume
n	reaction order
$k\,(\mathrm{m^{3n-3}/s\,mol^{n-1}})$	rate constant
$c\,(\mathrm{mol/m^3})$	concentration
$c_S\,(\mathrm{mol/m^3})$	surface concentration
$D\,(\mathrm{m^2/s})$	effective diffusivity
L	half-width (or radius) of pellet
$z = \frac{x}{L}$	fractional distance from center of pellet (dimensionless distance)
$f = \frac{c}{c_S}$	ratio of concentration at point x relative to that at the surface
$\phi = L\sqrt{\frac{k \cdot c^{n-1}}{D}}$	Thiele modulus (a reaction "rate" over a diffusion "rate")
$p = \frac{df}{dz}$	concentration gradient
ϕ_c	The critical Thiele modulus. This is the Thiele modulus at which the concentration becomes zero at the center of the pellet.
$\eta = \left(\frac{1}{\phi^2}\right)\frac{df}{dz}\Big\vert_{z=1}$	efficiency factor
$C_1, C_2, C_3, \ldots$	integration constants
z_c	position at which the dead zone begins (only for $\phi \geq \phi_c$)
$T\,(K)$	temperature
$T_S\,(K)$	surface temperature
$k_{eff}\,(\mathrm{W/m\,K})$	effective thermal conductivity
$\Delta H_R\,(\mathrm{J/mol})$	reaction enthalpy
θ	dimensionless temperature
$\beta = \frac{(\Delta H_R) D c_S}{k_{eff} T_S}$	thermicity, a measure of non-isothermal effects
$k_S\,(\mathrm{m^{3n-3}/s\,mol^{n-1}})$	pre-exponential factor at the surface temperature
$E\,(\mathrm{J/mol})$	activation energy
$R_g = 8.314$	gas constant
$\phi_0 = L\sqrt{\frac{(n+1)k_S C_S^{n-1}}{2D}}$	generalized Thiele modulus
$\phi_{0,c}$	generalized, critical Thiele modulus

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