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Rational Approximations of Effectiveness Factor and General Diagnostic Criteria for Heat and Mass Transport Limitations

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I. INTRODUCTION

Reactions occurring in the presence of porous catalysts are accompanied by transport of heat and mass in the whole structure formed by the porous body and the fluid film surrounding the external surface. Under these circumstances the chemical process can take place in the presence of temperature and concentration gradients in the porous pellet as well as in the fluid layer formed around the particle.

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After the pioneering works of Thiele [1], Zeldovich [2], Wagner [3], Wheeler [4], and Weisz [5], a great number of contributions have been presented to study new aspects of the effect of diffusion on the observed rate of reaction and its role in modifying the activity and selectivity of porous catalysts. Relevant conclusions on this subject have been concisely set forth in the texts of Satterfield and Sherwood [6], Petersen [7], Satterfield [8], and more recently by Aris [9], Carberry [10], and Satterfield [11].

The present article is specifically designed to discuss the existing "rational approximation" to predict the effect of diffusional phenomena on the overall rate of reaction under a great variety of circumstances and also to show how some part of the theoretical development can be used to deduce two general criteria to establish the conditions where diffusional phenomena can be safely neglected.

The effectiveness factor, defined as the rate of reaction divided by the rate which would occur with no resistance to heat and mass transfer inside or outside the pellet, is an important parameter in reactor design calculations involving catalyst pellets. Moreover, since this parameter is needed in the design step by step along the reactor, a number of useful numerical techniques have been proposed in the past to overcome, in the shortest way, the numerical integration of mass and heat balances inside the pellets. Increasing experience in this field has shown that the orthogonal collocation procedures as described by Villadsen and Michelsen [12] seem to be the optimum technique. However, under steep changes in concentration and temperature the procedure can fail and some care should be taken although this normally leads to an increase in computational time.

The methods that will be reviewed in this article do not have this disadvantage and remain tractable in all circumstances. Under the worst conditions the whole method is reduced to the solution of a single nonlinear algebraic equation. The essential feature of the method is its ability of matching very well known asymptotic expressions of the effectiveness factor.

Another great concern in catalytic experimental work is to establish if the data obtained are free from all transport influences before they are processed to yield correct kinetic paramaters, activity, and selectivity of the catalysts. It will be shown that all the deduced theoretical criteria, recently reviewed by Butt [13] and Madon and Boudart [14], as well as any new cases can be encompassed by only two general criteria. One criterion applies to intraparticle effects while the other applies to interphase phenomena; each of them is independent of the other.

II. EFFECTIVENESS FACTOR ESTIMATION

A. Present Status

Effectiveness factor estimation is of great concern in heterogeneous catalytic chemical reactor analysis and design. The properties of the solution and its asymptotic behavior, as a function of relevant kinetic and diffusional parameters, is well established as reviewed by Aris [9]. Accurate numerical methods are available for computing effectiveness factor as pointed out by Villadsen and Michelsen [12]. A great number of particular solutions based on these general collocation techniques have been presented in the chemical engineering literature.

Catalytic chemical reactor design needs repeated effectiveness factor calculations for different sets of parameters, and this need is especially acute in the simulation of packed-bed reactors since local values of effectiveness factor are affected by local temperature and concentration changes, and as a consequence have to be determined for every point along the reactor except in the case of isothermal first-order irreversible kinetic behavior. The importance of this calculation has been recently emphasized by Froment and Bishoff [15].

However, the vast literature on this subject contains very few attempts to develop fast and sufficiently accurate approximations of the effectiveness factor. One possible alternative is the one-point collocation method of Stewart and Villadsen [16] that requires the solution of an algebraic nonlinear equation and the well-known asymptotic solution for the large Thiele module. A large inherent error exists in this crude approximation around the region where the "collocation solution" crosses the asymptote. Similar difficulties were observed by Paterson and Creswell [17], Karanth et al. [18], and Ramachandran et al. [19]. This is not a serious disadvantage since the accuracy of the calculations can be increased by taking more than one collocation point, although a system of nonlinear algebraic equations has to be solved and can be quite time consuming.

The first approximate attempt to predict the effectiveness factor for arbitrary kinetic expressions and pellet geometry was probably by Petersen [7] who suggested it as a general expression found for first-order irreversible reactions in a slab pellet but where the Thiele modulus was replaced by a "normalized" one obtained in terms of the asymptotic expression of the effectiveness factor. The same concept was advanced almost simultaneously by Aris [20, 21] and Bishoff [22].

It should be noted, however, that this approach, if true, will lead to a unique dependence of the effectiveness factor on this

"normalized" Thiele modulus. Unfortunately, it is well known that even for the simplest case the effect of pellet geometry is not accounted for by this simple representation.

Liu [23] proposed some empirical formulas which can only be applied to first- and second-order nonisothermal reactions. Though explicit, the method is not accurate and cannot deal with systems having steady-state multiplicity. Much more accurate is the empirical approximation of Jouven and Aris [24], but only for first-order nonisothermal reactions. The variational methods of Strieder and Aris [25] and Rester and Aris [26] as well as that of Jouven and Aris [24] have not found many applications since they are difficult to apply. More recently Rajadhyaksha et al. [27] presented an empirical formula aimed at predicting effectiveness factor values for large values of Thiele moduli for the case of Langmuir-Hinshelwood nonisothermal kinetics.

None of the forementioned methods reviewed, except the case of one collocation point, can be easily extended to rate expressions not covered in the corresponding articles. Moreover, the effect of pellet geometry, nonuniform catalytic activity distribution, and mass and thermal diffusivity dependence on concentration and temperature is by no means straightforward. Churchill [28], based on previous work (Churchill and Usagi [29]), suggested a new expression for the effectiveness factor that fits the asymptotic behavior for small and large values of the Thiele moduli. However, the effectiveness factor is only a function of the "normalized" Thiele modulus and so it cannot account for the effect of pellet geometry, reaction rate expression, and eventually a nonuniform activity distribution inside the catalyst pellet. Nevertheless, it is the first attempt to match asymptotic expressions through a so-called rational approximation. Churchill [28] has also shown the importance of these kinds of expressions when effectiveness factor calculations involving interphase resistances are required.

Very recently, and almost simultaneously, Wedel and Luss [30] and Gottifredi et al. [31, 32] presented approximate expressions for the effectiveness factor based on matching the asymptotic behavior of the effectiveness factor for small and large values of the Thiele moduli. However, their proposed expressions are rational approximations of the effectiveness factor and are capable of accounting for those effects neglected in Churchill's [28] analysis.

In the section "Rational Approximations" the main steps of these methods are outlined since they can be used for any specific particular situation except the multiple solutions region of the effectiveness factor-Thiele modulus plane.

As will be shown, the rational approximation does not require any iterative or interpolative computation scheme and, at most, the solution of a nonlinear algebraic equation and the numerical calculation of two integrals that would be necessary with any of the methods reviewed above.

B. Asymptotic Effectiveness Factor Behavior

Let us consider the case of a single reaction taking place in a porous catalytic pellet. The conservation of Species A at steady-state conditions is most conveniently described by a parabolic second-order ordinary differential equation which accounts for diffusive and reactive fluxes. It will first be assumed that interphase resistances can be neglected and afterwards it will be shown how they can be incorporated into a calculation scheme. The dimensionless mass balance for Reactant A can be written as

$$x^{-n}\frac{d}{dx}\left(x^n \mathcal{D}(C)\frac{dC}{dx}\right) = h^2 f(x) R(C) \tag{1}$$

where h is the Thiele modulus defined by

$$h^2 = (r_S L^2 / D_S C_S) \tag{2}$$

and $\mathcal{D}(C)$ and R(C) are the dimensionless diffusivity and rate of reaction, respectively, normalized in terms of their respective surface values (D_S and r_S):

$$R(C) = (r/r_S) \tag{3}$$

$$\mathcal{D}(C) = (D/D_S) \tag{4}$$

while f(x) is a normalized catalytic activity distribution function in such a way that

$$\int_0^1 (n+1) f(x) x^n dx = 1 \tag{5}$$

In writing Eq. (1) it is assumed that an explicit relation exists between the dimensionless concentration of any other reactant or product taking place in the single reaction and between temperature and concentration. Such relations are straightforward when effective diffusivities and thermal conductivity are assumed neither

dependent on temperature nor on concentration (see Gottifredi et al. [31]).

By x we denote the dimensionless coordinate directed from the center of the pellet (x = 0) to the external surface (x = 1) and n (0, 1, 2) denotes slab, cylindrical, or spherical pellets, respectively.

Appropriate boundary conditions for Eq. (1) are

$$C = 1,\ x = 1; \quad dC/dx = 0,\ x = 0 \tag{6}$$

Under realistic situations Eq. (1) does not have an analytical solution since the term R(C) is nonlinear with respect to C. However, from a chemical engineering point of view, one is not interested in solving Eq. (1) but rather in estimating the effectiveness factor defined as

$$\eta = (n + 1) \int_0^1 R(C) f(x) x^{n+1} dx \tag{7}$$

Since C(x) is not known, η cannot be estimated. However, Eq. (1) can be approximately solved by perturbation procedures either when $h << 1$ or when $h >> 1$.

In fact, when $h^2 << 1$, Eq. (1) itself suggests the following series as an approximate solution:

$$C = 1 + h^2 G_1(x) + h^4 G_2(x) + 0(h^6) \tag{8}$$

which after being replaced in R(C), $\mathcal{D}(C)$, and in Eq. (1), and collecting terms of equal power of h, produces the following set of linear ordinary equations:

$$\frac{d}{dx}(x^n G_1') = x^n f(x) \tag{9}$$

$$\frac{d}{dx}(x^n G_2') = x^n f(x) R'(1) G_1 - \mathcal{D}'(1) \frac{d}{dx}\left(G_1 \frac{dG_1}{dx}\right) \tag{10}$$

Where R'(1) and $\mathcal{D}'(1)$ denote the first derivatives with respect to C evaluated at C = 1. According to Eq. (8) and Conditions (6), Eqs. (9) and (10) are to be solved subject to

$$G_1(1) = G_2(1) = 0; \quad dG_1/dx = dG_2/dx = 0,\ x = 0 \tag{11}$$

Since the System (9)-(10) can be easily solved through standard analytical methods, it is possible to obtain a approximate expression for η, valid when $h^2 << 1$:

$$\eta = 1 - \sigma_1 h^2 + \sigma_2 h^4 + 0(h^6) \tag{12}$$

where:

$$\sigma_1 = -\int_0^1 (n+1)x^n f(x)R'(1)G_1 dx = -G_2'(0)(n+1) \tag{13}$$

and

$$\sigma_2 = (n+1)\int_0^1 x^n f(x)[R'(1)G_2 + R''(1)G_1^2/2]dx \tag{14}$$

On the other hand, when $h^2 \to \infty$, it is convenient to introduce the stretched coordinate

$$\xi = h(1 - x) \tag{15}$$

into Eq. (1) yielding

$$\frac{d}{d\xi}\left(\mathcal{D}(C)\frac{dC}{d\xi}\right) - \frac{n}{h}\left(1 + \frac{\xi}{h}\right)\mathcal{D}(C)\frac{dC}{d\xi} = R(C)f\left(1 - \frac{\xi}{h}\right) \tag{16}$$

with the following boundary conditions:

$$\begin{aligned} C &= 1 \quad & \xi &= 0 \\ C &\to 0 \quad & \xi &\to \infty \end{aligned} \tag{17a, b}$$

The solution to Eq. (16) can be represented by the following perturbation series:

$$C = \phi_0 + \frac{1}{h}\phi_1 + 0(h^{-2}) \tag{18}$$

Inserting Eq. (18) into Eq. (16) and collecting terms of equal power of h yields the following equations:

$$\frac{d}{d\xi}\left(\mathcal{D}(\phi_0)\frac{d\phi_0}{d\xi}\right) = f(1)R(\phi_0) \tag{19}$$

$$\frac{d}{d\xi}\left(\mathcal{D}'\phi_1\frac{d\phi_0}{d\xi} + \mathcal{D}(\phi_0)\frac{d\phi_1}{d\xi}\right) - n\mathcal{D}(\phi_0)\frac{d\phi_0}{d\xi} =$$

$$R'\phi_1 f(1) - R(\phi_0)f'\xi \tag{20}$$

where $\mathcal{D}'$ and R' denote derivatives with respect to C evaluated with $C = \phi_0$.

Following the elegant procedure of Wedel and Luss [30], it is possible to obtain an asymptotic expression for η as

$$\eta = \rho_1/h + \rho_2/h^2 + (h^2) \tag{21}$$

where

$$\rho_1 = +(n+1)\left|2\int_0^1 f(1)\mathcal{D}(\phi_0)R(\phi_0)d\phi_0\right|^{1/2} \tag{22}$$

$$\rho_2 = -\frac{(n+1)^2[n + \frac{1}{2}f'(1)/f(1)]}{\rho_1}\int_0^1 \mathcal{D}(\phi_0)p(\phi_0)d\phi_0 \tag{23}$$

and

$$p = -\left[2\int_0^{\phi_0} f(1)\mathcal{D}(\phi)R(\phi)d\phi\right]^{1/2} \tag{24}$$

It follows that the coefficients ρ_1 and ρ_2 in Eq. (21) can be calculated by analytical methods or by standard numerical computation techniques depending upon the form of $\mathcal{D}(\phi_0)$ and $R(\phi_0)$. Wedel and Luss [30], in their Table 1, summarize the cases of most practical interest for irreversible kinetic expressions with only one component and assuming $\mathcal{D}(\phi_0) = 1$, but including the nonisothermal situation for an m-th order irreversible expression.

C. Rational Approximations

Expressions (12) and (21) need to be matched over the whole range of h values. Further, it is known that, except for the multiple solution region, the effectiveness factor is a smooth function of the Thiele modulus.

As pointed out in the Introduction, the first attempt in producing a rational approximation of these two asymptotic expressions was due to Churchill [28] who proposed, for isothermal conditions,

$$\bar{\eta} = (1 + (h/\rho_1)^2)^{-1/2} = (1 + \bar{h}^2)^{-1/2} \tag{25}$$

where $\bar{h}$ is the normalized Thiele modulus. However, it is well known that η is not a unique function of $\bar{h}$. By expanding Eq. (25) when $\bar{h} \to 0$ and $\bar{h} \to \infty$, it is clearly seen that it coincides with the first terms of Eqs. (12) and (21).

The next logical step leads to the two parameter rational expression

$$\eta_1 = \frac{(1 + a^2\bar{h}^2)^{1/2}}{(1 + a\bar{h}^2)} \tag{26}$$

where the parameter "a" can now be used to fit asymptotic Expression (12) up to terms of the order of h^2. Expanding Eq. (26) in a Taylor series when $\bar{h}^2 \to 0$ and then comparing it with Eq. (12) yields

$$a = 1 \pm \sqrt{1 - 2\sigma_1\rho_1^2} \tag{27}$$

Equation (26) was in fact proposed by Gottifredi et al. [31]. It produced extremely good results for a great number of kinetic expressions under isothermal conditions. However, the positive root must be taken in Eq. (27) when the apparent reaction order is greater than 0.5 and the negative root when it is smaller than 0.5. Equation (26) was also recently tested by Gonzo and Gottifredi [33] for irreversible m-th order and Langmuir-Hinshelwood kinetic expressions under nonisothermal conditions with fairly good results except, of course, in the multiple solution region. As a rule it can be said that Eq. (26) produces estimates which are within 5% of the exact η values. One disadvantage of Eq. (26) is due to the form in which parameter "a" is defined. It should be noticed that "a" can become imaginary when $2\sigma_1\rho_1^2 > 1$. It was shown that under these circumstances "a" is assumed equal to 1. In such a way, Eq. (26) coincides with Eq. (25). Gottifredi et al. [32] have shown that this short way solution ($a = 1$ only when $2\sigma_1\rho_1^2 > 1$) also produces fairly good estimates since maximum deviations are below 8%. It should be stressed, however, that this is not the proper solution since, as is shown below, another

rational expression must be tried that will take into account more terms in the expansions when $h \ll 1$ or $h \gg 1$. It is interesting to note that for a first-order reaction, "a" is almost exactly equal to 1 for a cylindrical pellet and the maximum deviation with exact values of η is about 1%. Thus Churchill's expression (25) should be better than the classical generalization

$$\eta_T = \text{tangh}\,(h)/h \tag{28}$$

Equation (28) represents the case where $n = 0$, while Eq. (25) is almost exact when the intermediate situation ($n = 1$) is met.

Wedel and Luss [30] proposed a different type of rational expression since they tried to match Eqs. (12) and (21) with the following expression:

$$\eta_2 = (1 + b_1 h + b_2 h^2)/1 + b_3 h + b_4 h^2 + b_5 h^3 \tag{29}$$

thus allowing even and odd powers of h. This is an advantage since it permits one to find the five unknowns, b_1 to b_5, with only σ_1, ρ_1, and ρ_2 yielding

$$b_1 = b_3, \qquad b_4 = b_2 + \sigma_1$$

$$b_2 = \rho_1 b_5, \qquad b_5 = \frac{b_3 - \sigma_1\rho_1}{\rho_2 + \rho_1^2} \tag{30a, b, c, d, e}$$

$$b_3 = \frac{\rho_1\sigma_1}{1 - \sigma_1(\rho_2 + \rho_1^2)}$$

Wedel and Luss [30] performed a great number of test calculations with Eq. (29) for a spherical pellet, m-th order, and Langmuir-Hinshelwood kinetic expressions under isothermal and nonisothermal conditions. It was shown that some difficulties arise when $R'(1) < 1$ since b_5 must be evaluated through an empirical procedure. It was concluded, however, that with these modifications (see Wedel and Luss [30]), Eq. (29) produces extremely good results when compared with exact values as long as multiplicity is absent. Maximum deviations under isothermal conditions are well below 7% in the most unfavorable situation and about 15% when exothermic m-th order reactions must be considered.

Gottifredi et al. [32], in an attempt to overcome the problem of imaginary solutions for "a" in Eq. (27), proposed a more complete rational approximation in terms of h^2:

$$\eta_3 = \frac{(1 + a\hat{h}^2)^{1/2}}{(1 + a\hat{h}^2)} + \frac{d_1\hat{h}^2}{(1 + d_2\hat{h}^2)^2} \tag{31}$$

where a, d_1, and d_2 must be found by fitting asymptotic Expressions (12) and (21) for small and large values of h, respectively. They yield

$$\left|\left(1 - \frac{a^2}{8} - \frac{a}{2}\right)\frac{a^2}{\rho_1^4} - \sigma_2\right|^2 = \frac{4}{\rho_2}\left[\left(1 - \frac{a}{2}\right)\frac{a}{\rho_1^2} - \sigma_1\right]^3 \tag{32}$$

$$d_1 = \rho_1^2\rho_2 d_3; \quad d_2 = \rho_1^2 d_3 \tag{33}$$

where the auxiliary parameter d_3 was introduced:

$$d_3 = +\left|\left[\left(1 - \frac{a}{2}\right)\frac{a}{\rho_1^2} - \sigma_1\right]\Big/\rho_2\right|^{1/2} \tag{34}$$

Clearly, once "a" is found by solving the nonlinear algebraic Equation (32), d_3 can be calculated with Eq. (34) and d_1 and d_2 with Eq. (33). In all cases investigated, the values of "a" were between 1.1 and 4. This speeds up the trial and error procedure needed to solve Eq. (32). However, for calculations along a reactor, the previous solution of "a" can be used as first guess in the next step.

Equation (31) produces extremely good estimates of η. When compared with exact values, it is shown that maximum deviations are below 2%. However, from a practical point of view, Gottifredi et al. [32] concluded that, when $2\sigma_1\rho_1^2 < 1$, Eq. (26) should be used since under these circumstances maximum deviations are below 5%, while Eq. (31) should be applied when $2\sigma_1\rho_1^2 > 1$. However, Eq. (31) cannot handle η behavior within the multiple solutions region.

There are some other interesting features of approximate Expression (26) which deserve a comment. First of all, Eq. (26) predicts a maximum of η when

$$\hat{h}_m^2 = a^{-2}(a - 2) \tag{35}$$

and as the normalized Thiele modulus must always be positive such a maximum will exist only when $a > 2$. This can only be achieved when the positive root of Eq. (27) is taken and when $\sigma_1 < 0$. However, from Eqs. (13) and (9) it is easy to demonstrate that

$$\sigma_1 = (n + 1)R'(1)\int_0^1 x^{-n}\left[\int_0^x x^n f(x)dx\right]^2 dx \qquad (36)$$

Thus $\sigma_1 < 0$ necessarily implies $R'(1) < 0$. Second, it could be of interest to find the value of $\hat{h}$ below which $\eta > 1$. A very simple calculation with Eq. (26) can be used to establish necessary and sufficient conditions for $\eta > 1$:

$$\eta > 1 \quad \text{when} \quad \sigma_1 < 0 \text{ and } \hat{h}^2 < (1 - 2a^{-1}) \qquad (37)$$

These conditions can also be used to roughly define the region where multiple solutions can be met. It is interesting to note that a necessary condition to violate Luss's [34] uniqueness criterion, valid for $f(x) = 1$, is just $R'(1) < 0$. Gonzo and Gottifredi [33] concluded that Eq. (26) can also be safely used with severe exothermic reactions in the region where $\hat{h}^2 > (1 - 2a^{-1})$.

These brief comments regarding η behavior, as described by Eq. (26), are to show that with a very simple rational approximation it is possible to obtain a number of useful criteria.

It should be stressed, however, that those presented here are by no means all the rational expressions that can be proposed. In this sense an open field for a search for better and simpler expressions than those reviewed above exists.

D. Interphase Heat and Mass Transfer Effects

As was pointed out in Section II-B, when a single reaction is considered it is always possible to relate the concentration of any species and the temperature inside the pellet with the key component concentration. In fact, from the dimensionless mass and heat balances, when transport parameters are temperature and concentration independent, it can be shown that

$$C_i = \Gamma_i(C - 1) + 1$$
$$T = \beta(1 - C) + 1 \qquad (38a, b)$$

C_i is the dimensionless concentration of species i referred to its surface value ($C_{iS'}$) and T is the dimensionless temperature, also related to its surface value ($T_{S'}$), while Γ_i and β are given by

$$\Gamma_i = -\left(\frac{DC_S'}{D_i C_{Si}'}\right)\alpha_i \tag{39}$$

$$\beta = DC_S'(-\Delta H)/\kappa T_S' \tag{40}$$

α_i being the stoichiometric coefficient, $-\Delta H$ the heat of reaction, and κ the effective thermal conductivity of the pellet.

However, when significant concentration and temperature differences between pellet surface and the bulk of the fluid arise, the effectiveness factor as calculated in Section II-B must be corrected in order to refer to the main reaction rate in terms of its corresponding bulk value in the flowing fluid:

$$\eta_0 = \eta\left(\frac{r_S}{r_o}\right) \tag{41}$$

where the subscript "o' is used to denote bulk value.

Mass and heat balances at the external pellet surface should now be taken into account. We can write

$$\left(\frac{C_{io}'}{C_{iS}'} - 1\right)B_{imi} = \left.\frac{dC_i}{dx}\right|_{x=1} \tag{42}$$

$$\left(\frac{T_o'}{T_S'} - 1\right)B_{ie} = \left.\frac{dT}{dx}\right|_{x=1} \tag{43}$$

where B_{im} and B_{ie} represent Biot numbers for mass and heat transport:

$$B_{imi} = (k_{gi}L/D_i) \tag{44}$$

$$B_{ie} = (h_e L/\kappa) \tag{45}$$

It should also be noticed that from Eq. (2)

$$h_0^2 = h^2(r_o/r_S)(C_S'/C_o') \tag{46}$$

By combining Eqs. (42) and (43) with Eqs. (38a, b), (41), and (46), the following relations can be obtained:

$$\frac{C_{iS}'}{C_{io}'} = 1 - \frac{h_o^2 \eta_o \Gamma_{io}}{B_{imi}(n+1)} \tag{47}$$

$$\frac{T_S'}{T_o'} = 1 + \frac{\eta_o h_o^2 \beta_o}{B_{ie}(n+1)} \tag{48}$$

Equation (47) is also valid for the key component with $\Gamma_{io} = 1$. By setting the values of B_{imi}, B_{ie}, β_o, and the Arrhenius numbers, η can first be calculated with some adequate rational approximation by assuming negligible interphase resistances ($\eta = \eta_o$ and $h = h_o$). With this first approximation a correction is made with Eqs. (47) and (48) and the resulting values can be used to repeat the whole procedure until two successive calculations with Eqs. (47) and (48) indicate that convergence has been achieved. In a chemical reactor calculation the procedure can be speeded up by using values of h_o and η_o found in the previous step of the numerical calculation as a first guess.

The advantage of this procedure is due to the rational approximation since it allows a rapid calculation of η in each trial. Convergence is found very rapidly even with rather strong exothermic reactions as was shown by Gonzo and Gottifredi [33]. Moreover, under these conditions the interphase heat transfer limitation plays an important role and cannot be neglected since large temperature differences between pellet surface and the bulk of the fluid may build up. This increase of surface temperature produces a dramatic increase in the values of h in such a way that the second condition in Eq. (37) is not fulfilled. Thus rational approximations can also be used with strong exothermic reactions.

The trial and error procedure described here produces η estimates with the same deviations with respect to exact values as those in Section II-C for each rational approximation.

III. GENERAL DIAGNOSTIC CRITERIA FOR TRANSPORT LIMITATIONS

Criteria to establish whether or not mass and heat transfer resistances can be neglected are of great importance for catalytic

reactor design and in experimental studies dealing with heterogeneous catalytic systems.

Some useful experimental criteria do not require knowledge of kinetic parameters; for instance, that presented by Koros and Nowak [35]. The main advantage of the latter, as pointed out by Madon and Boudart [14], is that it can be used to establish inter- and intraphase mass and heat transport limitations with supported as well as with unsupported catalysts (Gonzo and Boudart [36] and Boudart et al. [37]). On the other hand, theoretical criteria save experimental efforts but require some knowledge of the kinetic behavior of the system to be analyzed. This is just the situation in chemical reaction simulation. However, when kinetic parameters are not known, their values must be estimated and this may be a very difficult task.

Theoretical criteria have been extensively reviewed since the first contribution of Weisz and Prater [38] which is strictly valid for first-order irreversible reactions. However, these contributions deal with some particular case, e.g., isothermal irreversible m-th order reactions (Hudgings [39] and Weisz and Hicks [40]) or just the effect of temperature gradients inside a catalyst (Anderson [41]). Excellent summaries of existing criteria were presented by Froment and Bishoff [15] and Butt [13] and very recently by Madon and Boudart [14].

The purpose of this section is to show that there is no need to assume any kinetic expression to deduce useful criteria for transport limitations. Only two expressions are needed, one for interphase and the other for interparticle mass and heat transport effects. These expressions are easily deduced from the equations in Section II-B and II-D, and it can be advanced that the resulting expressions encompass all previous results based on some particular assumptions.

Applications of these two criteria to experimental data are presented elsewhere [42].

The general criterion used to establish the absence of interparticle transport limitation is always written in the following fashion:

$$|1 - \eta| \leq 0.5 \tag{49}$$

However, to fulfill Condition (49), h^2 must be small and so Eq. (12) can be used to rewrite Eq. (49) in a more useful form:

$$|\sigma_1 h^2| = |R'(1)\alpha h^2| \leq 0.05 \tag{50}$$

where, according to Eq. (36),

$$\alpha = (n + 1) \int_0^1 x^{-n} \left[\int_0^x x^n f(x) dx \right]^2 dx \tag{51}$$

Thus α only depends on the pellet geometry and $f(x)$, while the chemical kinetic behavior is concentrated in the term $R'(1)$. All existing interparticle criteria are summarized in Eq. (50). It is always applicable except when $R'(1) = 0$ since, in that case $\sigma_1 h^2$ in Eq. (50) must be replaced by $\sigma_2 h^4$. Typical values of α are given by Gonzo and Gottifredi [42] for linear and parabolic decaying activity distributions. When $f(x) = 1$:

$$\alpha = \left[(n + 1) (n + 3) \right]^{-1} \tag{52}$$

It is interesting to notice that a concentration or temperature dependence on diffusivity has no direct consequence on the criterion given by Eq. (50). However, it can have some indirect effect on $R'(1)$. Expressions for $R'(1)$ are given by Wedel and Luss [30] in their Table 1 and for other cases by Gonzo and Gottifredi [42] in their Table 2. Nevertheless, it is not a difficult task to generate $R'(1)$ for any particular situation.

When external transport phenomena are to be considered, the criterion to establish negligible effect can be written as

$$\left| 1 - \frac{\eta_o}{\eta} \right| \leq 0.05 \tag{53}$$

According to Eq. (41), however:

$$\frac{\eta_o}{\eta} = \frac{r_S}{r_o} = F(C^*) \tag{54}$$

where

$$C^* = \frac{C_S'}{C_o'} = 1 - \frac{\eta_o h_o^2}{(n + 1) B_{im}} \tag{55}$$

On physical grounds it will be expected that

$$\varepsilon = \frac{\eta_o h_o^2}{(n + 1) B_{im}} << 1 \tag{56}$$

if Criterion (53) is to be fulfilled. Expanding F(C*) in a Taylor series results in

$$F(C^*) = 1 + F'(1)\varepsilon + 0(\varepsilon^2) \tag{57}$$

where F'(1) denotes the first derivative of F(C*) with respect to C* evaluated at C* = 1.

Placing Eq. (57) into Eq. (54) and the result into Eq. (53) yields

$$|F'(1)\ \varepsilon| \leq 0.05 \tag{58}$$

It should be stressed that Eq. (58) was deduced without any particular assumptions except the existence of a single reaction.

Equation (58) can be regarded as the general inequality required to establish the absence of interphase transport limitations. It is valid for any kind of kinetic expression, pellet geometry, and activity distribution function inside the pellet, and encompasses all previously deduced expressions for particular situations.

As examples of applications, some particular cases will be considered. Let us first analyze the case of a reversible reaction where the dimensional rate of reaction is well described by a power law kinetic expression:

$$r = k\left(C'^{m}C_B'^{q} - \frac{1}{K}C_C'^{w}C_D'^{z}\right) \tag{59}$$

where K denotes the thermodynamic equilibrium constant and m, q, w, and z are the orders of reaction for the key component and Species B, C, and D, respectively. Assuming that the effect of temperature on K can be neglected, the criterion as given by Eq. (50) will take the following form:

$$\frac{r_{ob}L^2}{DC_S'} \leq \frac{(0.05/\alpha)}{\left|m + q\Gamma_B - \gamma\beta - \frac{1}{K'}(w\Gamma_C + z\Gamma_D)\right|} \tag{60}$$

where

$$K' = K\left[C'^{m}C_B'^{q}/C_C'^{w}C_D'^{z}\right]_S \tag{61}$$

$$\gamma = E/RT_S' \tag{62}$$

E is the activation energy of the forward specific rate constant k, and R is the universal gas constant. Expression (60) was not deduced before because the procedures previously presented had been worked out to solve only particular cases and some of these deductions required considerable effort.

Moreover, the example of Eq. (59) was so chosen to show that Eq. (60) summarizes all previous findings. In fact, Anderson's [41] criterion for establishing negligible temperature differences inside the pellet can be easily deduced from Eq. (60) for irreversible reactions ($K' \to \infty$) and when $|\gamma\beta| \gg m + q\Gamma_B$. On the other hand, Kubota and Yamanaka's [43] criterion is found when $K' \to \infty$ and $|m - \gamma\beta| \gg q\Gamma_B$.

From Eq. (60) it can be concluded that isothermal conditions prevail inside the pellet when

$$|\gamma\beta| \leq 0.05 \left[m + q\Gamma_B - \left(\frac{1}{K'}\right)\left(w\Gamma_C + z\Gamma_D\right) \right] \tag{63}$$

which can be considered an extension of Mears' [44] criterion which is strictly valid for irreversible ($K' \to \infty$) m-th order ($m \gg q\Gamma_B$) reactions.

Gonzo and Gottifredi [42] illustrated the application of the general expression (50) for Langmuir-Hinshelwood kinetic expressions. The effect of adsorbing species, such as reaction products, can also be taken into account following Roberts and Satterfield's [45] procedure to get the dimensionless rate of reaction.

As a second example let us analyze the case of an irreversible (m, p)-th-order reaction but with the aim of establishing the particular conditions where interphase resistances are negligible. F(C*) becomes

$$F(C^*) = C^{*m}\left[1 - \lambda_B(1 - C^*)\right]^p \exp\left(\frac{\gamma_o \phi(1 - C^*)}{1 + \phi(1 - C^*)}\right) \tag{64}$$

where

$$\lambda_B = \Gamma_{Bo}(B_{imB}/B_{im}); \qquad \phi = \beta_o(B_{im}/B_{ie}) \tag{65}$$

Application of Criterion (58) yields

$$\left(\frac{r_{ob}R^2}{DC_o'}\right) \leq \frac{(n + 1)0.05B_{im}}{|m + \lambda_B p - \phi\gamma_o|} \tag{66}$$

which can also be considered an extension of Mears' [46] results deduced for the particular case of an irreversible m-th order reaction.

It is worth mentioning that Gonzo and Gottifredi [42] compared the general criteria of Eq. (50) with the experimental results of Wu and Nobe [47] who measured η values for NO reduction with ammonia on cylindrical pellets with fairly good success. It was also shown that Criterion (58) when applied to the experimental results of Kehoe and Butt [48], who investigated benzene hydrogenation, predicts negligible external heat transfer resistance when temperature differences between the pellet surface and the bulk of the fluid are below 2 K.

IV. CONCLUSIONS

Rational approximations reviewed here give accurate results with minimal computational effort as long as multiplicity is absent. As discussed in Section II-C, Expression (26) accurately predicts effectiveness factor values under isothermal conditions provided the apparent reaction order is greater than 0.5. Maximum deviations are below 5%. When the reaction order is less than 0.5 the modified procedure of Wedel and Luss [30] (see Eq. 29) can be used with maximum deviations of about 7% even with Langmuir-Hinshelwood kinetic behavior and very strong rate depressions due to adsorption mechanisms. Gottifredi et al. [32] have shown that Expression (31) can produce extremely good effectiveness factor values with irreversible (m, p)-th-order kinetic expressions also taking into account the effect of nonuniform catalytic activity inside the pellet. Maximum deviation is below 3%.

When nonisothermal conditions are met, Wedel and Luss [30] concluded that their rational approximation produces fast and accurate results except in the multiple solutions region. Gonzo and Gottifredi [33] investigated the predictions obtained with the simple Expression (26) under nonisothermal conditions, concluding that it can be used in most realistic situations. Of course, it is not useful when multiplicity is present. As an example, results from Eq. (26) were compared with experimental and numerical predictions of Maymó and Smith [54] and showed that rational approximation deviations are within experimental error. Maymó and Smith's [54] experimental conditions were designed to meet very strong thermal effects.

Nevertheless, it could be that new rational approximations will be proposed in the near future to produce even better effectiveness factor predictions. However, it can be concluded that the

present rational approximations are versatile in their applicability to different rate expressions and provide sufficient accuracy for most chemical reactor analysis and simulation.

It must be stressed that this review was devoted to the single reaction case because not much work has been done on complex reaction systems. Pawlowski [49] and Roberts [50] performed an asymptotic analysis for the case of parallel reactions, assuming different values of reaction orders. Roberts [50] also developed expressions to estimate selectivity and the maximum effect of pore diffusion. More recently Cukierman and Lemcoff [51] developed an approximate asymptotic expression for the effectiveness factor when the Thiele moduli of both reactions are very large. The authors of this review have completed an investigation showing that the rational expression procedure can also be used with reasonable success for a parallel reaction system.

Schilson and Amundson [52] have also attempted effectiveness factor calculations for complex reaction system with a procedure developed by the same authors in a previous paper [53]. Since the heat generation is approximated by a linear function of temperature, a successive iteration scheme must be used to obtain the final results.

Another important feature of rational approximations of the effectiveness factor is the possibility of considering, with small extra effort, the effect of interphase heat and mass transfer which can play an important role in many realistic situations.

Finally, it was shown that with asymptotic perturbation procedures it is possible to derive two useful general criteria to establish the absence of interparticle and interphase mass and heat transport limitations in heterogeneous reaction systems. They can be readily applied to different rate expressions, geometry, and also take into account the activity distribution function inside the pellet.

REFERENCES

[1] E. W. Thiele, Ind. Eng. Chem., 31, 916 (1939).
[2] Y. B. Zeldovich, Zh. Fiz. Khim. USSR, 13, 163 (1939).
[3] C. Wagner, Z. Phys. Chem., A193, 1 (1943).
[4] A. Wheeler, in Catalysis, Vol. 2 (P. H. Emmett, ed.), Reinhold, New York, 1955.
[5] P. B. Weisz, Z. Phys. Chem. N.F., 11, 1 (1957).
[6] C. N. Satterfield and T. K. Sherwood, The Rate of Diffusion in Catalysis, Addison-Wesley, Reading, Massachusetts, 1963.

[7] E. E. Petersen, Chemical Reaction Analysis, Prentice-Hall, Englewood Cliffs, New Jersey, 1965.
[8] C. N. Satterfield, Mass Transfer in Heterogeneous Catalysis, M.I.T. Press, Cambridge, Massachusetts, 1970.
[9] R. Aris, The Mathematical Theory of Diffusion and Reaction in Permeable Catalysts, Claredon, Oxford, 1975.
[10] J. J. Carberry, Chemical and Catalytic Reaction Engineering, McGraw-Hill, New York, 1976.
[11] C. N. Satterfield, Heterogeneous Catalysis in Practice, McGraw-Hill, New York, 1980.
[12] F. Villadsen and M. L. Michelsen, Solution of Differential Equation Model by Polynomial Approximation, Prentice-Hall, Englewood Cliffs, New Jersey, 1978.
[13] J. B. Butt, Reaction Kinetics and Reactor Design, Prentice-Hall, Englewood Cliffs, New Jersey, 1980.
[14] R. J. Madon and M. Boudart, Ind. Eng. Chem., Fundam., In Press.
[15] G. Froment and K. Bishoff, Chemical Reactor Analysis and Design, Wiley, New York, 1980.
[16] W. E. Stewart and F. Villadsen, AIChE J., 15, 28 (1969).
[17] W. R. Paterson and D. L. Creswell, Chem. Eng. Sci., 26, 605 (1971).
[18] N. G. Karanth, H. P. Koh and R. Hughes, Ibid., 29, 451 (1974).
[19] P. A. Ramachandran, E. K. T. Kam, and R. Hughes, Ibid., 31, 244 (1976).
[20] R. Aris, Ind. Eng. Chem., Fundam., 4, 227 (1965).
[21] R. Aris, Ibid., 4, 487 (1965).
[22] K. Bishoff, AIChE J., 11, 351 (1965).
[23] S. L. Liu, Ibid., 16, 742 (1970).
[24] F. G. Jouven and R. Aris, Ibid., 18, 402 (1972).
[25] W. Strieder and R. Aris, J. Inst. Math. Its Appl., 8, 328 (1971).
[26] S. Rester and R. Aris, Chem. Eng. Sci., 27, 347 (1972).
[27] R. A. Rajadhyaksha, K. Vasudeva, and L. Doraiswamy, J. Catal., 41, 61 (1976).
[28] S. W. Churchill, AIChE J., 23, 208 (1977).
[29] S. W. Churchill and R. Usagi, Ibid., 18, 1121 (1972).
[30] S. Wedel and D. Luss, Chem. Eng. Commun., 7, 245 (1980).
[31] J. C. Gottifredi, E. E. Gonzo, and O. D. Quiroga, Chem. Eng. Sci., 36, 705 (1981).
[32] J. C. Gottifredi, E. E. Gonzo, and O. D. Quiroga, Ibid., 36, 713 (1981).
[33] E. E. Gonzo and J. C. Gottifredi, Lat. Am. J. Heat Mass Transfer, To Be Published.

[34] D. Luss, Chem. Eng. Sci., 26, 1713 (1971).
[35] R. Koros and E. Nowak, Ibid., 22, 740 (1967).
[36] E. E. Gonzo and M. Boudart, J. Catal., 52, 462 (1978).
[37] M. Boudart, A. Aldag, J. E. Benson, N. A. Dougharty, and G. C. Harkins, Ibid., 6, 92 (1966).
[38] P. B. Weisz and C. D. Prater, Adv. Catal., 6, 143 (1954).
[39] R. R. Hudgings, Chem. Eng. Sci., 23, 93 (1968).
[40] P. B. Weisz and J. S. Hicks, Ibid., 17, 265 (1962).
[41] J. B. Anderson, Ibid., 18, 147 (1963).
[42] E. E. Gonzo and J. C. Gottifredi, J. Catal., To Be Published.
[43] H. Kubota and Y. Yamanaka, J. Chem. Eng. Jpn., 2, 238 (1969).
[44] D. E. Mears, Ind. Eng. Chem., Process Des. Dev., 10, 541 (1971).
[45] G. W. Roberts and D. Satterfield, Ind. Eng. Chem., Fundam., 4, 288 (1965).
[46] D. E. Mears, J. Catal., 20, 127 (1971).
[47] S. C. Wu and K. Nobe, Ind. Eng. Chem., Prod. Res. Dev., 16, 136 (1977).
[48] J. P. Kehoe and J. Butt, AIChE J., 18, 347 (1972).
[49] J. Pawlowski, Chem.-Ing.-Tech., 33, 492 (1961).
[50] G. W. Roberts, Chem. Eng. Sci., 27, 1409 (1972).
[51] A. L. Cukierman and N. O. Lemcoff, Lat. Am. J. Chem. Eng. Appl. Chem., 9, 57 (1979).
[52] R. E. Schilson and N. R. Amundson, Chem. Eng. Sci., 13, 237 (1961).
[53] R. E. Schilson and N. R. Amundson, Ibid., 13, 226 (1961).
[54] J. A. Maymó and J. M. Smith, AIChE J., 12, 845 (1966).