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General Diagnostic Criteria for Transport Limitation in Porous Solid Chemical Reactions

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Theoretical criteria for establishing the absence of heat and mass transport limitations are of fundamental importance in chemical reactor engineering. Many criteria have been proposed in the past, but they cover only particular situations. This work shows that only two general expressions are needed to establish the absence of either intraparticle or interphase mass and heat transport. They encompass all previous theoretical findings and cover new cases. Moreover, when properly applied, the procedure can be used to generate useful criteria for systems with more than one reaction.

INTRODUCTION

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 kinetic studies dealing with heterogeneous catalytic systems.

Some useful experimental criteria do not require the knowledge of kinetic parameters, for instance, that presented by Koros and Nowak (*1*). The main advantage of the latter, as pointed out by Madon and Boudart (*2*), 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 (*3*) and Boudart *et al.* (*4*)). On the other hand, theoretical criteria save experimental efforts but require some knowledge of the kinetic behavior of the system to be analyzed. When kinetic parameters are not known their values must be estimated and this may be very difficult.

Theoretical criteria has been extensively reviewed since the first contribution of Weisz and Prater (*5*) which is strictly valid for first-order irreversible reactions. However, all contributions deal with some particular case, e.g., isothermal irreversible *m*th-order reactions (*6, 7*) or just the effect of temperature gradients inside a catalyst pellet (*8*). A summary of existing criteria was presented by Butt (*9*) and recently by Madon and Boudart (*2*).

Our purpose 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 for interphase and intraparticle mass and heat transport effects, respectively. The expressions are obtained by means of a simple perturbation procedure, previously developed by the authors (*10, 11*). The resulting expressions include, of course, all previously deduced results based on some particular assumptions. It must be stressed, however, that as in all previous theoretical analysis, the deduced criteria cannot be applied to a given situation without the knowledge of the kinetic expression as well as the value of its parameters.

The two general expressions will be used to analyze well-known experimental works in order to check the sensitivity of the deduced criteria. The effect of a nonuniform catalytic activity distribution is also taken into account for the first time.

ANALYSIS

A. Intraparticle transport limitations. Let us consider first the problem of estimat-

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ing the effectiveness factor (η) in a catalytic pellet where a single chemical reaction takes place. It is assumed that the dimensionless rate of reaction can be expressed as some arbitrary function (F) of the dimensionless concentration of the key component (C). This can always be achieved since the concentrations of other components and the temperature are easily related:

$$C_i = \lambda_i(C - 1) + 1 \tag{1}$$

$$T = \beta(1 - C) + 1, \tag{2}$$

where:

$$\lambda_i = -(D\, C_s'\, \alpha_i/D_iC_{si}') \tag{3}$$

$$\beta = D\, C_s'(-\Delta H)/\kappa\, T_s', \tag{4}$$

D being the effective diffusivity, κ the effective thermal conductivity, ΔH the heat of reaction, α_i the stoichiometric coefficient, C' the dimensional concentration of the key component, and subscripts i and s denote the ith component and surface value, respectively. Further it will be assumed that inside the pellet a nonuniform catalytic activity can exist which will be represented in terms of the normalized function $f(x)$ where x is the spatial coordinate. Thus:

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

Where $n = 0, 1, 2$ is to denote slab, cylindrical, or spherical geometry.

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

$$|1 - \eta| \leq 0.05, \tag{6}$$

where η is the effectiveness factor:

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

The dimensionless balance for the key component, under these circumstances, can be written as:

$$\frac{d^2C}{dx^2} + \frac{n}{x}\frac{dC}{dx} = h^2 f(x)F(C), \tag{8}$$

where $h = R(r_s/DC_s')^{1/2}$ and R is the pellet characteristic dimension. Boundary conditions are:

$$\frac{dC}{dx} = 0 \quad \text{at } x = 0;$$

$$C = 1 \quad \text{at } x = 1. \tag{9}$$

However, to fulfill condition (6) the Thiele modulus (h) must be small and Eq. (8) suggests for itself the following series solution:

$$C = 1 + h^2A(x) + 0(h^4). \tag{10}$$

After substituting Eq. (10) into Eq. (6) and collecting terms of like powers of h it can be shown that the auxiliary function $A(x)$ must be the solution of the following linear differential equation:

$$\frac{d^2A}{dx^2} + \frac{n}{x}\frac{dA}{dx} = f(x) \tag{11}$$

subject to:

$$\frac{dA}{dx} = 0 \quad \text{at } x = 0;$$

$$A = 0 \quad \text{at } x = 1. \tag{12}$$

Replacing Eq. (1) into Eq. (7) an expanding $F(C)$ in Taylor serie yields:

$$\eta = 1 + h^2\, \alpha\, F'(1) + 0(h^4), \tag{13}$$

where $F'(1)$ denotes the first derivative of F evaluated at $C = 1$ and

$$\alpha = -\int_0^1 (n + 1)f(x)A(x)x^n dx. \tag{14}$$

Now the criterion expressed by Eq. (6) can be rewritten in a more useful form:

$$|\alpha\, h^2F'(1)| \leq 0.05, \tag{15}$$

clearly α only depends on the pellet geometry and $f(x)$ while the kinetic behavior of the reaction system is concentrated on F' (1).

The resulting Eq. (15) can be regarded as the general criterion needed to establish the absence of intraparticle transport limitations. In fact it is valid for any kind of kinetic expression under nonisothermal conditions and also takes into account the effect of a nonuniform catalytic activity distribution inside a pellet of any shape.

All previously deduced expressions are particular cases of our expression (15).

B. Interphase transport limitations. When external transport phenomena are analyzed mass and heat balances at the external pellet surface must be considered:

$$\left(\frac{C'_o}{C'_s} - 1\right) B_{im} = \left.\frac{dC}{dx}\right|_{x=1} = \frac{h^2\eta}{(n+1)} \quad (16)$$

$$\left(\frac{T'_o}{T'_s} - 1\right) B_{ie} = \left.\frac{dT}{dx}\right|_{x=1} = -\beta \frac{h^2\eta}{(n+1)} \quad (17)$$

$$\left(\frac{C'_{o_i}}{C'_{s_i}} - 1\right) B_{im_i} = \left.\frac{dC_i}{dx}\right|_{x=1} = \lambda_i \frac{h^2\eta}{(n+1)} \quad (18)$$

where B_{ie} and B_{im} are the heat and mass Biot numbers and the subindex "o" is to denote bulk values. Taking into account η and h^2 definitions:

$$\frac{\eta_o}{\eta} = \frac{r_s}{r_o} \quad (19)$$

$$\frac{h^2}{h_o^2} = \left(\frac{C'_o}{C'_s}\right)\left(\frac{r_s}{r_o}\right). \quad (20)$$

Equations (16), (17), and (18) can now be used to provide a direct relation between surface concentration and temperature to their corresponding bulk values:

$$C^* = \left(\frac{C'_s}{C'_o}\right) = 1 - \frac{\eta_o h_o^2}{(n+1)B_{im}} = 1 - \varepsilon \quad (21)$$

$$C_i^* = \left(\frac{C'_{is}}{C'_{io}}\right) = 1 - \rho_i(1 - C^*) = 1 - \rho_i\varepsilon \quad (22)$$

$$T^* = \frac{T'_s}{T'_o} = 1 + \varphi(1 - C^*) = 1 + \varphi\varepsilon, \quad (23)$$

where

$$\rho_i = \lambda_{io}\left(\frac{B_{im}}{B_{im_i}}\right) \quad (24)$$

$$\varphi = \beta_o\left(\frac{B_{im}}{B_{ie}}\right) \quad (25)$$

and ε is defined by Eq. (21).

The criterion to establish the absence of interphase transport limitation can be expressed as:

$$\left|1 - \frac{\eta_o}{\eta}\right| \le 0.05. \quad (26)$$

According to Eq. (19) it can be shown that:

$$\frac{\eta_o}{\eta} = F_o(C^*) \quad (27)$$

since through Eqs. (22) and (23) F_o can be reduced to a unique function of C^*. To fulfill Eq. (26) ε must be small and then $F_o(C^*)$ can be expanded into a Taylor series, resulting in:

$$F_o(C^*) = F_o(1) + F'_o(1)\varepsilon + 0(\varepsilon^2), \quad (28)$$

where $F'_o(1)$ is to denote the first derivative of $F_o(C^*)$ evaluated at $C^* = 1$. By putting Eq. (28) into Eq. (27) and this into Eq. (26) the criterion can be expressed in the more direct form:

$$|F'_o(1)\varepsilon| \le 0.05. \quad (29)$$

This expression was deduced without any assumption except the existence of a single reaction.

Thus Eq. (29) 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 previous deduced expressions for particular situations.

DISCUSSION

The effect of nonuniform catalytic activity distribution on α is presented in Table 1 for three pellet shapes. This effect can be of great importance in some cases although it was not taken into account in previous contributions. In order to show the effect of the kinetic expression on $F'(1)$ three cases are presented in Table 2. Case "a" is for a general power law reversible reaction assuming an isothermal regime. Case "b" is for Langmuir–Hinshelwood kinetics where the

TABLE 1

Value of α

Activity distribution	$f(x)$	$n = 0$	$n = 1$	$n = 2$
Constant	1	1/3	1/8	1/15
Lineal	$a_1 x$	1/5	1/12	1/21
Parabolic	$a_2 x^2$	1/7	1/16	1/27

inhibition of the rate of reaction by the products concentration is considered under isothermal conditions. Case "c" is for a nonisothermal irreversible $(m;b)$th order power law kinetic expression. None of these cases have been previously analyzed. Our method reduces the whole problem to a very simple algebraic expression of C which can be readily differenciated to obtain $F'(1)$.

Let us assume $f(x) = 1$, spherical geometry and an isothermal reversible reaction of case (a). Then the criterion to establish the absence of intraparticle mass transport limitation results in:

$$\frac{r_{\text{ob}}R^2}{DC'_{\text{s}}} \leq \frac{0.75}{\left(\frac{K'}{K'-1}\right)\left\{m + b\,\lambda_{\text{B}} - \frac{1}{K'}(c\lambda_{\text{C}} + d\lambda_{\text{D}})\right\}}, \quad (30)$$

where $K' = K\,[C'^{m}_{\text{A}}\,C'^{b}_{\text{B}}/C'^{c}_{\text{C}}\,C'^{d}_{\text{D}}]_{\text{s}}$ and r_{ob} is the observed rate of reaction. Equation (30) reduces to the result derived by Hudgins (*6*) when $K' \rightarrow \infty$, and $\lambda_{\text{B}} \rightarrow 0$. In fact this would be the case of a pseudo-mth-order irreversible reaction. Under the same conditions a Langmuir–Hinshelwood kinetic expression (case (b) of Table 2) would lead to the following inequality:

$$\frac{r_{\text{ob}}R^2}{DC'_{\text{s}}} \leq 0.75\,(1 + K_{\text{I}}) \quad (31)$$

with

$$K_{\text{I}} = \left(K_{\text{A}}C'_{\text{As}} + \sum_j K_j\lambda_j C'_{j\text{s}}\right)\Big/\left[1 + \sum_j K_j(1 - \lambda_j)C'_{j\text{s}}\right].$$

TABLE 2

Expressions of $F(C)$ and $F'(1)$ for Different Cases

Case	Kinetic expression	$F(C)$	$F'(1)$
(a)	$r = K\left(C_{\text{A}}{}^m C_{\text{B}}{}^b - \frac{1}{K}C_{\text{C}}{}^c C_{\text{D}}{}^d\right)$	$\left(\frac{K'}{K'-1}\right)C^m(C-\Lambda_{\text{B}})^b\lambda_{\text{B}}{}^b\left[1 - \frac{(C-\Lambda_{\text{C}})^c(C-\Lambda_{\text{D}})^d}{K^*C^m(C-\Lambda_{\text{B}})^b}\right]$	$\frac{K'}{K'-1}\left[m + b\lambda_{\text{B}} - \frac{1}{K'}(c\lambda_{\text{C}} + d\lambda_{\text{D}})\right]$
(b)	$r = \frac{kC_{\text{A}}}{1 + K_{\text{A}}C_{\text{A}} + \sum_j K_jC_j}$	$\frac{C(1+K_{\text{I}})}{1+K_{\text{I}}C}$	$\frac{1}{1+K_{\text{I}}}$
(c)	$r = KC_{\text{A}}{}^m C_{\text{B}}{}^b$	$C^m[\lambda_{\text{B}}(C-1)+1]^b\exp\left[\frac{\gamma\beta(1-C)}{\beta(1-C)+1}\right]$	$m + b\lambda_{\text{B}} - \gamma\beta$

This rather simple result shows the importance of the effect of rate inhibition by products on the criterion. In fact, the larger the value of K_1 the smaller will be the importance of mass transport on the observed rate of reaction. This effect was pointed out by Petersen (*12*) as a disadvantage of the Weisz and Prater (*5*) criterion.

Finally from case (c) it can be shown that Eq. (15), for the case of a spherical pellet with uniform catalitic activity can be written as:

$$\frac{r_{ob}R^2}{DC_s'} \leq \frac{0.75}{|m + \lambda_B b - \gamma\beta|} \tag{32}$$

γ being the Arrhenius number. Eq. (32) reduces to Anderson's (*8*) criterion when $|\gamma\beta| \gg (m + \lambda_B b)$. However, in most circumstances this situation is not met. On the other hand Eq. (32) reduces to Kubota and Yamanaka's (*13*) criterion when $\lambda_B b \ll m$. It is also clear that when:

$$|\gamma\beta| \leq 0.05(m + \lambda_B b) \tag{33}$$

isothermal conditions must prevail. This result can be considered as an extension of Mears' (*15*) results valid for an irreversible mth-order reaction.

The criterion deduced for interphase transport limitation is wholly independent of the corresponding intraparticle criterion. In fact, it applies for any value of η_o. However, from Eq. (29) and the definition of ε it is clearly seen that the effect of external transport is increasingly important as $h_o \to \infty$. It is interesting to reanalyze case (c) taking into account external mass and heat transfer phenomena. The expression for $F_o(C^*)$ becomes:

$$F_o(C^*) = C^{*m}[1 - \rho_B(1 - C^*)]^b \exp\left\{\frac{\gamma_o\varphi(1 - C^*)}{1 + \varphi(1 - C^*)}\right\} \tag{34}$$

which allows rewriting the criterion for interphase transport limitation as:

$$\frac{r_{ob}R^2}{DC_o'} \leq \frac{(n + 1)0.05B_{im}}{|m + \rho_B b - \varphi\gamma_o|}. \tag{35}$$

This expression encompasses the isothermal case analyzed by Mears (14) when $m \gg |\rho_B b - \varphi\gamma_o|$. When heat transfer resistance prevails $|\gamma_o\varphi| \gg (m + \rho_B b)$, Mears' (*15*) results is readily obtained. It should be noticed that in Eq. (32), as well as in Eq. (35), compensation of mass and temperature gradients can reduce the denominator to nearly zero and apparently the criterion will always be fulfilled. In this case further terms in the expansion (Eqs. (10) and (28)) must be taken into account involving magnitudes to the order of h^4 or ε^2 instead of h^2 and ε, respectively. It should be noticed that due to compensation (only with exothermic reactions) the criteria can be fulfilled though perceptible temperature and concentration gradients are already present.

Comparison with experimental results. Wu and Nobe (*16*) studied the reduction of NO with ammonia. They measured the rate of reaction on cylindrical pellets of 3.175 mm in diameter and length. All the data required to check the intraparticle criterion are given except the Knudsen effective diffusivity of the reacting components which is estimated with a tortuosity factor of 2. Resulting values are:

$$D_{NO} = 0.012 \text{ cm}^2 \text{ s}^{-1}; \frac{D_{NO}}{D_{NH_3}} = 0.753.$$

Results are given in Table 3. It can be seen that the criterion is not fulfilled in all runs except runs 11 and 32 where experimental values of η are 0.92 and 1.0, respectively. From these results in can be concluded that the criterion for interparticle mass transport limitations can be safely used. As soon as it is disobeyed experimental values of η differ significantly from 1.

The second study is that of Kehoe and Butt (*17*), where results for benzene hydrogenation on supported nickel catalyst are presented. We selected experimental runs where the external mass transport resitence was negligible. Equation (35) reduces in this case to:

TABLE 3

Application of Intraparticle Mass Transport Criterion

Run number[a]	$P_{NO} \times 10^6$ (atm)[b]	$P_{NH_3} \times 10^6$ (atm)	$r_{ob} \times 10^4$ (mol cm^{-3} h^{-1})	λ_{NH_3}	T (°K)	$\frac{R^2 r_{ob}}{D_{NO}C'_{NO}}$	$\frac{0.4}{0.2 + 0.12\,\lambda_{NH_3}}$	$\eta = \frac{r_{ob}}{r_s}$
3	495	356	2.037	0.698	638	12.56	1.41	0.26
8	485	990	2.525	0.246	633	15.76	1.74	0.30
12	750	430	1.670	0.876	588	6.27	1.31	0.35
15	750	736	1.232	0.511	538	4.23	1.53	0.51
1	495	356	0.535	0.698	488	2.52	1.41	0.64
4	485	445	0.387	0.547	458	1.76	1.51	0.85
11	750	430	0.409	0.876	453	1.18	1.31	0.92
32	1350	1117	0.662	0.607	458	1.07	1.47	1

[a] Wu and Nobe (*19*).
[b] 1 atm = 101.3 kPa.

$$\frac{r_{ob}R^2}{DC'_o} \leq \frac{0.1B_{ie}}{|\gamma_o\beta_o|}. \qquad (36)$$

Since Kehoe and Butt (*17*) also present temperature differences between bulk and surface values, it is shown in Table 4 that the criterion is fulfilled up to a temperature difference of 2.5°K.

CONCLUSIONS

Our main result is to establish with only two criteria the absence of interparticle and interphase heat and mass transport limitations in catalyzed heterogeneous reaction systems. These two criteria apply to any kind of kinetic expression under either isothermal or nonisothermal conditions. Each of them is applied independently to establish either the interparticle or the interphase transport limitations. As shown above, previous results are encompassed by the two general expressions deduced here. It should be noted that they cannot be applied to a given situation if the kinetic expression is not known as well as the values of its parameters.

As a new feature, the effect of pellet geometry and of a nonuniform catalytic activity distribution are considered.

The deduced criteria are very sensitive when compared with experimental results. When inequalities (15) and (29) are slightly fulfilled more precise parameter estimation is needed before neglecting heat and mass transport phenomena.

TABLE 4

Application of Interphase Heat Transport Criterion

Run number[a]	γ_o	β_o	B_{ie}	$\left(\frac{C'_o - C'_s}{C'_o}\right) \times 100$	$r_{ob} \times 10^6$ (mol cm^{-3} s^{-1})	$\frac{R^2 r_{ob}}{DC'_o}$	$\frac{0.1B_{ie}}{\gamma_o\beta_o}$	°K T'_o	°K T'_s	°K $\Delta T'$
10	6.77	0.020	29.7	0.2	0.2726	2.52	21.93	299	299	0
8	6.77	0.020	24	0.3	0.2839	2.50	17.7	299	300	1
9	6.77	0.020	17.2	0.4	0.2745	2.54	12.7	299	301	2
25	6.19	0.078	29.7	0.5	2.350	5.54	6.15	327	229.5	2.5
28	6.17	0.110	29.7	0.4	2.957	5.12	4.38	328	332	4
24	6.12	0.078	24	0.7	2.831	6.74	5.03	331	336.5	5.5
23	5.94	0.083	17.2	1.2	5.057	11.69	3.48	341	351	10

[a] Kehoe and Butt (*18*).

It was shown that compensation could occur when highly exothermic reactions are involved. Under these circumstances the criteria can be fulfilled but with perceptible concentration and temperature gradients.

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