JOURNAL OF CATALYSIS **21**, 321-329 (1971)

On the Asymptotic Behavior of Noncatalytic Gas–Solid Reactions

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Received August 13, 1970

The asymptotic effectiveness factor for the reaction between a porous solid and a gas is calculated. Surface area and effective diffusivity variation are taken into account as well as temperature profiles. The isothermal effectiveness factor can be written in terms of the isothermal "catalytic" effectiveness factor (constant surface area and effective diffusivity) and a correction factor, h_I^+. It is demonstrated that this correction factor is dependent on porous structure but independent on reaction mechanism. On the other hand, the nonisothermal effectiveness factor can be written in terms of the nonisothermal "catalytic" effectiveness factor, the isothermal correction factor, h_I^+, and a second correction factor which takes into account the influence of the transport coefficients variation in the Damköhler's analogy used to relate temperature to gaseous composition.

NOMENCLATURE

$A, B, C, D,$	reaction components
a	surface area of B per unit volume, L^2/L^3
a^*	dimensionless surface area of B, $a^* = a/a_o$
Ar	Arrhenius number, $Ar = E/R_gT_s$
b, d	stoichiometric coefficients
c	molar concentration, g-mole/L^3
c_A^*	dimensionless concentration of A, $c_A^* = c_A/c_{As}$
c_B^*	dimensionless concentration of B, $c_B^* = c_B/c_{Bo}$
D_A	effective diffusivity of A, L^2/θ
D_A^*	dimensionless effective diffusivity of A, $D_A^* = D_A/D_{Ao}$
E	activation energy, Q/g-mole
e	coefficient defined in Eq. (30)
G	coefficient defined in Eq. (31)
g	coefficient defined in Eq. (30)
$(-\Delta H)$	heat of reaction, Q/g-mole
h_o	initial generalized Thiele modulus, $h_o = L_o\left[\frac{\gamma+1}{2}\frac{k'a_oc_{As}{}^{\gamma-1}}{D_{Ao}}\right]^{0.5}$
h^+	correction factor to Thiele modulus
I	function defined in Eq. (52)
J	function defined in Eq. (53)
k'	reaction rate constant per unit surface area
k'^*	dimensionless reaction rate constant, $k'^* = k'(T)/k'(T)_s$
L	characteristic length of porous solid
n	exponent in Eq. (34)
q	coefficient in Eq. (33)
r	reaction rate per unit volume, g-mole/$L^3\theta$
r_A^*	dimensionless reaction rate, $r_A^* = r_A/r_{As}$
R	radial position of the interface between ash layer product and front of reaction zone, L
R^*	dimensionless radial position

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	of the interface between ash layer product and front of reaction zone, $R^* = R_s/R_0$
R_g	gas constant, Q/g-mole °K
t	time, θ
T	temperature, °K
T^*	dimensionless temperature, $T^* = T/T_s$
x	ratio of thermal conductivities, $x = \lambda_S/\lambda_F$
z	rectangular coordinate, L
z^*	dimensionless rectangular coordinate, $z^* = z/L$

Subscripts

c	catalytic
F	fluid
I	isothermal
i	internal
o	initial value
S	solid
s	interface between ash layer product and front of reaction zone
t	true density of solid phase

Greek Letters

β	dimensionless number, $\beta = D_{Ac}(-\Delta H)C_{As}/\lambda_o T_s$
γ	reaction order with respect to A
δ	reaction layer thickness
ϵ	porosity
ϵ^*	dimensionless porosity, $\epsilon^* = \epsilon_S/\epsilon_o$
ϵ'	porosity, Eqs. (32) and (33)
η_i	internal effectiveness factor
λ	effective thermal conductivity, Q/L °K
λ^*	dimensionless effective thermal conductivity, $\lambda^* = \lambda/\lambda_0$
ξ	correction factor, defined in Eq. (50)
ϕ, ϕ_1, ϕ_2,	coefficients defined in Eq. (48)

INTRODUCTION

Let us consider the reaction between the gas A and the porous solid B according to

$$A_{(g)} + bB_{(s)} = C_{(g)} + dD_{(s)}. \tag{1}$$

The mathematical description of this reaction is given by the mass balance equations of components A and B and the thermal energy balance (Fig. 1)

$$\nabla \cdot D_A \nabla c_A = r_A, \tag{2}$$

$$-\frac{\delta c_B}{\delta t} = br_A, \tag{3}$$

and

$$\nabla \cdot \lambda \nabla T = -(-\Delta H)r_A, \tag{4}$$

where the pseudo steady-state assumption has been applied to Eqs. (2) and (4), and equimolar counterdiffusion is assumed in Eq. (2). Pseudo steady-state assumption has been analyzed for the shrinking core model taking into account mass (*1*) and heat transfer effects (*2*).

It is obvious that there is no analytical solution to the set of Eqs. (2)–(4). There is, however, a limiting case in which the treatment of these equations simplifies very much. This case arises when reactant A is consumed completely inside solid B at some distance from its outer surface. Provided some working hypotheses are introduced, it is possible to obtain an analytic solution for the consumption of the solid as a function of time (*3*, *4*). These assumptions are:

(a) The just mentioned hypothesis of A consuming completely inside solid B. This consumption must take place in a dis-

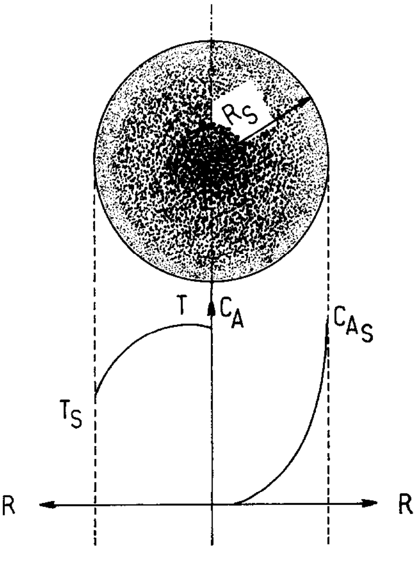

FIG. 1. General picture of the system.

tance $\delta \ll L$, where L is the characteristic length of the porous solid;

(b) Irreversible γ-order reaction with respect to A;

(c) A pseudo steady-state in Eqs. (2) and (4);

(d) The initial condition is given by the time at which profiles of c_A and c_B are just developed;

(e) For a given porous structure, there is a relationship between the surface area of B and its concentration;

(f) There is a relationship between effective diffusivity and porosity, and

(g) By assuming effective diffusivity and surface area of B are constant, a relationship between c_A and c_B is obtained for the isothermal case. For nonisothermal systems, the Damköhler's analogy obtained with constant transport coefficients is also included in the development (*5, 6*). It is to be emphasized that this assumption of constancy of transport coefficients and surface area is only applied for this calculation.

Taking into account these hypotheses, Eq. (2) was integrated once by the Clairaut substitution to obtain the internal effectiveness factor (*3, 4*), which can be written as follows:

$$\eta_i = h^+ R^{*^2}/h_o, \tag{5}$$

where h^+ is a correction factor accounting for the effect of surface area and effective diffusivity variation inside the porous solid. In the nonisothermal case, it also accounts for the effect of temperature profiles on the effectiveness factor (*6*). The value of h^+ appears dependent on the porous structure model, but independent on time since concentration profiles are repeated as solid is consumed (*4, 6*).

Furthermore, the mass balance equation of B was written in terms of the effectiveness factor and integrated to obtain the rate of consumption of B as a function of time (*4, 6*). It is seen that once the value of h^+ is provided, Eq. (2) is no longer used. Nevertheless, the assumption (g) used in this method introduces an error in the calculation of h^+.

The objective of this study is to calculate h^+, neglecting that assumption of constancy of surface area and transport coefficients for the isothermal and the nonisothermal cases. In addition, that study will provide a knowledge of the system properties in the asymptotic region.

EQUATIONS

As has been shown for catalytic systems (*7*) in the asymptotic region of the effectiveness factor (high Thiele modulus), Eq. (2) can be written as that for slab geometry, provided a proper characteristic length is used in the Thiele modulus. Hence, Eq. (2) turns out to be

$$\frac{d}{dz} D_A \frac{dc_A}{dz} = r_A. \tag{6}$$

By using the Clairaut substitution, Eq. (6) can be integrated once to obtain

$$\frac{dc_A}{dz} = (1/D_A)\left[2\int_0^{c_A} D_A r_A dc_A\right]^{0.5}, \tag{7}$$

where the following boundary condition was used,

$$c_A = 0; \qquad dc_A/dz = 0 \qquad \text{at } z = 0. \tag{8}$$

The value of h^+ for the asymptotic zone can be evaluated from Eq. (7) as has been shown elsewhere (*4–6*):

$$\eta_i = [(\gamma + 1)/2](D_{As}/D_{Ao})[(dc_A^*/dz^*)_s/h_o^2]R^{*^2} = h^+ R^{*^2}/h_o, \tag{9}$$

where

$$h^+ = \left[(\gamma + 1)\int_0^1 D_A^* r_A^* dc_A^*\right]^{0.5}, \tag{10}$$

and $c_A^* = c_A/c_{As}$; $z^* = z/L$; $R^* = R_s/R_0$; $D_A^* = D_A/D_{Ao}$; $r^* = r_A(a)/r_{As}(a_o)$.

Assuming now that concentration profiles are repeated in the partially reacted solid as time goes on, we can write

$$\frac{Dc_B}{Dt} = \frac{\delta c_B}{\delta t} + \frac{dz_s}{dt}\frac{\delta c_B}{\delta z} = 0, \tag{11}$$

where dz_s/dt is the velocity of the boundary between ash layer and reaction front.

On the other hand, by writing a macroscopic balance for components A and B at the interface it follows that

$$c_{Bo}dz_s/dt = -bD_{As}(dc_A/dz)_s. \tag{12}$$

From Eqs. (3), (7), (11) and (12) we obtain

$$dc_B/dz = -r_A c_{Bo}\left[2\int_0^{c_{As}} D_A r_A dc_A\right]^{-0.5}. \tag{13}$$

Eqs. (7) and (13) can be equated to give

$$dc_A/dc_B = -2\left[\int_0^{c_A} D_A r_A dc_A\right]^{0.5} \times\left[\int_0^{c_{As}} D_A r_A dc_A\right]^{0.5}\Big/ D_A r_A c_{Bo}. \tag{14}$$

By introducing Eq. (10) in Eq. (14) and using dimensionless variables it follows that

$$dc_A^*/dc_B^* = -2h^+ \times\left[(\gamma+1)^{-1}\int_0^{c_A^*} D_A^* r_A^* dc_A^*\right]^{0.5}\Big/ D_A^* r_A^*. \tag{15}$$

Eq. (15) can also be written as follows;

$$d\left[(\gamma+1)\int_0^{c_A^*} D_A^* r_A^* dc_A^*\right]^{0.5} = -h^+ dc_B^*, \tag{16}$$

which can be transformed to

$$(\gamma+1)D_A^* r_A^* dc_A^* = -2(1-c_B^*)h^{+^2} dc_B^*, \tag{17}$$

where the boundary condition $c_A^* = 0$ for $c_B^* = 1$ has been used.

As $D_A^* = D_A^*(c_B^*)$ and $r_A^* = r_A^*(c_A^*, c_B^*)$ it will be necessary to separate the variables in order to simplify the evaluation of Eq. (17).

The reaction rate can be written as

$$r_A^* = k'^*(c_A^*)c_A^{*^\gamma} a_i^*(c_B^*), \tag{18}$$

where an irreversible γ-order reaction has been considered and the general case of nonisothermal reaction was taken into account by means of the function $k'^*(c_A^*)$ arising from Eqs. (2) and (4).

By separating variables in Eqs. (17) and (18), the following result is obtained:

$$(\gamma+1)k'^* c_A^{*^\gamma} dc_A^* = -2(h^{+^2}/D_A^* a_i^*)(1-c_B^*)dc_B^*. \tag{19}$$

The coefficient h^+ can be evaluated from Eq. (19) by integration using the following boundary conditions:

$$\begin{aligned} c_A^* &= 0; \quad & c_B^* &= 1, \text{ and} \\ c_A^* &= 1; \quad & c_B^* &= 0. \end{aligned} \tag{20}$$

(As a matter of fact the last boundary condition is not taking into account the external surface area of the partially reacted solid).

Hence, Eq. (19) yields

$$h^+ = \left[\frac{(\gamma+1)\int_0^1 k'^* c_A^{*^\gamma} dc_A^*}{2\int_0^1 (D_A^* a_i^*)^{-1}(1-c_B^*)dc_B^*}\right]^{0.5}. \tag{21}$$

From Eq. (21) the value of h^+ can be easily evaluated without knowing the relationship between c_A^* and c_B^*; this makes an important difference with the method outlined before. In that sense, the mathematical treatment which leads to Eq. (21) has the advantage of separating the c_A^* and c_B^* dependent variables in different integrals. As will be shown later this property provides a useful way to report data in both the isothermal and nonisothermal cases.

Furthermore, by integrating Eq. (19), the $c_A^*(c_B^*)$ relationship can be obtained as

$$\frac{\int_0^{c_A^*} k'^* c_A^{*^\gamma} dc_A^*}{\int_0^1 k'^* c_A^{*^\gamma} dc_A^*} = -\frac{\int_1^{c_B^*} (D_A^* a_i^*)^{-1}(1-c_B^*)dc_B^*}{\int_0^1 (D_A^* a_i^*)^{-1}(1-c_B^*)dc_B^*}. \tag{22}$$

For isothermal systems ($k'^* = 1$) with the condition $D_A^* = a_i^* = 1$ (assumption g) Eq. (22) yields as a particular case the relationship used in previous papers (*4*, *6*).

$$c_A^* = [1-c_B^*]^{2/\gamma+1} \tag{23}$$

It is possible now to visualize how the variable coefficients k'^*, D_A^* and a_i^* affect the relationship given by Eq. (22) as well as the value of h^+ in Eq. (21).

ISOTHERMAL SYSTEMS

For isothermal systems $k'^* = 1$ and Eqs. (21) and (22) turn out to

$$h_I^+ = \left[2\int_0^1 (D_A^* a_i^*)^{-1}(1 - c_B^*)dc_B^*\right]^{-0.5}, \tag{24}$$

where the subscript I indicates the isothermal case, and

$$c_A^* = -\left[\frac{\int_1^{c_B^*} (D_A^* a_i^*)^{-1}(1 - c_B^*)dc_B^*}{\int_0^1 (D_A^* a_i^*)^{-1}(1 - c_B^*)dc_B^*}\right]^{0.5}. \tag{25}$$

In order to evaluate the integrals of Eqs. (24) and (25), it is necessary to develop the following relationships;

$$a_i^* = a_i^*(c_B^*) \text{ and} \tag{26}$$

$$D_A^* = D_A^*(c_B^*). \tag{27}$$

$a_i^*(c_B^*)$ relationship

The $a_i^*(c_B^*)$ relationship depends on the pore structure model used to represent the solid reactant. As has been done elsewhere (*4*) three different models are used:

(i) Dispersed-solid model,

$$a_i^* = (c_B^*)^{2/3}; \tag{28}$$

(ii) Petersen model,

$$(a_i^*)^3 + e(a_i^*)^2 + gc_B^*(1 - \epsilon_0)[c_B^*(1 - \epsilon_0) - 1] = 0, \tag{29}$$

where

$$e = G^2/(2G - 3) \text{ and } g = (G - 1)^2/\epsilon_0[(2G - 3)/3]^3, \tag{30}$$

with

$$4\epsilon_0 G^3 - 27G + 27 = 0; \tag{31}$$

(iii) Pore-generation model,

$$a_i^* = 1 + (q - 1)(\epsilon - \epsilon_0)/(\epsilon' - \epsilon_0) \quad \text{for } \epsilon \leqslant \epsilon', \tag{32}$$

and

$$a_i^* = q \quad \text{for } \epsilon \geqslant \epsilon'. \tag{33}$$

$D_A^*(c_B^*)$ relationship

A phenomenological dependence of the effective diffusivity on porosity that has been observed for a great number of porous materials can be written as

$$D_A^* = (\epsilon/\epsilon_0)^n, \tag{34}$$

where n varies from 1 to 3 (authors have used a value of $n = 2$ in previous studies (*4*)).

Furthermore, the porosity can be evaluated through

$$\epsilon = 1 - (c_B/c_{Bt}) - (c_D/c_{Dt}), \tag{35}$$

where the subscript t denotes the true density of the solid. Eq. (35) can be written exclusively in terms of c_B^*

$$\epsilon = \epsilon_s + c_B^*(\epsilon_0 - \epsilon_s). \tag{36}$$

Hence, by introducing Eq. (36) in Eq. (34) it follows,

$$D_A^* = [\epsilon^* + c_B^*(1 - \epsilon^*)]^n, \tag{37}$$

where

$$\epsilon^* = \epsilon_s/\epsilon_0. \tag{38}$$

From Eqs. (24), (28), (29), (32), (33), and (37), it can be seen that h_I^+ will depend on the porous structure model as well as on ϵ^* and n. However, it is to be emphasized that h_I^+ is independent upon reaction order or in general upon the chemical reaction kinetics provided a generalized Thiele modulus is used in Eq. (9).

RESULTS

As has been mentioned before, the value of h_I^+ or the $c_A^*(c_B^*)$ relationship will depend on a_i^* and D_A^* profiles in the partially reacted solid. Since the integrals in Eqs. (24) and (25) arise from kinetic concepts, it is obvious that results will be influenced by the way in which the mechanism of diffusion with simultaneous chemical reaction is affected by the profiles of a_i^* and D_A^*. The influence of a_i^* arises from the porous structure model under consideration.

The correction factor h_I^+ was calculated from Eq. (24) and is plotted in Fig. 2 as a function of ϵ^* for the different porous structure models. Points show the values obtained and reported elsewhere (*4*) with

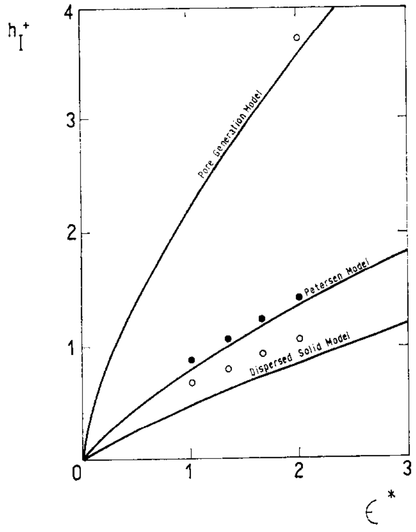

FIG. 2. Influence of ϵ^* upon h_I^+ for different porous structure models.

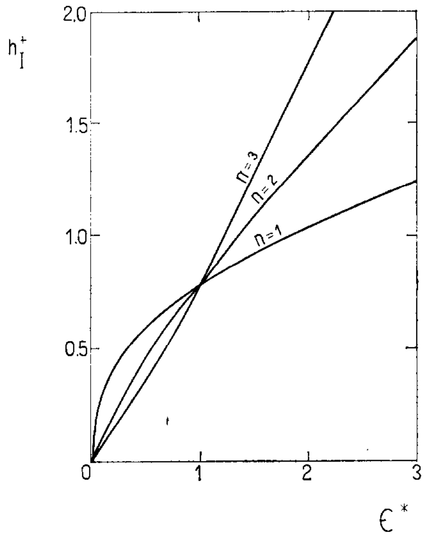

FIG. 3. Influence of ϵ^* upon h_I^+ for Petersen model and different values of n.

assumption (g). It is possible to observe that the values arising from this assumption are not too far from the curves coming out from Eq. (24) in all cases.

On the other hand the influence of D_A^* on h_I^+ and the $c_A^*(c_B^*)$ relationship will depend upon the value of ϵ^* and n. For $\epsilon^* = 1$ Eq. (37) yields $D_A^* = 1$ and there is not D_A^* profile. In other words, as porosity is not changing with reaction the effective diffusivity remains constant. This effect can be observed in Fig. 3 where the correction factor h_I^+ is plotted as a function of ϵ^* for different values of n. The Petersen model for $\epsilon_o = 0.303$ was considered here. Similar results were obtained for the dispersed-solid model. From Fig. 3 it can be seen that the differences in h_I^+ are not great for usual values of ϵ^* $(0.5 \leqslant \epsilon^* \leqslant 2.0)$ showing a low sensibility of D_A^* on h_I^+. Hence, it can be concluded that for the isothermal case, errors are not too high when applying assumption (g). However, as values of h_I^+ can be easily calculated from Eq. (24), the search for an analytical $c_A^*(c_B^*)$ relationship is no longer important.

NONISOTHERMAL SYSTEMS

For nonisothermal systems the value of k'^* must be expressed in terms of c_A^* in order to evaluate the integrals in Eqs. (21) and (22).

In conventional catalytic systems, this relationship arises from the Damköhler's analogy (*5*) which relates temperature and gaseous composition within the porous solid through Eqs. (2) and (4). Such a treatment leads to the following relationship:

$$k'^* = \exp\{Ar\beta(1 - c_A^*)/[1 + \beta(1 - c_A^*)]\} \tag{39}$$

where $Ar = E/R_gT_s$ and $\beta = D_{Ao}(-\Delta H) c_{As}/\lambda_o T_s$. However, this relationship was obtained assuming D_A, λ and ΔH were constant. This is not the case for gas–solid systems; hence, a new relationship $k'^*(c_A^*)$ must be developed. From Eqs. (2) and (4) we obtain

$$D_A(dc_A/dz) = -[\lambda/(-\Delta H)](dT/dz), \tag{40}$$

where the following boundary conditions were used

$$dc_A/dz = 0;\ dT/dz = 0, \text{ at } z = 0. \tag{41}$$

By integrating Eq. (40) we obtain

$$T - T_s = (-\Delta H) \int_{c_A}^{c_{As}} (D_A/\lambda) dc_A, \tag{42}$$

or, in dimensionless form

$$T^* - 1 = \beta \int_{c_A*}^{1} (D_A{}^*/\lambda^*) dc_A{}^*, \qquad (43)$$

where $T^* = T/T_s$ and $\lambda^* = \lambda/\lambda_0$. (44)

Hence, k'^* can be expressed as

$$k'^* = \exp\left[\frac{Ar\beta \int_{c_A*}^{1} (D_A{}^*/\lambda^*) dc_A{}^*}{1 + \beta \int_{c_A*}^{1} (D_A{}^*/\lambda^*) dc_A{}^*}\right]. \qquad (45)$$

For the particular case $D_A{}^* = \lambda^* = 1$, Eq. (45) reduces to Eq. (39). As $D_A{}^*$ and λ^* are functions of $c_B{}^*$ the solution of Eq. (45) requires an iterative method to be applied together with Eq. (22) which will provide the necessary relationship between $c_A{}^*$ and $c_B{}^*$. Once the iterative procedure is ended the correct relationship $c_A{}^*(c_B{}^*)$ is obtained as well as the value of h^+. However, we need first to develop the relationship $\lambda^* = \lambda^*(c_B{}^*)$ or $\lambda^* = \lambda^*(\epsilon)$.

For unconsolidated porous media the expression developed by Kunii and Smith (*8*) can be used

$$\lambda/\lambda_F = \epsilon + (1 - \epsilon)0.95/[\phi + (2/3x)], \qquad (46)$$

where $x = \lambda_S/\lambda_F$, with λ_S being the thermal conductivity of the solid phase and λ_F that one of the fluid phase. In turn

$$\phi = \phi_2 + (\phi_1 - \phi_2)(\epsilon - 0.260)/0.216 \qquad (48)$$

ϕ_1 and ϕ_2 are plotted as a function of x (*8*). The dimensionless effective thermal conductivity λ^* can be evaluated from Eqs. (46) and (48) for given values of ϵ and ϵ_0.

On the other hand, for consolidated porous media we can use (*9*)

$$\lambda^* = (\lambda_S/\lambda_F)^{\epsilon_0 - \epsilon} = (x)^{\epsilon_0 - \epsilon}. \qquad (49)$$

It is now easy to evaluate both, the $c_A{}^*(c_B{}^*)$ relationship and the value of h^+ for the nonisothermal system. We should remember that in a previous study (*6*) the nonisothermal h^+ was calculated taking into account the influence of $D_A{}^*$ and $a_i{}^*$ profiles as well as temperature gradients in the reactant solid but constant transport coefficients were assumed in the Damköhler's analogy when evaluating the relationship $k'^*(c_A{}^*)$ (Eq. (39)).

Hence, let us introduce a correction factor defined as

$$\xi = \frac{h^+ \text{ calculated with Eq. (45)}}{h^+ \text{ calculated with Eq. (39)}}. \qquad (50)$$

From Eqs. (21), (39), and (45) it follows that ξ can be written as

$$\xi = \left[\frac{\int_0^1 (c_A{}^{*\gamma})[\exp I] dc_A{}^*}{\int_0^1 (c_A{}^{*\gamma})[\exp J] dc_A{}^*}\right]^{0.5}, \qquad (51)$$

where

$$I = \frac{Ar\beta \int_{c_A*}^{1} (D_A{}^*/\lambda^*) dc_A{}^*}{1 + \beta \int_{c_A*}^{1} (D_A{}^*/\lambda^*) dc_A{}^*}, \qquad (52)$$

and

$$J = \frac{Ar\beta(1 - c_A{}^*)}{1 + \beta(1 - c_A{}^*)}. \qquad (53)$$

Hence, ξ will depend upon

$$\xi = \xi(\epsilon^*, n, Ar, \beta, x, \gamma, \text{porous structure model}). \qquad (54)$$

For isothermal systems $\xi = 1$; for $\epsilon^* = 1$ as porosity is not changing with reaction, both transport coefficients are constant and again $\xi = 1$.

By introducing Eqs. (50) and (51) in Eq. (9) we obtain

$$\eta_i = (\xi/h_0) \times \left[(\gamma + 1) \frac{\int_0^1 (c_A{}^*)^\gamma [\exp J] dc_A{}^*}{\int_0^1 (2/D_A{}^* a_i{}^*)(1 - c_B{}^*) dc_B{}^*}\right]^{0.5} \times R^{*^2}. \qquad (55)$$

On the other hand, Eq. (9) for a catalytic system can be written as follows ($D_A{}^* = a_i{}^* = \lambda^* = 1$):

$$\eta_{i_c} = f(Ar, \beta, \gamma)/h_0 = \left\{[(\gamma + 1)/h_0{}^2] \int_0^1 (c_A{}^{*\gamma})[\exp J] dc_A{}^*\right\}^{0.5}, \qquad (56)$$

where the subscript c denotes the catalytic case. In turn, from Eqs. (55) and (56) we obtain

$$\eta_i = \xi \eta_{i_c} \left[\int_0^1 (2/D_A{}^* a_i{}^*)(1 - c_B{}^*) dc_B{}^*\right]^{-0.5} R^{*^2} \qquad (57)$$

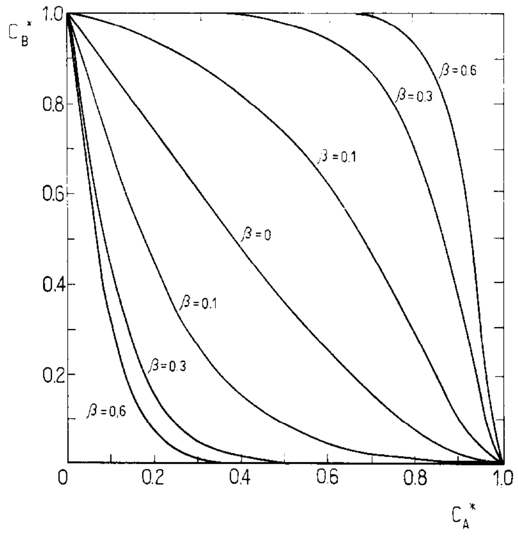

Fig. 4. Relationship between c_A^* and c_B^* for Petersen model, $Ar = 40$, $\epsilon^* = 1$, and different values of β.

On the other hand, by using Eq. (24) it follows

$$\eta_i = \xi h_I{}^+\eta_{I_c}R^{*^2}. \quad (58)$$

Eq. (58) gives an important relationship since it allows the calculation of the nonisothermal effectiveness factor for a gas–solid reaction (with variable transport coefficients and surface area) in terms of the catalytic effectiveness factor and two correction factors, $h_I{}^+$ and ξ.

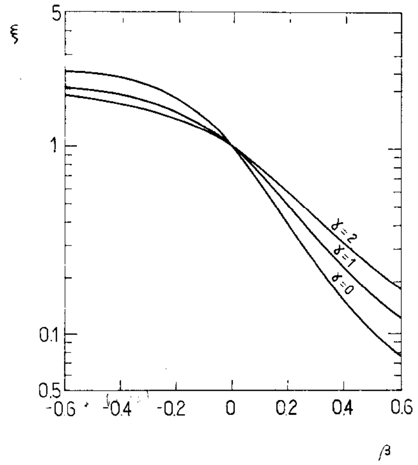

Fig. 5. Influence of β upon ξ for dispersed solid model, $Ar = 20$, $\epsilon^* = 0.67$, $x = 1000$, and different values of γ.

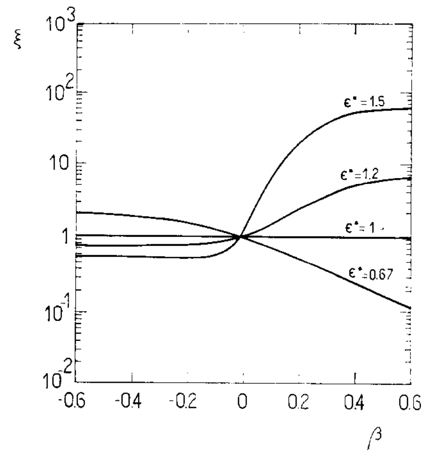

Fig. 6. Influence of β upon ξ for dispersed solid model, $Ar = 20$, $\gamma = 1$, $x = 1000$, and different values of ϵ^*.

Results

The $c_A^*(c_B^*)$ relationship is shown in Fig. 4 for the Petersen model ($\epsilon_o = 0.303$), $\epsilon^* = 1$, $Ar = 40$ and different values of β. As $\epsilon^* = 1$, Eqs. (45) or (39) can be used without distinction. It can be seen that, for a given value of c_B^*, c_A^* decreases as the heat of reaction increases if the reaction is exothermic. The opposite effect is observed for endothermic reactions.

Figures 5, 6, and 7 show the influence of different parameters upon the correction factor ξ for the dispersed-solid model. We

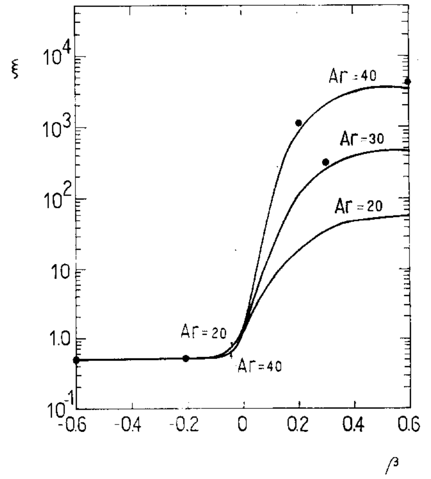

Fig. 7. Influence of β upon ξ for dispersed solid model, $\epsilon^* = 1.5$, $\gamma = 1$, $x = 1000$, and different values of Ar.

remember that $\xi = 1$ for $\beta = 0$ and/or $\epsilon^* = 1$. The parameters Ar, β, and ϵ^* influence directly upon ξ through the Damköhler's analogy; on the other hand, the reaction order γ and the porous-structure model influence upon ξ through the $c_A^*(c_B^*)$ relationship.

The influence of β and γ is shown in Fig. 5. It is seen that the parametric sensibility of γ is not too high.

The influence of β and ϵ^* is shown in Fig. 6. As ϵ^* modifies the transport coefficients of the porous solid, its influence will be high for exothermic reactions as can be verified from Fig. 6.

In the same way, the influence of Ar is very high for exothermic reactions (Fig. 7). The points shown in this figure correspond to the Petersen model. It is seen that the influence of the porous structure is very low.

Furthermore, in the calculations involved in Figs. 5–7 a value of $x = 1000$ was used; calculations performed with $x = 500$ and $x = 1500$ showed the influence of x was negligible.

CONCLUSIONS

The asymptotic effectiveness factor for a nonisothermal gas–solid reaction with variable coefficients can be written in terms of the nonisothermal catalytic effectiveness factor and two correction factors: the first one which accounts for the influence of effective diffusivity and surface area profiles in the isothermal case and is independent on the reaction mechanism and the second one which accounts for the influence of variable transport coefficients when relating temperature and gaseous composition within the porous solid.

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