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Kinetics of Gas–Solid Reactions: Influence of Reaction Order and Temperature Profiles

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The irreversible, γ order reaction between a gas and a spherical porous solid is analyzed under isothermal and nonisothermal conditions. Effective diffusivity and surface area profiles inside the reactant solid are taken into account. An analytic solution for the rate of variation of solid size is obtained provided the gaseous reactant is consumed completely inside the porous solid. The moving boundary model arises as a particular case of the general solution obtained.

NOMENCLATURE

A, B, C, D	reaction components
a	total surface area of B per unit volume, L^2/L^3
a_i	internal surface area of B per unit volume, L^2/L^3
a_i^*	dimensionless internal surface area of B, $a_i = a_i/a_{i_0}$
b, d	stoichiometric coefficients
c_A	molar concentration of A, mole$/L^3$
c_A^*	dimensionless concentration of A, $c_A = c_A/c_{A_s}$
c_B	molar density of B, mole$/L^3$
c_B^*	dimensionless concentration of B, $c_B = c_B/c_{B_0}$
$\bar{c}_B^*$	mean value defined in Eq. (28)
c_D	molar density of D, mole$/L^3$
c_D^*	dimensionless concentration of D, $c_D = c_D/c_{D_s}$
D_A	effective diffusivity of A in the porous solid, L^2/θ
E	activation energy (cal/mole)
g	coefficient defined in Eq. (13)
G	coefficient defined in Eq. (14)
ΔH	heat of reaction (cal/mole)
h_0	generalized Thiele modulus, $h_0 = L_0 \{[(\gamma + 1)/2]k'_s a_{i_0} c_{A_s}^{\gamma-1}/D_{A_0}\}^{0.5}$
h^+	correction factor defined in Eq. (23)
I	variable defined in Eqs. (50) and (51)
k'	reaction rate constant per unit surface area
k^*	dimensionless reaction rate constant, $k^* = k'/k'_s$
L	characteristic length, $L = V/S$
M	dimensionless parameter, $M = 1 + h^+(1 - \alpha_0)/\alpha_0 h_0$
n_B	number of moles of B (mole)
r	radial coordinate, L
r^*	dimensionless coordinate, $r^* = r/R_0$
R	radius
R^*	dimensionless radius of the shrinking core, $R^* = R_s/R_0$

R_g	gas constant
r_A	reaction rate per unit volume, mole/$L^3\theta$
r'_A	reaction rate per unit surface area, mole/$L^2\theta$
S	geometrical area, L^2
t	time, θ
$^*t$	dimensionless time, $t^* = bk'_s c_{A_s}{}^{\gamma} a_0 \alpha_0 t / c_{B_0}$
T	temperature (°K)
V	volume, L^3
z	rectangular coordinate, L
z^*	dimensionless coordinate, $z^* = z/L_0$
Greek Letters	
α	fractional surface area, α = external surface area/total surf. area
β	dimensionless parameter, $\beta = D_{A_0}(-\Delta H) c_{A_s} / \lambda_0 T_s$
γ	reaction order respect to reactant A
δ	dimensionless parameter, $\delta = \mathrm{A}r\beta$
ϵ	porosity
ϵ^*	dimensionless porosity, $\epsilon^* = \epsilon_s/\epsilon_0$
η	overall effectiveness factor, defined in Eq. (15)
η_i	internal effectiveness factor, defined in Eq. (16)
λ	effective thermal conductivity, cal/L °K θ
Subscripts	
0	initial value
s	evaluated at the boundary between ash layer and reaction zone
f	evaluated at the coordinate where the gaseous reactant is completely consumed

INTRODUCTION

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

$$A_{(g)} + bB_{(s)} = C_{(g)} + dD_{(s)}, \qquad (1)$$

which is represented in Fig. 1.

This reaction was analyzed in a previous paper (*4*) in order to calculate the solid consumption rate as a function of time taking into account the influence of the effective diffusivity profiles in the porous solid, and that of internal surface area of B per unit volume. The mass balances for A and B were the starting point:

$$\epsilon \frac{\partial c_A}{\partial t} = \nabla \cdot D_A \nabla c_A - r_A, \qquad (2)$$

$$-\frac{\partial c_B}{\partial t} = b r_A, \qquad (3)$$

where ϵ is the porosity of the solid, c_A the molar concentration of A, c_B the molar concentration of B, D_A the effective diffusivity of A in the porous pellet and r_A the reaction rate per unit volume.

The reaction rate was expressed as:

$$r_A = k' a_i c_A, \qquad (4)$$

where k' is the reaction rate constant per unit surface area.

The solid consumption as a function of time must be obtained from the simultaneous solution of Eqs. (2) and (3). However this solution is difficult to obtain since ϵ, D_A, and a_i are variable coefficients which depend upon the way in which solid B is consumed.

The devised method of solution introduced four fundamental working hypotheses: (i) Pseudo steady state for reactant A was assumed; (ii) The system was isothermal; (iii) Reaction was irreversible and first order with respect to A; and (iv) Reactant A was consumed at some distance from the outer surface of solid B.

The objective of the present study was to obtain a similar solution but without taking into account the working hypotheses 2 and 3. In other words both, γ order irreversible reaction as well as the nonisothermal case will be considered.

As the treatment will be essentially the same already mentioned (*4*) let us summarize briefly the general procedure:

1. In order to evaluate the law of varia-

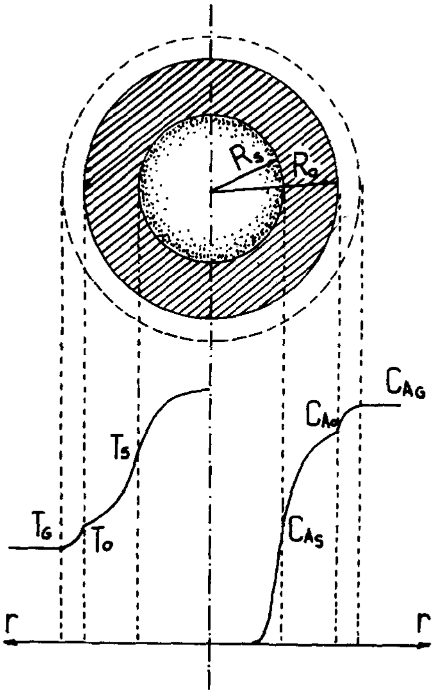

FIGURE 1

tion of the coefficients D_A and a_i some relationships of the type:

$$D_A = D_A(c_B), \tag{5}$$

$$a_i = a_i(c_B), \tag{6}$$

will be necessary.

2. In addition, Eqs. (2) and (3) can be interpreted to mean that both c_A and c_B are functions of position and time and therefore c_B is a function of c_A and position. But a relationship,

$$c_B = c_B(c_A), \tag{7}$$

independent on position may be obtained to make both equations (2 and 3) independent. This relationship, which has been obtained by assuming D_A and a_i as constant in Eqs. (2) and (3), can be introduced into Eq. 2 and the integration performed once. In this integration D_A and a_i are taken as variable coefficients by means of the relationships (5), (6), and (7).

3. Once the solution has been obtained (usually in terms of an effectiveness factor), it is introduced into a macroscopic balance for solid B. By integration of this balance the desired conversion-time relationship is obtained.

4. When the nonisothermal case is considered, the Damköhler's relationship (*5*) relating c_A and T must be used when solving Eq. (2) as well as when obtaining the $c_B - c_A$ function of Eq. (7).

Let us now deal with the functions (5) and (6). The relationship of Eq. (5) has been analyzed elsewhere (*4*) being:

$$D_A = \frac{D_{A_0}}{2}[1 - c_B^*(1 - \epsilon_0) - c_D^*(1 - \epsilon_s)]^2, \tag{8}$$

where $c_B^* = c_B/c_{B_0}$. ϵ_0^2, $c_D^* = c_D/c_{D_s}$ and c_{B_0}, ϵ_0, c_{D_s} and ϵ_s are the molar densities and porosities of the solid reactant and the solid product, respectively.

By considering that

$$c_D^* = 1 - c_B^*, \tag{9}$$

which is valid when there is no change in pellet volume during reaction, Eq. (8) turns out to:

$$D_A^* = [\epsilon^* + c_B^*(1 - \epsilon^*)]^2, \tag{10}$$

where $\epsilon^* = \epsilon_s/\epsilon_0$ and $D_A^* = D_A/D_{A_0}$.

The function in Eq. (6) will be dependent upon the porous structure of the solid and as has been done before (*4*) it will be analyzed for unconsolidate and consolidate media:

a. The dispersed solid model. The porous solid is made of small non porous particles whose number and shape remain unchanged as solid is consumed. For this case:

$$a_i^* = c_B^{*2/3}, \tag{11}$$

where $a_i^* = a_i/a_{i_0}$ and a_{i_0} is the internal surface area per unit volume at initial conditions.

b. Petersen model (*6*). The porous solid is made of a network of cyclindrical pores randomly interconnected. For this case:

$$a_i^{*3} + ea_i^{*2} + gc_B^*(1 - \epsilon_0)[c_B^*(1 - \epsilon_0) - 1] = 0, \tag{12}$$

where

$$e = \frac{G^2}{2G - 3} \quad \text{and} \quad g = \frac{27[G - 1]^2}{\epsilon_0[2G - 3]^3}, \tag{13}$$

with

$$G^3 - \frac{27}{4\epsilon_0} G + \frac{27}{4\epsilon_0} = 0. \quad (14)$$

Both, Eqs. (10) and (12) provide the necessary relationships to relate D_{A} and a_i in terms of solid concentration.

Let us define now an overall effectiveness factor (*3*) for a spherical pellet as:

$$\eta = \frac{(-\,dn_{\mathrm{A}}/dt)}{r'_{\mathrm{A}_s} V_0 a_0} = (1 - \alpha_0)\eta_i + \alpha_0 \mathrm{R}^{*^2}, \quad (15)$$

where η_i is the internal effectiveness factor given by:

$$\eta_i = \frac{D_{\mathrm{A}_s} S_s (dc_{\mathrm{A}}/dz)|_s}{r'_{\mathrm{A}_s} \mathrm{V}_0 a_{i_0}} \quad (16)$$

where V_0 is the initial volume of the solid, a_0 its total initial surface area per unit volume, a_{i_0} its internal initial surface area per unit volume, S_s the geometrical area of the boundary of the reaction zone and r'_{A_s} is the reaction rate of A per unit surface area at this boundary.

By writing Eq. (16) in dimensionless form it follows:

$$\eta_i = \frac{[(\gamma + 1)/2](D_{\mathrm{A}_s}/D_{\mathrm{A}_0})(dc_{\mathrm{A}}^*/dz^*)|_s R^{*^2}}{h_0^2}, \quad (17)$$

with

$$h_0 = L_0 \left[\frac{\gamma + 1}{2} \frac{k'_s a_{i_0} c_{\mathrm{A}_s}{}^{\gamma - 1}}{D_{\mathrm{A}_0}} \right]^{0.5}, \quad (18)$$

where $L_0 = V_0/S_0$, D_{A_0} is the effective diffusivity for the initial condition ($\epsilon = \epsilon_0$) and the dimensionless coordinate in Eq. (17) was defined as $z^* = z/L_0$.

On the other hand, if reactant A is consumed in a thin layer within the solid B, Eq. (2) will reduce to:

$$\frac{d}{dz} D_{\mathrm{A}} \frac{dc_{\mathrm{A}}}{dz} = k' a_i c_{\mathrm{A}}{}^{\gamma}. \quad (19)$$

Equation 19 can be integrated once by using the Clairaut substitution (*2*) to obtain:

$$\frac{dc_{\mathrm{A}}}{dz} = \frac{1}{D_{\mathrm{A}}} \left[2 \int_0^{c_{\mathrm{A}}} D_{\mathrm{A}} k' a_i c_{\mathrm{A}}{}^{\gamma} dc_{\mathrm{A}} \right]^{0.5} \quad (20)$$

By evaluating Eq. (20) in the boundary between reaction zone and product layer and writing it in dimensionless form it follows:

$$\left. \frac{dc_{\mathrm{A}}^*}{dz^*} \right|_s = 2h_0 \frac{D_{\mathrm{A}_0}}{D_{\mathrm{A}_s}} \times \left[\frac{1}{(\gamma + 1)} \int_0^1 D_{\mathrm{A}}^* k^* a_i^* c_{\mathrm{A}}^{*^{\gamma}} dc_{\mathrm{A}}^* \right]^{0.5} \quad (21)$$

where $k^* = k'/k'_s$.

By introducing Eq. (21) into Eq. (17) it is obtained:

$$\eta_i = \frac{R^{*^2}}{h_0} \left[(\gamma + 1) \int_0^1 D_{\mathrm{A}}^* k^* a_i^* c_{\mathrm{A}}^{*^{\gamma}} dc_{\mathrm{A}}^* \right]^{0.5} \quad (22)$$

The term inside brackets in Eq. (22) measures the influence of D_{A} and a_i profiles upon the internal effectiveness factor in the isothermal system, as well as the effect of temperature profiles in the nonisothermal one.

It can be seen as a correction for the Thiele modulus h_0. By calling:

$$h^+ = [(\gamma + 1) \int_0^1 D_{\mathrm{A}}^* k^* a_i^* c_{\mathrm{A}}^{*^{\gamma}} dc_{\mathrm{A}}^*]^{0.5}, \quad (23)$$

the internal effectiveness factor can be expressed as:

$$\eta_i = \frac{h^+ R^{*^2}}{h_0}. \quad (24)$$

For catalytic systems the correction factor h^+ will be one in the isothermal case and a function of heat and mass transfer parameters in the nonisothermal one.

Nevertheless, as it has been pointed out before, for noncatalytic systems a $c_{\mathrm{B}}^* - c_{\mathrm{A}}^*$ relationship will be necessary in order to relate $D_{\mathrm{A}}^*(c_{\mathrm{B}}^*)$ and $a_i^*(c_{\mathrm{B}}^*)$ with c_{A}^* and to perform the integral of Eq. (23).

ISOTHERMAL SYSTEM

Relationship Between c_{B}^* and c_{A}^*

For isothermal systems and by assuming the product $D_{\mathrm{A}}^* \cdot a_i^*$ as constant the $c_{\mathrm{B}}^* - c_{\mathrm{A}}^*$ relationship was obtained elsewhere (*4*) as:

$$c_{\mathrm{B}}^* = 1 - (c_{\mathrm{A}}^*)^{(\gamma+1)/2}. \quad (25)$$

Values of h^+ were calculated for the two

TABLE 1

VALUES OF h^+ FOR THE ISOTHERMAL CASE AND OF h^+/h_c^+ FOR THE NONISOTHERMAL CASE (any order)[a]

ϵ^*	1	1.33	1.67	2.00
Dispersed solid model				
	0.67	0.79	0.92	1.05
Petersen model($\epsilon_0 = 0.303$)				
	0.90	1.09	1.27	1.46

[a] Values were approximated to the second decimal.

porous structure models by introducing Eqs. (10), (11), and (25) or (10), (12), and (25) into Eq. (23) and taking into account that for the isothermal case it is $k^* = 1$. These values are shown in Table 1. It is to be observed that h^+ is independent upon the reaction order γ.

The overall effectiveness factor can be readily calculated by introducing Eq. (24) into Eq. (15) to obtain:

$$\eta = (1 - \alpha_0)\frac{h^+R^{*^2}}{h_0} + \alpha_0 R^{*^2}. \qquad (26)$$

Calculation of Solid Consumption

By writing a macroscopic mass balance at the boundary of the solid reactant it follows:

$$-\frac{dn_B}{dt} = bk' c_{A_s}{}^{\gamma} a_0 V_0 \eta \qquad (27)$$

If Eq. (26) is introduced into Eq. (27) it is seen that some relationship $n_B - R^*$ will be necessary in order to integrate it. We will obtain that relationship as a function of the reaction order.

Let us define a dimensionless mean molar density of B in the partially reacted solid such as:

$$\bar{c}_B{}^* = \frac{3}{R^{*3}}\int_0^{R^*} c_B{}^* r^{*^2} dr^* \qquad (28)$$

where $r^* = r/R_0$ and $R^* = R_s/R_0$ Hence:

$$n_B = c_{B_0} V_s \bar{c}_B{}^* \qquad (29)$$

On the other hand, it has been shown elsewhere (*4*) that for high Thiele modulus the following relationship can be written:

$$-(dc_B/dz) = k' a_i c_{B_0} c_A{}^{\gamma} / D_{A_s} (dc_A/dz)|_s. \qquad (30)$$

By writing Eq. (30) in dimensionless form and introducing Eq. (21) the following result is obtained:

$$\begin{aligned}(dc_B{}^*/dz^*) &= -\,h_0 a_i{}^* c_A{}^{*^{\gamma}}/h^+ \\ &= -(h_0 a_i{}^*)/h^+(1 - c_B{}^*)^{2\gamma/(\gamma+1)} \qquad (31)\end{aligned}$$

where $c_B{}^*$ was related to $c_A{}^*$ according to Eq. (25)

By assuming $a_i{}^* = 1$ and taking into account that:

$$z^* = z_s{}^*, \qquad c_B{}^* = 0, \qquad (32)$$

Eq. (31) can be integrated to obtain:

$$c_B{}^* = 1 - \exp[-(h_0/h^+)(z_s{}^* - z^*)] \quad \text{for } \gamma = 1, \qquad (33)$$

and

$$c_B{}^* = 1 - \left\{1 - (h_0/h^+)\left[\frac{1-\gamma}{1+\gamma}\right]\cdot(z_s{}^* - z^*)\right\}^{(1+\gamma)/(1-\gamma)} \quad \text{for } \gamma \neq 1. \qquad (34)$$

For values of $0 \leq \gamma < 1$ the reactant A is completely consumed at a finite coordinate $z_f{}^*$. As for $z^* \leq z_f{}^*$ it is $c_B{}^* = 1$ and $c_A{}^* = 0$, Eq. (34) will be only valid for $z^* \geq z_f{}^*$. The value of $z_f{}^*$ can be obtained from Eq. (34) as:

$$z_f{}^* = z_s{}^* - \frac{1+\gamma}{1-\gamma}\frac{h^+}{h_0} \qquad (35)$$

By introducing Eqs. (33), (34), and (35) into Eq. (28) and taking into account that $z^* = 3r^*$ it is obtained:

$$\bar{c}_B{}^* = 1 - \frac{\gamma+1}{2}p + \frac{(\gamma+1)^2}{3(3-\gamma)}p^2 - \frac{(\gamma+1)^3}{18(2-\gamma)(3-\gamma)}p^3 \text{ for } 0 \leq \gamma < 1, \qquad (36)$$

$$\bar{c}_B{}^* = 1 - p + \frac{2}{3}p^2 - \frac{2}{9}\mathrm{p}^3\left[1 - \exp\left(-\frac{3}{\mathrm{p}}\right)\right] \text{ for } \gamma = 1, \qquad (37)$$

and

$$\bar{c}_B{}^* = 1 - \frac{\gamma + 1}{2}\,p + \frac{(\gamma + 1)^2}{3(3 - \gamma)}\,p^2 - \frac{(\gamma + 1)^3}{18(2 - \gamma)(3 - \gamma)} \times p^3 \left\{1 - \left[1 + \frac{\gamma - 1}{\gamma + 1}\frac{3}{\mathrm{p}}\right]^{(4-2\gamma)/(1-\gamma)}\right\} \quad \text{for } \gamma > 1, \tag{38}$$

where $p = h^+/h_0R^*$.

For $0 \leq \gamma < 1$ the integral of Eq. (28) was performed straightforward from 0 to $R_f{}^*$ and by using Eq. (34) from $R_f{}^*$ to $R_s{}^*$.

For the assumption of high Thiele modulus already done it can be proved that the exponential term of Eq. (37) and terms in p with power two or higher in Eqs. (36), (37), and (38) are negligible from the R^* — t^* relationship standpoint. Thus Eqs. (36), (37), and (38) reduce to a general expression for any order $\gamma \geq 0$:

$$\bar{c}_B{}^* = 1 - \frac{\gamma + 1}{2}\,\frac{h^+}{h_0R^*}. \tag{39}$$

Of course these simplications are not good for $R^* \rightarrow 0$. Anyway for this case the asymptotic assumption already done is no longer valid.

By introducing Eq. (39) into Eq. (29) and taking into account that $V_s = V_0R^{*^3}$, the following equation is obtained:

$$n_B = c_{B_0}V_0\left[\mathrm{R}^{*^3} - \frac{\gamma + 1}{2}\,\frac{h^+R^{*^2}}{h_0}\right]. \tag{40}$$

Hence by introducing Eqs. (26) and (40) into Eq. (27), it follows:

$$-\left[3R^{*^2} - (\gamma + 1)\,\frac{h^+R^*}{h_0}\right]\frac{dR^*}{dt^*} = MR^{*^2}, \tag{41}$$

where

$$t^* = bk'c_{A_s}{}^{\gamma}a_0\alpha_0t/c_{B_0} = bk'c_{A_s}{}^{\gamma}t/L_0c_{B_0}$$

and

$$M = 1 + \left(\frac{1 - \alpha_0}{\alpha_0}\,\frac{h^+}{h_0}\right)$$

Equation 41 can be integrated with the initial condition:

$$t^* = 0, \qquad R^* = 1, \tag{42}$$

to yield:

$$Mt^* = 3(1 - R^*) + (\gamma + 1)\,\frac{h^+}{h_0}\ln R^*. \tag{43}$$

Equation (43) gives the size–time relationship for a spherical isothermal pellet with an irreversible γ order reaction provided the gaseous reactant is consumed completely inside the porous solid. This solution is of direct application when there are no concentration gradients in the gaseous boundary layer and in the ash layer. Otherwise for $\gamma \neq 1$ a numerical solution must be used with Eq. (41) and the equations for mass transfer in the product layer and the boundary layer around the pellet.

Equation (43) contains, as a very important particular case, the expression for the moving boundary model which is obtained when:

$$\frac{1 - \alpha_0}{\alpha_0}\,\frac{h^+}{h_0} \rightarrow 0. \tag{44}$$

in such a case Eq. (43) reduces to:

$$t^* = 3(1 - R^*). \tag{45}$$

NONISOTHERMAL SYSTEM

Relationship Between c_B and c_A

In order to apply the procedure already analyzed it is necessary to evaluate some $c_B{}^*$ — $c_A{}^*$ relationship for the nonisothermal case.

This relationship will be obtained as before by assuming that the effective diffusivity and the surface area per unit volume are constant. In addition it will be also necessary to assume as constant the value of λ the effective thermal conductivity.

By assuming steady state Damköhler (*5*) found a relationship between temperature, T and concentration of the gaseous reactant, c_A inside a porous solid in which a reaction takes place. This relationship leads to the following expression (*8*):

$$k^* = \exp\left[\frac{\mathrm{A}r\beta(1 - c_A{}^*)}{1 + \beta(1 - c_A{}^*)}\right], \tag{46}$$

where $\beta = D_{A_0}(-\Delta H)c_{A_s}/\lambda_0T_s$, $Ar = E/R_gT_s$, and $k^* = k'/k'_s$.

For the particular case in which the temperature difference within the solid ($T - T_s$) is small, Petersen (7) has shown that:

$$k^* = \exp \delta(1 - c_A^*), \qquad (47)$$

where $\delta = A r \beta$.

The introduction of Eq. (47) into the dimensionless form of Eq. (20) by assuming that D_A and a_i are constant yields:

$$\frac{dc_A^*}{dz^*} = 2h_0 \times \left[\frac{1}{\gamma + 1} \int_0^{c_A^*} c_A^{*\gamma} \exp[\delta(1 - c_A^*)] dc_A^*\right]^{0.5}, \qquad (48)$$

which can be integrated to obtain:

$$\frac{dc_A^*}{dz^*} = 2h_0 I(\gamma + 1)^{-0.5}, \qquad (49)$$

where

$$\begin{aligned} I &= \left[e^{\delta}\delta^{-(\gamma+1)} \int_0^{c_A^*} x^{\gamma} e^{-x} dx\right]^{0.5} \\ &= \left\{e^{\delta}\delta^{-(\gamma+1)}\left[\Gamma(\gamma + 1) - \int_{c_A^*}^{\infty} x^{\gamma} e^{-x} dx\right]\right\}^{0.5} \\ &= \left\{e^{\delta}\delta^{-(\gamma+1)} \times \sum_{n=0}^{n=\infty} \left[\frac{(-1)^n (\delta c_A^*)^{(\gamma+n+1)}}{n!(\gamma + n + 1)}\right]\right\}^{0.5}. \qquad (50) \end{aligned}$$

There are tables for evaluating the incomplete gamma function, so that the series are not useful except for large or small (δc_A^*) (our case is only represented by small values of that term). For integer values of γ, Eq. (50) simplifies to

$$I = \left\{e^{\delta}\delta!\delta^{-(\gamma+1)} \times \left[1 - e^{-\delta c_A^*} \sum_{n=0}^{n=\gamma} [(\delta c_A^*)^n/n!]\right]\right\}^{0.5}, \qquad (51)$$

which is easily applied.

On the other hand, by introducing Eq. (47) into Eq. (30) and writing it in dimensionless form we obtain

$$-dc_B^*/dz^* = [2/(\gamma + 1)]h_0^2(c_A^*)^{\gamma} \times \{\exp[\delta(1 - c_A^*)]\}/(dc_A^*/dz^*)_s, \qquad (52)$$

where $(dc_A^*/dz^*)_s$ is obtained from Eq. (49), evaluating it at s.

Dividing Eq. (52) by (49) it follows

$$-dc_B^*/dc_A^* = (c_A^*)^{\gamma}\{\exp[\delta(1 - c_A^*)]\}/2II_s, \qquad (53)$$

where I_s is the value of I (Eqs. (50) and (51)) for $c_A^* = 1$.

Integration of Eq. (53) with the boundary condition $c_B^* = 0$ for $c_A^* = 1$ yields

$$c_B^* = 1 - [I(c_A^*)/I_s]. \qquad (54)$$

Equation (54) gives the relationship between c_B^* and c_A^* for the nonisothermal, irreversible, γ order reaction with respect to A. The chosen boundary condition for the integration of Eq. (53) implies that the time required for the development of the c_B^* profile is negligible. In other words, we assumed that, from the starting point, the $c_B^*(c_A^*)$ relationship is established. This may be a good assumption provided the gaseous reactant is consumed completely in a narrow thickness inside the porous solid, which was one of our working hypotheses. Otherwise, conversion should be >0 for our initial condition.

On the other hand, the introduction of Eq. (47) into Eq. (22) yields:

$$\eta_i = \frac{1}{h_0} R^{*2} \left\{(\gamma + 1) \int_0^1 D_A^* a_i^* c_A^{*\gamma} \exp[\delta(1 - c_A^*)] dc_A^*\right\}^{0.5}, \qquad (55)$$

which will turn out to Eq. (24) by defining:

$$h^+ = \left\{(\gamma + 1) \int_0^1 D_A^* a_i^* c_A^{*\gamma} \exp[\delta(1 - c_A^*)] dc_A^*\right\}^{0.5}, \qquad (56)$$

where h^+ is now a correction factor for the Thiele modulus due to D_A^*, a_i^* and T profiles. When D_A and a_i are constant, h^+ reduces to a correction factor h_c^+ due to temperature profiles only, which is the function of δ used in catalysis (7). The only limitation in the calculation of h^+ is that we assumed constant coefficients (D_A, a_i and λ) when the calculation of the $c_B - c_A$ relationship was performed. This assumption was used twice: (a) to relate c_A to T, and (b) to relate finally c_B to c_A.

TABLE 2
VALUES OF h^+ FOR THE NONISOTHERMAL CASE[a]

ϵ^*	1			1.33			1.67			2.00		
δ γ:	0	1	2	0	1	2	0	1	2	0	1	2
					Dispersed solid model							
−5	0.30	0.38	0.43	0.35	0.45	0.51	0.41	0.52	0.58	0.47	0.59	0.67
−2	0.44	0.51	0.54	0.52	0.60	0.64	0.60	0.69	0.74	0.69	0.79	0.84
2	1.20	0.99	0.90	1.42	1.17	1.06	1.64	1.36	1.23	1.87	1.55	1.40
5	3.64	2.26	1.67	4.31	2.68	1.98	4.98	3.09	2.29	5.68	3.53	2.62
					Petersen model (ϵ_0 = 0.303)							
−5	0.40	0.51	0.57	0.48	0.61	0.69	0.56	0.72	0.81	0.65	0.82	0.93
−2	0.59	0.68	0.73	0.71	0.82	0.87	0.83	0.95	1.02	0.96	1.10	1.17
2	1.61	1.34	1.21	1.94	1.61	1.45	2.27	1.88	1.70	2.61	2.17	1.96
5	4.90	3.05	2.25	5.88	3.66	2.71	6.89	4.29	3.17	7.94	4.94	3.66

[a] Values were approximated to the second decimal.

We understand it is the first one which may be mainly criticized especially when dealing with exothermic reactions, since the influence of T upon the reaction rate is greater than that of c_A or c_B.

Values of h^+ were calculated by numerical integration of Eq. (56) taking into account Eq. (54) to obtain the functionality D_A^* (c_A^*) and $a_i^*(c_A^*)$. Results are shown in Table 2. Table 2 shows that the more exothermic the reaction, the higher is the value of h^+.

We can compare the value of the nonisothermal h^+ for a given porous structure model and different values of ϵ^*, γ, and δ to that for the nonisothermal catalytic case for same values of γ and δ. The ratio h^+/h_c^+ results independent on γ and δ and it is equal to the isothermal h^+ of Table 1. This is of upmost practical importance since knowing the values of γ and δ for our porous reactant solid we can calculate h_c^+ (which is independent on the porous structure model) and then, using Table 1 with the porous structure model and ϵ^* for the particular case it is possible to calculate the value of the nonisothermal h^+.

Calculation of Solid Consumption

From the isothermal case it can be seen that the contribution of the c_B profile to solid consumption rate is reasonably small for high Thiele modulus. On the other hand, it must be expected that in the nonisothermal case it will be the temperature profile rather than the c_B profile which will mainly affect the solid consumption rate. By neglecting the contribution of the c_B profile to the rate of solid consumption $(c_B^* \cong 1)$, Eq. (29) reduces to:

$$n_B = c_{B_0} V_0 R^{*^3}. \qquad (57)$$

The introduction of Eqs. (26) and (57) into Eq. (27) yields in dimensionless form:

$$-3(dR^*/dt^*) = M, \qquad (58)$$

where t^* and M, have the same meaning as before except that M involves now a nonisothermal h^+. The integration of Eq. (58) with the boundary condition of Eq. (42) yields:

$$Mt^* = 3(1 - R^*). \qquad (59)$$

Equation (59) is the solution for the size–time relationship in a spherical, nonisothermal pellet which is consumed by an irreversible γ order reaction with respect to the gaseous reactant and provided this reactant is consumed completely inside the porous solid. The influence of temperature gradients, as well as of effective diffusivity and internal surface area, is measured by the correction factor h^+ included in M.

When gaseous film or product layer

resistances are important, a numerical solution must be used with mass and heat transfer equations in both resistances as well as with Eqs. (26), (41), and (58).

CONCLUSIONS

The rate of variation of size in a spherical porous solid has been calculated when it reacts with a gas under asymptotic conditions.

Even though temperature gradients inside the porous solid were taken into account the analytic solution obtained is simple. The solution contains as a particular case the Moving Boundary Model.

In addition, it is shown that the ratio between the effectiveness factor for the reactant solid (with D_A, a_i and T profiles) and that for a catalyst (with T profiles) under the same references conditions is independent on reaction order and on transfer parameters being only dependent upon the porous structure of the reactant solid. This provides a simple method to evaluate the parameter h^+ under nonisothermal conditions.

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