JOURNAL OF CATALYSIS 17, 1-9 (1970)

Kinetics of Gas–Solid Reactions

Influence of Surface Area and Effective Diffusivity Profiles

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Received February 28, 1969

The isothermal reaction between a gas and a porous solid was studied theoretically. The conversion-time relationship for the solid is calculated for an irreversible, first-order reaction with respect to the gaseous reactant and taking into account the diffusional resistances of the gas film and the ash layer. This calculation is performed assuming the gaseous reactant is consumed inside the porous solid, but taking into account the way in which this consumption affects the porosity and hence the available surface area and the effective diffusivity. The effectiveness factor used in such a calculation is also developed in this paper and is expressed as a correction factor to the Thiele modulus.

NOMENCLATURE

A,B,C,D	reaction components
a	total (BET) surface area of solid B per unit volume, L^2/L^3
a_e	outer surface area of solid B for reaction per unit volume, $a_e = S_e \epsilon'_B f/V$, L^2/L^3
a_i	internal surface area of solid B per unit volume, L^2/L^3
a^*	dimensionless surface area of solid B per unit volume, $a^* = a/a_0$
b,d	stoichiometric coefficients
c	molar concentration, moles/L^3
c^*_A	dimensionless concentratoin of A, $c^*_A = c_A/c_{A_g}$
c^*_B	dimensionless concentration of B, $c^*_B = c_B/c_{B_0}$
c_t	true molar density of solid, moles/L^3
$\mathfrak{D}$	diffusivity through pores, L^2/θ
D_A	effective diffusivity of A in reaction zone, L^2/θ
D'_A	effective diffusivity of A in ash layer, L^2/θ
e	coefficient defined in Eq. (37)
e'	coefficient defined in Eq. (48)
g	coefficient defined in Eq. (11)
h	Thiele modulus, $h = L(k' a_{i_0} c_{A_s}{}^{\gamma-1}/D_{A_0})^{0.5}$
h^+	correction factor to Thiele modulus, defined in Eqs. (6) and (42)
i,j,p,v,w	coefficients in Eq. (14)
k	reaction rate coefficient per unit volume, θ^{-1}
k'	reaction rate coefficient per unit surface area, L/θ
k_{A_g}	mass transfer coefficient, L/θ
L	characteristic length, $L = V/S$, L
m	generalized Thiele modulus defined in Eq. (6)
N	coefficient in Eq. (44)
n	number of moles, moles
Bi_k	Biot number for mass transfer through boundary layer, $\mathrm{Bi}_k = k_{A_g}/k' \epsilon'_B f$
Bi_p	Biot number for mass transfer through ash layer, $\mathrm{Bi}_p = D'_A/R_e k' \epsilon'_B f$
O,P,Q,T,U,W	coefficients in Eq. (52), defined in Eq. (53)
q	coefficient in Eqs. (15) and (16)

q'	coefficient in Eq. (53)
r_A	reaction rate of A per unit volume, moles of $A/\theta L^3$
r'_A	reaction rate of A per unit surface area, moles of $A/\theta L^2$
r	particle radius of solid B in dispersed solid model, Eqs. (8) and (9), L
r^*	dimensionless pore radius in Petersen model, Eqs. (11) and (12), $r^* = r/r_0$
R	pellet radius, L
R^*	dimensionless pellet radius, $R^* = R/R_0$, L
S	geometrical area, L^2
t	time, θ
t^*	dimensionless time, $t^* = br'_{A_g}\epsilon'_B ft/R_0 c_{B_0}$
u	variable defined in Eq. (44)
V	volume, L^3
w'	coefficient defined in Eq. (46)
x	conversion
z	distance, L

Subscripts

e	solid–gas interface
g	bulk gaseous phase
0	initial value
s	boundary between ash layer and reaction zone

Superscripts

0	reference condition

Greek Letters

α	dimensionless surface area of solid B, $\alpha = a_e/(a_e + a_{i0})$
β	dimensionless surface area of solid B, $\beta = (1 - \alpha)/\alpha$
γ	reaction order
ϵ	voidage
ϵ_B	volumetric fraction of solid B
ϵ'_B	surface fraction of solid B at boundary between ash layer and reaction zone
η	overall effectiveness factor (OEF)
η_i	internal effectiveness factor (IEF)
Ω	labyrinth factor

INTRODUCTION

Let us consider the reaction between the porous solid B and the gas A (Fig. 1),

$$A_{(g)} + B_{(s)} = C_{(g)} + D_{(s)}, \tag{1}$$

which according to Eq. (1) can lead to the production of gas C and the porous solid D which can remain as an ash layer surrounding the reactant B. It is assumed that the reaction takes place isothermally.

As the objective of the present study was to calculate the conversion-time relationship for the solid B, we started by writing the equations of change for both reactants, letting c_A denote the concentration of A and c_B the concentration of B at any point,

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

$$-\frac{\partial c_B}{\partial t} = b r_A. \tag{3}$$

In these equations ϵ is the porosity, D_A is the effective diffusivity of A, and r_A is the reaction rate. All of these depend on the way in which the solid B is consumed; the porosity because the solid disappears, the diffusivity because the pore structure is opened up, and the reaction rate because it depends on the internal surface area per

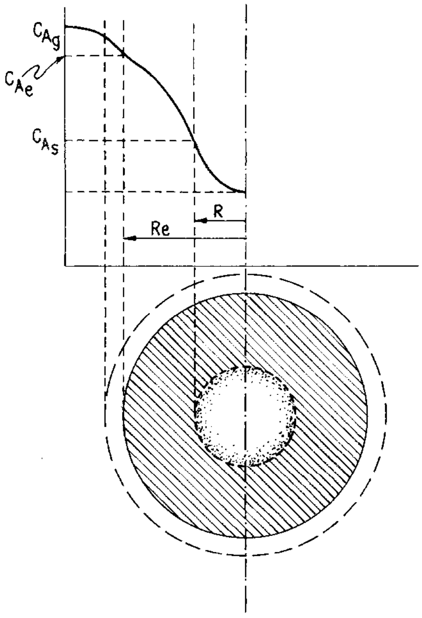

FIG. 1. General picture of the reacting system.

unit volume, a_i. Moreover, since the reaction proceeds at a rate which depends on position, profiles of varying ϵ, D_A, and a_i are developed which must be taken into account in solving Eqs. (2) and (3). The dependence of r_A and a_i and of D_A on ϵ is given by the pair of equations

$$r_A = k'a_i f_i(c_A), \tag{4}$$

$$D_A = f_2(\epsilon, \Omega), \tag{5}$$

where Ω is the labyrinth factor.

Consequently, once a model of the pore structure is stated, Eqs. (2) to (5) can be solved provided Eq. (3) is written in terms of the pore wall variation. This solution has been performed numerically for a random pore distribution (*11*). Others have solved Eqs. (2) and (3) by avoiding the discrete picture for the pseudo-steady state (*2*, *7*, *8*) or by analogy with a transient absorption with chemical reaction (*9*).

Nevertheless, in all these solutions (*2*, *7–9*) the constancy of surface area of B and effective diffusivity of A were assumed.

The influence of effective diffusivity profiles was taken into account (*17*) by means of numerical solution of Eqs. (2) and (3) for a first-order reaction with respect to B, second-order with respect to A, and using the pseudo-steady-state assumption.

In this study we tried to obtain an analytic solution of Eqs. (2) and (3), taking into account the variation of the surface area of B and the effective diffusivity of A due to the transient behavior of the pore structure.

THE SEARCH FOR AN ANALYTIC SOLUTION

Let us first state the hypotheses which are sufficiently unsophisticated to enable us to obtain the desired solution. The fundamental hypotheses are: (i) Reaction takes place isothermally. (ii) Reactant A is consumed completely inside solid B at some distance from its outer surface. (iii) Pseudo-steady state is reached for reactant A.

The second assumption implies that the internal effectiveness factor (IEF) (*5*) will lie on the so-called asymptotic region (*12*, *4*). The third assumption was discussed in a general fashion by Danckwerts (*6*) and applied to gas–solid reactions by Bischoff (*3*) and Wen (*17*).

Thus, we foresee that the IEF (*5*) must be expressed by

$$\eta_i = 1/m = h^+/h, \tag{6}$$

where m is a generalized Thiele modulus which can be calculated by the method proposed by Bischoff (*4*); h is the Thiele modulus which corresponds to the solid B without surface area and diffusivity gradients, namely, the Thiele modulus for initial conditions. From this, the meaning of h^+ is obvious: it is a correction factor due to the existence of surface area and effective diffusivity profiles inside the porous solid B. Furthermore, it will be important to analyze the influence of the surface area and effective diffusivity profiles upon h^+ for different pore structure patterns.

However, the three fundamental hypotheses are not sufficient to obtain an analytic solution of Eqs. (2) and (3), and we need, in addition, some assumptions which will be used first to express the surface area and effective diffusivity as functions of the dependent variables (c_A or c_B) and then to show that Eqs. (2) and (3) can be solved separately.

Let us analyze the relationships we need briefly. Regarding the first purpose, it is known that once a pore structure has been established, there is a relationship between the surface area and the concentration of the solid (c_B). If, in addition, it is assumed that the effective diffusivity of A depends only upon porosity, then it will be also a function of solid concentration. Hence, Eqs. (2) and (3) could be written in terms of c_A and c_B as dependent variables. These are obtained in Sects. a and b, below.

On the other hand, if some relationship between c_A and c_B, and between c_A and c_D, can be derived from reasonable assumptions, Eqs. (2) and (3) can be handled as uncoupled. This is obtained in Sect. c.

a. Relationship between surface area and solid concentration. We will look for a function

$$a^*_i = a^*_i(c^*_B), \tag{7}$$

for different pore patterns. It is seen that the relationship between surface area and solid concentration in Eq. (7) was written in terms of dimensionless variables. The functionality in Eq. (7) is relatively easy to obtain if it is assumed that no new pores are generated by the reaction. There are two well-defined cases:

1. One case is that of a pellet which is made by compaction of small nonporous particles. As in this case the solid is the dispersed phase, we will call it the "dispersed solid model."

For this model the surface area per unit volume is given by

$$a_{\mathrm{i}} = (3r^2/r_0{}^3\phi_{\mathrm{s}})\epsilon_{\mathrm{B}_0}. \tag{8}$$

On the other hand, if the number of particles per unit volume remains constant and particles do not change their shape during reaction, it follows that

$$c_{\mathrm{B}} = c_{\mathrm{B}_0}(r^3/r_0{}^3). \tag{9}$$

By introducing Eq. (8) in (9) we obtain

$$a^*{}_{\mathrm{i}} = (c^*{}_{\mathrm{B}})^{2/3}. \tag{10}$$

2. The other case is that of cylindrical pores randomly interconnected, which has been developed by Petersen (*11*); hence, we will call it the "Petersen model."

Accordingly to this model,

$$a^*{}_{\mathrm{i}} = \frac{(\frac{2}{3})g - r^*}{(\frac{2}{3})g - 1}\, r^*, \tag{11}$$

$$c^*{}_{\mathrm{B}} = (1/\epsilon_{\mathrm{B}_0})\left(1 - \frac{g - r^*}{g - 1}\, r^{*2}\right), \tag{12}$$

where g is given by

$$g^3 - \frac{27g}{4\epsilon_0} + \frac{27}{4\epsilon_0} = 0. \tag{13}$$

Consequently, the expression for the relationship between a_{i} and c_{B} is of some complexity. Nevertheless, for $\epsilon_0 = 0.30$ (which is the initial porosity of many solids), that relationship is well approximated by an equation of the type

$$a^*{}_{\mathrm{i}} = i + jc^*{}_{\mathrm{B}} - pc^{*2}{}_{\mathrm{B}} + \frac{v}{w + c^*{}_{\mathrm{B}}}, \tag{14}$$

where: $i = 0.56$, $j = 1.43$, $p = 0.97$, $v = 0.0137$, $w = 0.0244$.

It is interesting to compare these two models by their respective influence upon h^+.

As it has been said before, a different case is given when new pores are generated. In this case the surface area of the solid could increase many times that of the original, as was shown by Walker (*16*). Obviously, the probability of generating new pores depends upon the physicochemical and structural properties of the solid phase. Thus, it is very difficult to make any prediction.

Hence, what we shall do here is to take a simple, idealized, variation of $a^*{}_i$ with some parameter of the solid. According to the experiments of Walker (*16*) for carbon combustion in the zone in which A seems to be exhausted inside the solid, a sound idealized variation of $a^*{}_{\mathrm{i}}$ with porosity will be of the form

$$a^*{}_{\mathrm{i}} = 1 + \frac{q - 1}{\epsilon' - \epsilon_0}(\epsilon - \epsilon_0) \quad \text{for } \epsilon \leq \epsilon', \tag{15}$$

and

$$a^*{}_{\mathrm{i}} = q \qquad \text{for } \epsilon \geq \epsilon', \tag{16}$$

where $q > 1$. Walker's observed value was $q \simeq 8$. We will call this the "pore generation model."

The relationship obtained between $a^*{}_{\mathrm{i}}$ and $c^*{}_{\mathrm{B}}$ allow us to express the reaction rate of A as a function of the dimensionless concentrations $c^*{}_{\mathrm{A}}$ and $c^*{}_{\mathrm{B}}$ [the porosity in Eq. (15) can be readily transformed in terms of solid concentration].

b. Relationship between effective diffusivity and solid concentration. The effective diffusivity in porous media depends upon the geometry of the pores. There is a well-known relationship in terms of the voidage ϵ and the labyrinth factor Ω

$$D_{\mathrm{A}} = \mathfrak{D}_{\mathrm{A}}\epsilon/\Omega. \tag{17}$$

This expression has been simplified by some authors assuming that

$$\Omega = 1/\epsilon. \tag{18}$$

In such a case Eq. (17) reduces to

$$D_{\mathrm{A}} = \mathfrak{D}_{\mathrm{A}}\epsilon^2 = D_{\mathrm{A}_0}(\epsilon/\epsilon_0)^2, \tag{19}$$

where ϵ_0 is the voidage of the original solid B. Equation (18) has been observed to check Walker's experimental data (*16*) for carbon combustion and Satterfield's collection of data (*13*) for many porous solids.

Besides its empirical nature, Eq. (18)

represents a particular case of the Wakao–Smith model for diffusion (*15*) when there are only micropores. Alternatively, Eq. (19) can be written as follows:

$$D_A = D_{A_0}(1/\epsilon_0^2)\left(1 - \frac{c_B}{c_{tB}} - \frac{c_D}{c_{tD}}\right)^2. \qquad (20)$$

c. Relationship between gaseous and solid concentrations. So far we have expressed the two variable coefficients in Eqs. (2) and (3) as a function of c_B and c_D.

If we are now able to assume a relationship between c_A, c_B, and c_D, Eq. (2) could be written in terms of c_A, and so it could be solved without taking into account Eq. (3). In order to get such a relationship among concentrations we will assume that the surface area and the effective diffusivity are constant and that the reaction is irreversible and γ order with respect to A.

The constancy of the surface area and effective diffusivity is only used to get a relationship among c_A, c_B, and c_D. Once this relationship has been obtained, Eq. (2) will be solved, taking the surface area and effective diffusivity as variable coefficients. The relationship so derived is approximately correct, but the final result shows an excellent agreement between theory and experiment.

Taking into account the three fundamental hypotheses and the assumptions just mentioned, Eq. (2) turns out to be, if it is written in dimensionless form,

$$\frac{d^2c^*_A}{dz^{*2}} = m(c^*_A)^\gamma. \qquad (21)$$

Equation (21) is valid for any geometry whenever the Thiele modulus is large enough, because most of the reaction then takes place near the outer surface.

Taking into account that c_A is uniform on the outer surface of the solid and falls to zero inside it, Eq. (21) can be integrated once by the Clairaut substitution to give

$$\frac{dc^*_A}{dz^*} = [2/(\gamma + 1)]mc_A{}^{*(\gamma+1)/2} \qquad (22)$$

At the same time,

$$\frac{dn_B}{dt} = \frac{d}{dt}\int_0^V c_B\,dV, \qquad (23)$$

but for high Thiele modulus it can be assumed that $c_B \simeq c_{B_0}$; hence, Eq. (23) can be simplified to

$$\frac{dn_B}{dt} = c_{B_0}S\frac{dz_s}{dt}. \qquad (24)$$

On the other hand, Eq. (3) can be written as follows:

$$\frac{dc_B}{dz} = \frac{bkc_A{}^\gamma}{dz_s/dt}. \qquad (25)$$

But taking into account that

$$-\frac{dn_B}{dt} = bD_AS\left.\frac{dc_A}{dz}\right|_s, \qquad (26)$$

then, from Eqs. (24) and (26) it follows that Eq. (25) can be written as

$$-\frac{dc_B}{dz} = \frac{kc_{B_0}c_A{}^\gamma}{D_A(dc_A/dz)_s}. \qquad (27)$$

Equation 27 can be written in terms of dimensionless variables, as follows:

$$-\frac{dc^*_B}{dz^*} = mc_A{}^{*\gamma}. \qquad (28)$$

Consequently, from Eqs. (22) and (28) it follows that

$$-\frac{dc^*_A}{dc^*_B} = [2/(\gamma + 1)]c_A{}^{*(1-\gamma)/2}. \qquad (29)$$

The relationship between c^*_A and c^*_B is then readily obtained taking into account that the boundary conditions are,

$$\begin{aligned} &\text{at the center:} && c^*_A = 0 && c^*_B = 1,\\ &\text{at the reaction front:} && c^*_A = 1 && c^*_B = 0. \end{aligned} \qquad (30)$$

The following result is obtained:

$$c^*_B = 1 - c_A{}^{*(\gamma+1)2}. \qquad (31)$$

Furthermore, at the same time, the following relationship holds:

$$-d\frac{dc_B}{dt} = b\frac{dc_D}{dt} \qquad (32)$$

Hence, by a similar treatment to that we have just done, it can be shown that

$$c^*_D = c_A{}^{*(\gamma+1)/2}. \qquad (33)$$

The relationship between c^*_A and c^*_B given by Eq. (31) was also obtained by

Ishida (*7*) by analytical integration of Eqs. (2) and (3) and numerically by Ausman (*1*) for a spherical solid and for the particular case $\gamma = 1$.

By substituting now Eqs. (31) and (33) into Eqs. (7) and (20), it is seen that Eq. (2) can be written in terms of c_A exclusively. We are then able to integrate Eq. (2) once to obtain the effectiveness factor; obviously the so-calculated effectiveness factor will take into account the profiles of surface area and effective diffusivity through the porous solid. On the other hand, the mass balance for B can be written as follows

$$-\frac{dn_B}{dt} = br'_{A\,r}\eta V, \tag{34}$$

where η is the overall effectiveness factor (OEF) (*5*).

By introducing the calculated effectiveness factor, Eq. (34) can then be integrated to obtain the desired solution.

Calculation of the Effectiveness Factor

By introducing Eq. (31) into Eq. (7), it follows that

$$a^*_i = a^*_i(c^*_A). \tag{35}$$

Assuming that the reaction is irreversible and first order with respect to A and by introducing Eqs. (31) and (33) into Eq. (20), it follows that

$$D_A = D_{A_0}(1 + ec^*_A)^2, \tag{36}$$

where

$$e = \frac{1}{\epsilon_0}\left(\frac{c_{B_0}}{c_{tB}} - \frac{c_{D_s}}{c_{tD}}\right) = \frac{\epsilon_s - \epsilon_0}{\epsilon_0}. \tag{37}$$

So far we have related the variable coefficients of Eq. (2) to c_A.

For high Thiele modulus and pseudo-steady-state conditions, Eq. (2) simplifies to

$$\frac{d}{dz} D_A \frac{dc_A}{dz} - r_A = 0, \tag{38}$$

but taking into account Eqs. (4, 10, 14–16, 31, and 36), Eq. (38) can be written as follows:

$$\frac{d}{dz^*} f(c^*_A) \frac{dc^*_A}{dz^*} - hc^*_A a^*_i(c^*_A) = 0, \tag{39}$$

where $f(c^*_A)$ indicates the influence of c^*_A upon D_A, and $a_i(c^*_A)$ that of c^*_A upon a^*_i.

The function $f(c^*_A)$ is given by Eq. (36) and that of $a^*_i(c^*_A)$ arises from the introduction of Eq. (31) into Eqs. (10, 14, or 16–17) according to the pore structure model which has been selected.

Remembering

$$\frac{dc^*_A}{dz^*} = m = 1/\eta_i \tag{40}$$

and applying the Clairaut substitution to Eq. (39), the following result is obtained:

$$m = h\left[2 \int_0^1 (1 + ec^*_A)^2 c^*_A a^*_i(c^*_A)\, dc^*_A\right]^{-0.5}. \tag{41}$$

Thus, taking into account Eq. (6), it is seen that

$$h^+ = \left[2 \int_0^1 (1 + ec^*_A)^2 c^*_A a^*_i(c^*_A)\, dc^*_A\right]^{0.5}, \tag{42}$$

where the parameter e measures the influence of effective diffusivity profiles upon h^+.

Integration of Eq. (42) is performed below for the three proposed pore structure models and for different values of e (for the pores generation model we take q as the parameter).

Dispersed solid model. By introducing Eq. (31) (for $\gamma = 1$) into Eq. (11), the latter in Eq. (42), and integrating, it follows that

$$h^+ = \{2[e^2(\tfrac{3}{5}N^2u^{5/3} - \tfrac{3}{4}Nu^{8/3} + \tfrac{3}{11}u^{11/3} - \tfrac{3}{8}N^2u^{8/3} + \tfrac{6}{11}Nu^{11/3} - \tfrac{3}{14}u^{14/3})]_0^1\}^{0.5}, \tag{43}$$

where

$$N = 1 + (1/e) \text{ and } u = 1 - c^*_A. \tag{44}$$

The value of h^+ was calculated for different values of e, and the results are shown in Table 1.

Petersen model. By introducing Eq. (31) (for $\gamma = 1$) into Eq. (14), the latter in Eq. (42), and integrating, one obtains

$$h^+ = [2(E + F + G + I + J + K + M)]^{0.5}, \tag{45}$$

where

$E = (i + j - p)/2,$

$F = [2p - j + 2e(i + j - p)]/3,$

$$G = e(4p - 2j) - p + e^2(i + j - p)$$
$$H = e[2p(e - 1) - ej]/5,$$
$$I = e/^2p6$$
$$J = -v\left(1 + w' \ln \frac{w' - 1}{w'}\right),$$
$$K = 2ve\left[\frac{(w' - 1)^2 - w'^2}{2} + 2w' + w'^2 \ln \frac{w' - 1}{w'}\right],$$
$$M = e^2d\left\{\frac{(w' - 1)^3 - w'^3}{3} - \frac{3w'}{2}[(w' - 1)^2 - w'^2] - 3w' - w'^3 \ln \frac{w' - 1}{w'}\right\},$$

where

$$w' = 1 + w. \tag{46}$$

The value of h^+ was calculated for different values of e, and the results are shown in Table 1.

TABLE 1

Influence of Pore Model Parameters upon h^+

Ash layer porosity ϵ_s	Correction factor, h^+		
	Dispersed solid model		Petersen model,
	$\epsilon_0 = 0.20$	$\epsilon_0 = 0.30$	$\epsilon_0 = 0.30$
0.20	0.68		
0.30	0.855	0.68	0.90
0.40	1.05	0.795	1.09
0.50	1.14	0.925	1.27
0.60	1.44	1.06	1.46

Pores generation model

$\epsilon_0 = 0.30$ $\epsilon_s = 0.60$ $\epsilon' = 0.40$

q	h^+
5	3.72
10	5.25
15	6.45
20	7.45

Pores generation model. If it is taken into account that for $\gamma = 1$

$$\epsilon = \epsilon_0 + e'c_A, \tag{47}$$

where

$$e' = \frac{c_{B_0}}{c_{tB}} - \frac{c_{D_s}}{c_{tD}}, \tag{48}$$

then, by introducing Eq. (47) into Eq. (15) and the latter and Eq. (16) into Eq. (42), an equation is obtained which can be integrated in two steps. The first integration will be between the limits

$$\epsilon = \epsilon_0 \qquad c^*_A = 0, \tag{49}$$
$$\epsilon = \epsilon' \qquad c^*_A = c^{*\prime}_A,$$

and the second one between

$$\epsilon = \epsilon' \qquad c^*_A = c^{*\prime}_A, \tag{50}$$
$$\epsilon = \epsilon_s \qquad c^*_A = 1.$$

According to Eq. (47),

$$c^*_A = \frac{(\epsilon/\epsilon_0) - 1}{e}. \tag{51}$$

Hence, the whole integration gives

$$h^+ = \left\{2\left[\frac{(c^{*\prime}_A)}{2} + Oc^{*\prime 3}_A + Pc^{*\prime 4}_A + Qc^{*\prime 5}_A + T(1 - c^{*\prime 2}_A) + U(1 - c^{*\prime 3}_A) + W(1 - c^{*\prime 4}_A)\right]\right\}^{0.5} \tag{52}$$

where

$$O = e(2 + q')/3,$$
$$P = e^2(1 + 2q')/4,$$
$$Q = e^3q'/5,$$
$$T = q/2,$$
$$U = 2eq/3,$$
$$W = e^2q/4,$$
$$q' = (q - 1)/(\epsilon' - \epsilon_0) - 1. \tag{53}$$

The value of h^+ was calculated for an initial voidage of 0.30, a voidage of the ash layer of 0.60, $\epsilon' = 0.40$, and different values of q. These results are also shown in Table 1.

The results condensed in Table 1 show that the influence of the voidages (or the influence of e) upon h^+ is of the same order of magnitude for the dispersed solid and Petersen models, though they represent quite different pore patterns.

Calculation of Conversion-Time Relationship

Now we have to introduce Eq. (41) into Eq. (34) and to integrate it. However, to perform that integration, a relationship between n_B and V is necessary.

Relationship between n_B and V. Equation (34) can also be written as follows:

$$n_{\mathrm{B}} = c_{\mathrm{B}_0} \int_0^V c^*{}_{\mathrm{B}}\, dV. \tag{54}$$

If Eq. (31) (for $\gamma = 1$) is taken into account, then Eq. (54) can be written as follows:

$$n_{\mathrm{B}} = V\left[C_{\mathrm{B}_0} - \frac{\int_0^V c_{\mathrm{A}}\, dV}{C_{\mathrm{A}_s} V}\right] \tag{55}$$

The term containing the integral in Eq. (55) is the IEF for a zero-order reaction with respect to B, first-order with respect to A, and constant effective diffusivity, namely, for the conditions for which the relationship between $c^*{}_{\mathrm{A}}$ and $c^*{}_{\mathrm{B}}$ was calculated.

For our later development, that term does not represent the true IEF. However, the form of Eq. (55) makes the influence of that term very small, especially when we consider that our development is only valid for high Thiele modulus. Hence, it can be assumed that

$$n_{\mathrm{B}} = c_{\mathrm{B}_0} V(1 - \eta_{\mathrm{i}}). \tag{56}$$

Equation (56) can be transformed into a rate expression by differentiating it with respect to time:

$$\frac{dn_{\mathrm{B}}}{dt} = c_{\mathrm{B}_\bullet} \frac{dV}{dt}\left(1 - \frac{h^+}{h}\right). \tag{57}$$

Two alternate expressions of Eq. (57) are

$$\frac{dn_{\mathrm{B}}}{dt} = c_{\mathrm{B}_0} \frac{dV}{dt}\left(1 - \frac{h^+}{Lh_0}\right), \tag{58}$$

$$\frac{dn_{\mathrm{B}}}{dt} = c_{\mathrm{B}_0} \frac{d}{dt}\left(V - \frac{L_0 S_s h^+}{h_0}\right). \tag{59}$$

It is seen from Eq. (59) that the first term inside the parentheses represents the conversion contribution due to the swept volume and the second term that due to cross section variation. Hence, for a solid with slab geometry, Eq. (59) reduces to an expression which is identical to that used for the MBM. It is seen that now we are able to integrate Eq. (34) to obtain the conversion-time relationship.

Calculation of the conversion-time relationship. The OEF for a spherical solid is given by (*5*):

$$\eta = \frac{\alpha + (1 - \alpha)(h^+/h_0)}{1 + \left[\frac{R^2}{\mathrm{Bi}_k} + \frac{R(1 - R)}{\mathrm{Bi}_p}\right]\left(1 + \frac{1 - \alpha}{\alpha}\frac{h^+}{h}\right)}, \tag{60}$$

where

$$\alpha = a_{\mathrm{e}}/(a_{\mathrm{e}} + a_{\mathrm{i}_0}) \text{ and } a_{\mathrm{e}} = 3\epsilon'{}_{\mathrm{B}} f/R. \tag{61}$$

In addition, the right-hand side of Eq. (34) can be written in terms of the dimensionless radius according to Eq. (59).

By introducing Eq. (60) into Eq. (34), taking into account that Eq. (34) is equal to Eq. (59), and assuming that the term $\epsilon'{}_{\mathrm{B}} f$ remains constant as solid B is consumed, the following result is obtained:

$$\frac{dR^*}{dt^*} = \frac{1 + \beta_0(h^+/h_0)}{\left(1 - \frac{2h^+}{3R^* h_0}\right) \times \left\{1 + \left[\frac{R^{*^2}}{\mathrm{Bi}_k} + \frac{R^*(1 - R^*)}{\mathrm{Bi}_p}\right]\left(1 + \frac{h^+}{h_0}\right)\right\}} \tag{62}$$

where

$$\beta = (1 - \alpha)/\alpha \text{ and } t^* = br'{}_{\mathrm{A_g}}\epsilon'{}_{\mathrm{B}} ft/R_0 c_{\mathrm{B}_0}. \tag{63}$$

Equation (62) can be integrated between $t^* = 0$ and $t^* = t^*$ to give:

$$\begin{aligned} t^* = {} & \frac{1}{3}\left(\frac{1}{\mathrm{Bi}_k} - \frac{1}{\mathrm{Bi}_p}\right)(1 - R^{*^3}) \\ & + \frac{1}{3}\left(\frac{3}{2\mathrm{Bi}_p} - \frac{h^+}{h_0 \mathrm{Bi}_k} + \frac{h^+}{h_0 \mathrm{Bi}_p}\right)(1 - R^{*^2}) \\ & + \frac{1}{1 + (\beta_0 h^+/h_0)} - \frac{2}{3h_0 \mathrm{Bi}_p}(1 - R^*) \\ & + \frac{2}{3[\beta_0 + (h_0/h^+)]} \ln R^*. \end{aligned} \tag{64}$$

Let us remember that the instant $t^* = 0$ is the time at which the profiles of c_{A} and c_{B} were just developed.

In addition, from Eq. (56) it follows that

$$x_{\mathrm{B}} = 1 - \left(1 - \frac{h^*}{R^* h_0}\right) R^{*^3}. \tag{65}$$

Equation (65) together with Eq. (64) yield the desired relationship between conversion and time.

Equation (64) implies the most general solution for the size-time relationship in the asymptotic region of the IEF for an isothermal, irreversible, first-order reaction with respect to A and different pore structure models whose influence is measured by the parameter h^+.

There are four terms in Eq. (64) which describe the contribution to conversion due to the c_B profile: those which contain h^+ in the second term; that which contains $2h^+/3$ in the third term, and the last, logarithmic, term. The other terms represent the conversion contribution due the volume swept out as the core shrinks. Equation (64) contains a very important particular case, that of the moving boundary model.

If the Thiele modulus approaches infinity, that is to say the c_A profile approaches a step function on the outer surface of solid B, Eq. (64) will reduce to

$$t^* = \frac{1}{3}\left(\frac{1}{\mathrm{Bi}_k} - \frac{1}{\mathrm{Bi}_p}\right)(1 - R^{*3}) + \frac{1}{2\mathrm{Bi}_p}(1 - R^{*2}) + (1 - R^*), \quad (66)$$

and Eq. (65) will reduce to

$$x_B = 1 - R^{*3}, \quad (67)$$

provided $R^* \neq 0$.

Equation (66) can in turn be reduced to simpler expressions in three limiting cases: (i) when both Biot numbers approach infinity, namely, when the surface reaction controls; (ii) when the Biot number of the boundary layer approaches infinity and that of the ash layer approaches zero, that is to say, when diffusion through the ash layer is the controlling step; and (iii) when the Biot number of the ash layer approaches infinity, but that of the boundary layer approaches zero, in which case, the reaction is controlled by diffusion through the boundary layer.

In the last two cases, the expression for the dimensionless time obviously changes; thus when ash layer is the controlling resistance, $t^* = 6D'_A b c_{A_g} t / R_0^2 c_{B_0}$, and when the boundary layer is the controlling resistance, $t^* = 3k_{A_g} b c_{A_g} t / R_0^2 c_{B_0}$.

CONCLUSIONS

An analytic solution was obtained for the conversion-time relationship when a porous solid reacts with a gas. This solution contains the contribution to reaction due to outer surface area of solid reactant and hence it approaches the moving boundary model as a limiting case. Surface area and effective diffusivity profiles through porous solid due to reaction were taken into account. Influence of pore structure pattern was measured by means of a correction factor of the initial Thiele modulus. The main assumptions are: the system is isothermal; the reaction is irreversible and first order with respect to the gaseous reactant; the Thiele modulus is large; and the pseudo-steady state for the gaseous reactant is reached.

ACKNOWLEDGMENT

Suggestions and remarks of Professor Rutherford Aris are gratefully acknowledged.

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