化學 및 冶金工程에서 流固體間에 일어나는 非觸媒的 反應의 速度論 : II. 單一多孔質固體의 反應*

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Kinetics of Non-Catalytic Fluid-Solid Reactions in Chemical and Extractive Metallurgical Processes: Part II. Reaction of a Single Porous Particle

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요　　약

이 總說의 第一部에서 본 바와 같이 非孔質固體의 境遇에는 化學 反應과 diffusion 또는 mass transfer 가 連鎖的으로 일어나 體系的인 處理가 比較的 容易하다. 그러나 固體가 처음부터 多孔性인 境遇에 는 化學反應과 pore diffusion이 並行하여 일어나기 때문에 그 數學的인 處理가 복잡하여 最近까지 이 分野의 理論이 매우 不振되어 있었다. 지난 數年동안에 이러한 反應系의 重要性이 認識됨에 따라 몇몇 硏究그룹으로 부터의 硏究結果가 發表된바있다. 이 第二部에서는 이러한 多孔性 固體의 反應 速度論을 檢討한다. 다음 두部에서는 氣體를 媒介로 하여 일어나는 두 固體間의 反應과 工業的으로 重要한 多粉體系의 反應을 取扱하고저 한다.

Abstract

As was seen in Part I, the treatment of the reaction of a nonporous solid particle is relatively straightforward. When the solid is initially porous, analysis becomes rather involved due to the fact that chemical reaction and diffusion occur in parallel. Only recently, some noteworthy developments and articles have been reported as the importance of this type of systems is being recognized more and more. In this Part II, recent advances on the reaction of a porous solid particle will be discussed. In the next two parts, we will describe the reactions between two solids proceeding through gaseous intermediates and the treatment of industrially important multiparticle systems.

*Part I: *Hwahak Konghak*, **14** (1976), 3.

When the reactant solid is initially porous, the fluid reactant will diffuse into the solid while reacting with it on its path. Thus, chemical reaction and diffusion occur in parallel over a diffuse zone rather than at a sharp boundary. The reaction of a porous solid has not been studied as extensively as that of a nonporous solid. Only recently has it received much attention from a number of research groups. As in the case of a nonporous solid, it is important to understand the relative importance of chemical kinetics and transport phenomena. The resistance to mass and heat transport may significantly influence the apparent activation energy, the apparent reaction order, and the dependence of overall rate on the size and other structures of the particle.

2.1 Reactions in which no solid product is formed

Examples of such reactions are the combustion of porous carbon, the formation of nickel carbonyls from relatively pure nickel, the dissolution of porous minerals, and the Boudouard (or solution-loss) reaction between porous carbon and carbon dioxide. This type of reactions may in general be described by the following:

$$A(\text{fluid}) + bB(\text{solid}) \rightarrow \text{fluid products} \quad (53)$$
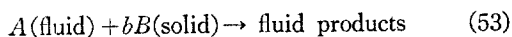
In the case of nonporous solids reacting without forming a solid product layer, it was shown that the overall reaction may be controlled by chemical reaction or by external mass transfer. In the case of porous solids, the diffusion of fluid reactants within the pores of the solid creates an additional regime where the overall reaction is strongly influenced by the pore diffusion (but not controlled by it).

2.1.1 *Uniformly-reacting porous particles*

At low temperatures where intrinsic kinetics is slow the fluid species can diffuse deeply into the interior of the solid, and reaction occurs throughout the solid under a uniform concentration of fluid A that is same as its bulk value. Thus all the kinetic measurements will yield intrinsic values.

One of the first models on the gasification of solids, taking into account the changes in pore structure by the consumption of solid, is due to Petersen[32], who assumed that the solid contains uniform cylindrical pores with random intersections. Without going into the detailed description of mathematical derivation, the result of the model will be summarized. When the diffusion through the pores is rapid and hence offers little resistance, the concentration of the reactant is uniform throughout the particle and the rate of reaction per unit volume of solid is given by the following:

$$\text{Rate per volume} = k\left(\frac{\varepsilon_0}{r_0}\right)\frac{(2G-3\xi)\xi}{G-1}C_A^n \quad (54)$$

where

k = gas-solid reaction rate constant,
ε_0 = initial porosity of the solid,
r_0 = inital radius of pores,
$\xi = r/r_0$ (r = pore radius at anytime)
C_A = concentration of reactant A

and G is the root of

$$\frac{4}{27}\varepsilon_0 G^3 - G + 1 = 0 \quad (55)$$

the variation of ξ with time is obtained by integrating

$$-\frac{dr}{dt} = \frac{bk}{\rho_s}C_A^n \quad (56)$$

to give

$$\xi = 1 + \frac{t}{\tau_c} \quad (57)$$

where

$$\tau_c \equiv \frac{r_0 \rho_s}{bkC_A^n} \quad (58)$$

The relationship between the conversion X and time is given by[5]

$$X = \frac{\varepsilon_0}{1-\varepsilon_0}\left[(1+\frac{t}{\tau_c})^2\left(\frac{G-1-t/\tau_c}{G-1}\right)-1\right] \quad (59)$$

It is emphasized that this expression is valid only when diffusion offers little resistance and hence the fluid concentration is uniform within the solid. When diffusion offers a significant resistance, the concentration and reaction rate will vary with position inside the particle. This problem has been treated by Petersen[32] and, more recently, by Hashimoto and Silveston[33].

Applying the model to the reaction of porous graphite with carbon dioxide, Petersen[32] found a reasonable agreement, despite the assumptions that the pores are cylindrical and uniform in size and the neglect of the coalescence of adjacent pores as they grow. Furthermore, this model is one of the few models that contain the realistic feature that the surface area may increase with reaction, go through a maximum and then decrease.

2.1.2 *Reactions occurring under the strong limitation of pore diffusion or under the control of external mass transfer*

As the reaction becomes faster, the fluid reactants cannot penetrate deeply into the solid without reacting. Under these conditions, the reaction will mostly occur in a narrow region near the external surface consuming the solid from the surface into the center. The situation is described in *Fig. 8*.

We will illustrate the quantitative aspects of such a reaction for an irreversible reaction. Since the reaction mainly occurs in a narrow layer near the external surface, the reaction zone may be considered flat regardless of the actual overall geometry of the solid. The mass balance, therefore, may be written in one direction only:

$$D_e \frac{d^2C_A}{dx^2} - kS_v C_A^n = 0 \qquad (60)$$

where x is the distance normal to the external surface and S_v is the surface are per unit volume.
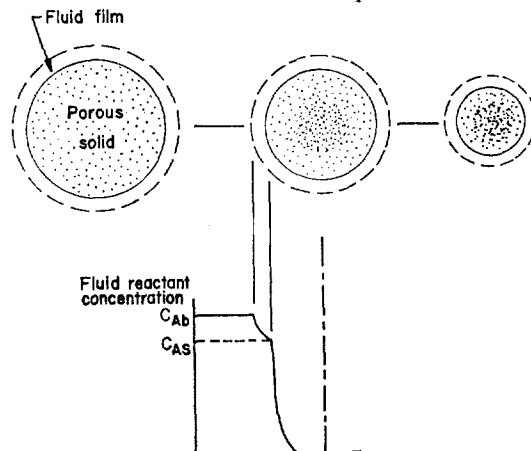

Fig. 8. Reaction of a porous particle without forming a solid product layer and shrinking in overall size.

Here, we made the assumption that the bulk flux is negligible, which is valid for equimolar counter diffusion or when A is present at low concentrations. The case of substantial volume change due to reaction will be examined later. The boundary conditions are:

$$C_A = C_{As} \qquad \text{at } x=0 \quad \text{(outer surface of the soid)} \quad (61)$$

and

$$C_A = \frac{dC_A}{dx} = 0 \qquad \text{as } x \to \infty \qquad (62)$$

The first boundary condition assumes a negligible resistance due to external mass transfer. The effect of external mass transfer can easily be incorporated as shown later. The second boundary condition is justified when it is recognized that the pellet dimension is much larger than the thin layer in which the fluid reactants are completely exhaused. This condition is satisfied when the following inequality is valid[2]:

$$\frac{V_p}{A_p} \sqrt{\left(\frac{n+1}{2}\right) \frac{kS_v C_A^{n-1}}{D_e}} > 3 \qquad (63)$$

The solution of Eq. (60) is given by*

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*Substitute $p \equiv \dfrac{dC_A}{dx}$ and thus $\dfrac{d^2C_A}{dx^2} = p\dfrac{dp}{dC_A}$ and solve for p with C_A as the independent variable.

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$$\left. \frac{dC_A}{dx} \right|_{x=0} = -\left(\frac{2}{n+1} \frac{kS_v}{D_e} C_A^{n+1} \right)^{1/2} \qquad (64)$$

From the concentration gradient at the external surface $(x=0)$, the overall rate per unit external surface area can be obtained as follows:

$$n_A = -D_e \left(\frac{dC_A}{dx} \right)_{\substack{\text{at external} \\ \text{surface}}} = \left(\frac{2}{n+1} kS_v D_e \right)^{\frac{1}{2}} C_{As}^{\frac{n+1}{2}}$$

$$(65)$$

It is noted that the rate is proportional to $(kD_e)^{1/2}$ which means that the apparent activation energy is the arithmetic average of the activation energies of intrinsic reaction and diffusion:

$$E_{app} = \frac{E_r + E_d}{2} \qquad (66)$$

For the diffusion of gaseous reactant, $E_d \simeq 0$ and the apparent activation energy is one-half of the intrinsic value. The apparent reaction order is also changed:

$$n_{app} = \frac{n_{intrinsic} + 1}{2} \qquad (67)$$

Equation (65) shows why diffusion does not control the overall rate, that is, even when chemical reaction is fast (k large), a larger k still increases the overall rate. This is because chemical reaction and diffusion occur in parallel, not in series. The overall conversion of the solid may be described using n_A given by Eq. (65). The procedure is entirely analogous to that for a nonporous particle described previously.

Equating Eqs. (11) and (65), integrating, and substituting Eq. (27), we get

$$\frac{b \left(\frac{2}{n+1} kS_v D_e \right)^{1/2} C_{As}^{\frac{n+1}{2}}}{\rho_B} \left(\frac{A_p}{F_p V_p} \right) t$$

$$= 1 - (1-X)^{1/F_p} \equiv g_{Fp}(X) \qquad (68)$$

We have assumed that the external mass transfer offers little resistance. We shall examine the effect of external mass transfer subsequently. It is seen that the X-vs. $-t$ relationship is analogous for porous and nonporous solids. Thus, fre-

quently no distinction has been made in analyzing this type of a reaction whether the solid is porous or not. On closer inspection, however, the kinetics of the reaction of a porous solid is falsified by the influence of diffusion. Instead of intrinsic kinetic parameters, one obtains the apparent values of activation energy and reaction order. The kinetics is also strongly affected by the physical structure of the porous solid such as the specific surface area and the effective diffusivity.

The above analysis was made for a power-law kinetic expression. Many fluid-solid reactions may be more accurately described by the Langmuir-Hinshelwood type expression:

$$\text{Rate} = \frac{kC_A}{1 + KC_A} \qquad (69)$$

which can be shown[34], using appropriate transformation of variables, to represent, also a class of more complex mechanisms that account for a reversible surface chemical reaction and the adsorption of other species. When this kinetic expression is incorporated in Eq. (60), the result is:

$$n_A = (2kS_v D_e)^{1/2} \frac{[KC_{As} - \ln(1 + KC_{As})]^{1/2}}{KC_{As}} C_{As}$$

$$(70)$$

When there is a substantial change in fluid volume upon reaction, which is expected more likely in gas-solid reactions, the bulk of fluid species in the pores must be taken into account. If the volume increases upon reaction, as in $2C + O_2 \rightarrow 2CO$, the bulk outward flow of CO hinders the diffusion of O_2 into the solid. A reduction in volume has the opposite effect.

Thiele[35] first showed the effect of volume change on the rate of a catalytic reaction in a porous catalyst pellet. His work was extended later by Weekman and Gorring[36]. We can apply a similar analysis to fluid-solid noncatalytic reactions with which we are concerned here. The mass balance equation including the bulk flux term at constant pressure is as follows:

$$D_e \frac{d^2 C_A}{dx^2} - \frac{\theta/C_{As}}{1+\theta \cdot C_A/C_{As}} \left(\frac{dC_A}{dx}\right)^2 - kS_v C_A^n (1+\theta C_A/C_{As}) = 0 \qquad (71)$$

where $\theta \equiv (\nu-1) Y_{As}$ and ν is the the volume of fluid species produced per unit volume of fluid species reacted, and Y_{As} in the mole fraction of gas A at the pellet surface. Solution of Eq. (71) with the boundary conditions given in Eqs. (61) and (62) gives the overall rate of reaction per unit area of external surface as follows:

For a zeroth-order reaction $(n=0)$,

$$n_A = (2kS_v D_e)^{1/2} (1+\theta) \left[\frac{1}{\theta} ln(1+\theta)\right]^{1/2} C_{As}^{1/2} \qquad (72)$$

For a first-order reaction $(n=1)$,

$$n_A = (2kS_v D_e)^{1/2} (1+\theta) \left[\frac{1}{\theta} - \frac{1}{\theta^2} ln(1+\theta)\right]^{1/2} C_{As} \qquad (73)$$

For a second-order reaction $(n=2)$,

$$n_A = (2kS_v D_e)^{1/2} (1+\theta) \left[\frac{1}{2\theta} - \frac{1}{\theta^2}\right.$$
$$\left. + \frac{1}{\theta^3} ln(1+\theta)\right]^{1/2} C_{As}^{3/2} \qquad (74)$$

Up to now, we have implicitly assumed that the area of the external surface is negligible compared with S_v. This may not be valid for solids of very low porosity or very fast reaction. In such a case, the reaction occurring at the external surface may contribute significantly to the overall rate[37]. The rate of reaction at the external surface may be written as

$$n_A \underset{\substack{\text{external} \\ \text{surface}}}{} = kfC_{As}^n \qquad (75)$$

where f is the roughness factor for the external surface defined as the ratio of true area to the projected area of external surface. This term is added to Eqs. (65), (70), and (71) to obtain the total rate of reaction. This total rate of reation must be used to determine the conversion.

For a first-order reaction without appreciable volume change, the overall rate including the resistance due to the external mass transfer is

$$n_A = \frac{C_{Ab}}{\dfrac{1}{\left(\dfrac{2}{n+1}kS_v D_e\right)^{1/2}+kf} + \dfrac{1}{k_m}} \qquad (76)$$

It can be readily verified that the external mass transfer controls the overall rate when $k \rangle\rangle k_m$. When the external mass transfer offers little resistance $(k \langle\langle k_m)$, the overall rate becomes

$$n_A = \left[\left(\frac{2}{n+1}kS_v D_e\right)^{1/2} + kf\right] C_{Ab} \qquad (77)$$

When the contribution of the second term is small compared with that of the first, the expression reduces to that of Eq. (65) with C_{As} equal to C_{Ab}.

Nonisothermal behavior in reaction systems under consideration has been studied[5], based on the analysis by Petersen [2,38] for a nonisothermal catalytic reaction in a porous catalyst pellet. Only the result for a first-order reaction will be presented here. Then

$$n_A = (2k_s S_v D_e)^{1/2} \frac{(e^\delta - 1 - \delta)^{1/2}}{\delta} C_{As} \qquad (78)$$

where $k_s = k(T_s)$, $\qquad (79)$

the reaction-rate constant at external surface temperature, and where

$$\delta \equiv \gamma\beta \qquad (80)$$

$$\gamma \equiv E/R_g T_s \qquad (81)$$

$$\beta \equiv \frac{(-\Delta H) D_e C_{As}}{\lambda_e T_s} = \left(\frac{T-T_s}{T_s}\right)_{max} \qquad (82)$$

It has been assumed in deriving Eq. (78) that $\beta \langle\langle 1$, for which the solution is valid for values of $|\delta|$ up to at least 5. For other values of β the solution involves numerical integration, and the reader is referred to literatures[5,39].

2. 2 Reacions in which a product layer is formed

This type of a reaction is similar to those discussed in Section 1.4 of Part I except that the initial reactant solid is porous. The reaction can again be described by the following:

$$A(\text{fluid}) + bB(\text{solid}) = cC(\text{fluid}) + dD(\text{solid}) \qquad (83)$$
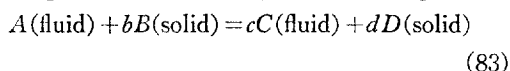
In a porous solid, the reaction occurs in a diffuse zone rather than a sharp interface. There is a gradual change in conversion of solid over the pellet. In general, the external layer will be completely reacted first and the thickness of the completely-reacted layer will grow towards the interior of the porous solid. Figure 9 illustrates the reaction of a porous solid in which a solid product layer is formed.
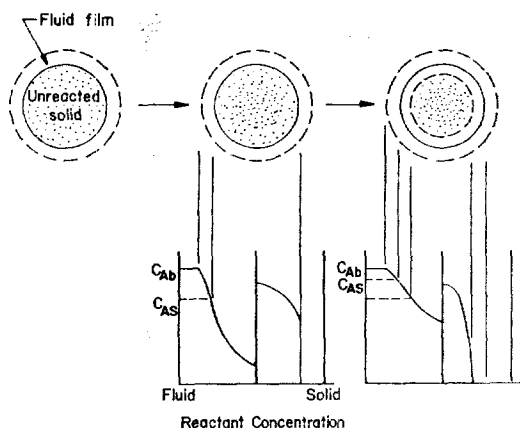
Fig. 9. Reaction of a porous particle forming a solid product layer.

When pore diffusion is fast compared with the rate of chemical reaction, the concentration of fluid reactant will be uniform throughout the pellet and the reaction will occur at a uniform rate. If chemical kinetics is much faster than the rate of diffusion, however, the reaction will occur in a narrow layer between the unreacted and the completely-reacted zones. This latter situation is identical to the diffusion-controlled shrinking-core reaction of a nonporous solid discussed previously. We will formulate equations

including both intrinsic chemical kinetics and diffusion, and derive the criteria for asymptotic regimes where a particular step controls the overall rate. The analysis will be made for an isothermal system of a first-order, irreversible reaction. (Extension to a reversible reaction can be found elsewhere[5]. We also neglect the structural changes that occur during the reaction, although certain aspects of such changes can be incorporated into the analysis as discussed by Szekely, Evans and Sohn[5].

The following discussion is based on the work of Sohn and Szekely[40~43]. Unlike those of many other investigators[44~48], their analysis is general in terms of solid geometry and gives approximate closed-form solutions valid for the cases that must otherwise be solved numerically. They also derive important criteria for asymptotic regimes for which simple, exact solutions are possible.

2. 2. 1 Mathematical formulation

Let us assume the porous solid to be an aggregate of fine grains. In order to facilitate the visualization and description of the model, we will assume that the grains have the shape of flat plates, long cylinders or spheres. * The external shape of the pellet may also be approximated by one of these geometries.

We will follow the procedure described elsewhere[40] in developing the mathematical equations for the generalized grain model. In addition to those already made above, the assumptions to be made are:

(1) The pseudosteady-state approximation is valid for determining the concentration profile of the fluid reactant within the pellet. [49,50]

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*The assumed shape of particles is to facilitate the visualization of the system. The real requirement is to know the variation in the rate of reaction with solid conversion in the absence of resistance due to intrapellet diffusion. This must always be determined by experiments.

(2) The resistance due to external mass transfer is negligible. (This assumption will be relaxed later and the effect of external mass transfer will be studied).

(3) Intrapellet diffusion is either equimolar counter-diffusion or occurs at low concentrations of diffusing species.

(4) Diffusivities are constant throughout the pellet.

(5) Diffusion through the product layer around the individual grain is fast. (This assumption will also be relaxed later).

The conservation of fluid reactant may be described by

$$D_e \Delta^2 C_A - v_A = 0 \tag{84}$$

where v_A is the local rate of consumption of the fluid reactant A, in moles per unit time per unit volume of pellet.

Within each grain, the conservation of solid reactant may be described by

$$-\rho_B \frac{\partial r_c}{\partial t} = bk C_A \tag{85}$$

where r_c is the distance from the center of symmetry to the reaction interface.

An expression for v_A may be obtained by determining the surface area for reaction available per unit volume of the pellet:

$$v_A = \alpha_B k \left(\frac{A_g}{V_g} \right) \left(\frac{A_g r_c}{F_g V_g} \right)^{F_g - 1} C_A \tag{86}$$

where α_B is the volume fraction of the pellet occupied by solid B.

Equations (84) and (85) may be expressed in dimensionless forms by introducing the following dimensionless variables:

$$\psi \equiv \frac{C_A}{C_{Ab}} \tag{87}$$

$$\xi \equiv \frac{A_g r}{F_g V_g} = \frac{r}{r_g} \tag{88}$$

$$t^* \equiv \left(\frac{bk C_{Ab}}{\rho_B} \frac{A_g}{F_g V_g} \right) t \tag{89}$$

$$\eta \equiv \frac{A_p R}{F_p V_p} = \frac{R}{R_p} \tag{90}$$

and

$$\sigma \equiv \frac{F_p V_p}{A_p} \sqrt{\frac{\alpha_B k}{D_e} \frac{A_g}{V_g}} \tag{91}$$

In the above, R is the distance from the center of geometry of the pellet. The dimensionless forms of Eqs. (84) and (85) are

$$\Delta^{*2} \psi - \sigma^2 \psi \xi^F g^{-1} = 0 \tag{92}$$

and

$$\frac{\partial \xi}{\partial t^*} = -\psi \tag{93}$$

where Δ^{*2} is the Laplacian operator with η as the position coordinate. The initial and boundary conditions for Eqs (92) and (93) are

$$\xi = 1, \qquad at \ t^* = 0 \tag{94}$$

$$\psi = 1, \qquad at \ \eta = 1 \tag{95}$$

$$\frac{d\psi}{d\eta} = 0, \qquad at \ \eta = 0 \tag{96}$$

For most practical purposes the desired results are in terms of the fraction of the solid reacted, instead of ψ or ξ, as a function of time. This is obtained as follows:

$$X = \frac{\int_0^1 \eta^{F_p - 1} (1 - \xi^{F_g}) d\eta}{\int_0^1 \eta^{F_p - 1} d\eta} \tag{97}$$

It is noted that the dimensionless representation of the governing equations indicates that the dependent variables ξ and ψ, and thus X, are related to t^* and η through a single parameter σ. This quantity σ is a measure of the ratio of the capacities for the system to react chemically and for it to diffuse reactants into the pellet. The modulus σ contains both structural and kinetic parameters and is very useful in characterizing the behavior of the system.

2.2.2 *Asymptotic behaviors*

When σ approaches zero, the overall rate is controlled by chemical kinetics, the diffusion being rapid compared with the rate of chemical reaction. Thus, the reactant concentration is uniform within the pellet and equal to that in the bulk ($\psi = 1$). This can be directly obtained from Eq. (92) with $\sigma = 0$. ξ is then independent of η and Eq. (93) is readily integrated to give:

$$\xi = 1 - t^* \qquad \text{for } 0 < t^* \leq 1$$

$$\tag{98}$$

$$\xi = 0 \qquad \text{for } t^* \geq 1$$

Using Eq. (97) we obtain the following relationship between X and t^*:

$$t^* = 1 - (1-X)^{1/F_g} \equiv g_{F_g}(X) \tag{99}$$

which is identical to Eq. (21) with $\sigma_s = 0$ for chemical-reaction control. Equation (99) provides a convenient means of determining the reaction rate constant from experimental data obtained under conditions where diffusional resistance is absent. When σ approaches infinity, the overall rate is controlled entirely by the diffusion of the gaseous reactant within the pellet. This case is identical to the diffusion controlled reaction of nonporous solids discussed previously in Section 1.4.4. The result can be expressed as follows [using Eq. (30)]:

$$P_{F_b}(X) = \frac{2F_p b D_e C_{Ab}}{\alpha_B \rho_B}\left(\frac{A_p}{F_p V_p}\right)^2 t \tag{100}$$

$$= \frac{2F_g F_p}{\sigma^2} t^* = \frac{t^*}{\hat{\sigma}^2} \tag{101}$$

where $P_{F_b}(X)$ has been defined in Eqs. (26). Equation (100) provides a convenient means of determining the effective diffusivity by plotting experimental data obtained under diffusion control according to this equation. Equation (101) suggests the following generalized modulus

$$\hat{\sigma} = \frac{\sigma}{\sqrt{2F_g F_p}} = \frac{V_p}{A_p}\sqrt{\frac{\alpha_B k}{2D_e}\frac{F_p}{\left(\frac{A_g}{F_g V_g}\right)}} \tag{102}$$

As will be seen subsequently, this generalized modulus enables us to determine the criteria for the chemically-controlled and diffusion-controlled asymptotic regimes. Furthermore, the numerical values of $\hat{\sigma}$ defining the respective asymptotic regimes will be the same for all combinations of grain and pellet geometries.

2.2.3 *Complete solutions*

Analytical solutions are possible for $F_g = 1$. The case of $F_p = 3$ and $F_g = 1$ has been solved

by Ishida and Wen [48], and the solution for the case of $F_p = F_g = 1$ is also available [40]. In other cases the solution must be obtained numerically. Results of numerical computation have been reported by Sohn and Szekely [40] as shown in *Figs.* 10 and 11.
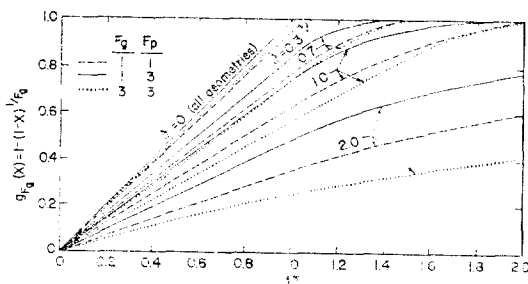
Fig. 10. Conversion function *vs.* reduced time for small values of $\hat{\sigma}$ [Adopted from H. Y. Sohn and J. Szekely, *Chem. Eng. Sci.*, 27 (1972), 763].
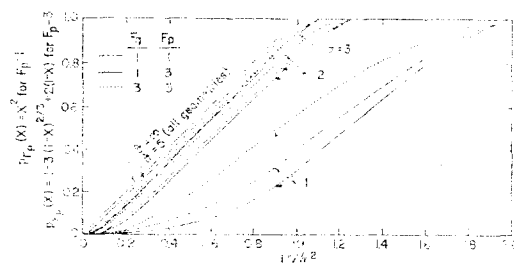
Fig. 11. Conversion function *vs.* reduced time for large values of $\hat{\sigma}$. [Adopted from H. Y. Sohn and J. Szekely. *Chem. Eng. Sci.*, 27 (1972), 763].

Figure 10 shows a plot of $g_{F_g}(X)$ *vs.* t^* for small values of $\hat{\sigma}$. The ordinate was so chosen as to allow the convenient presentation of the appropriate asymptotic solution of $g_{F_g}(X) = t^*$. It is apparent from this figure that the $\hat{\sigma} = 0$ asymptote is valid for $\hat{\sigma} < 0.3$ (or $\hat{\sigma}^2 < 0.1$), regardless of the geometry. Thus, when this

criterion is met, the system is under the control of the reaction of individual grains and the solution is given by Eq. (99) which eliminates the need for numerical computation.

Figure 11 shows a plot of $P_{F_p}(X)$ vs. $t^*/\hat{\sigma}^2$ for large values of $\hat{\sigma}$. The choice of the ordinate was dictated by the form of the asymptotic solution of Eq. (101). It is seen that the $\hat{\sigma}\to\infty$ asymptote is approached when $\hat{\sigma}>3.0$ (or $\hat{\sigma}^2>10$), again, regardless of the geometry.

The solution for $0.1<\hat{\sigma}^2<10$ depends on the geometries of the grain and the pellet. Sohn and Szekely[40] obtained the following closed-form approximate solution that is applicable to any combination of geometries:

$$t^*\simeq g_{F_g}(X)+\hat{\sigma}^2 p_{F_p}(X) \qquad (103)$$

The detailed derivation of this relation can be found in the original article.

Equation (103) provides not only a simple and easty-to-use relationship between X and t^*, but also a greater insight into the problem by clearly showing the relative importance of chemical reaction and diffusion through a parameter $\hat{\sigma}$. Another important feature of Eq. (103) is that the time required to attain a certain conversion is shown to be the sum of the time to reach the same conversion under chemical reaction control and that under the diffusion control.
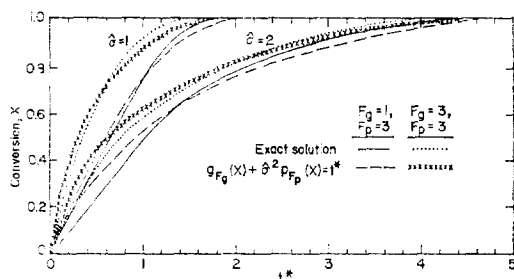

Fig. 12. Comparison of approximate solution with exact solution for $\hat{\sigma}=1$ and 2. [Adapted from H. Y. Sohn and J. Szekely, *Chem. Eng. Sci.*, **27**, (1972), 763].

This can be recognized by comparing Eq. (103) with Eqs. (99) and (101).

Comparison of Eq. (103) with exact solution is shown in *Fig.* 12.

The comparison is made for intermediate values of $\hat{\sigma}$ for which the difference is largest. The approximate solution is seen to be a satisfactory representation of the exact solution. For smaller and larger values of $\hat{\sigma}$, agreement is better than shown in this figure. In fact, the approximation is asymptotically correct as $\hat{\sigma}\to0$ or $\hat{\sigma}\to\infty$. Furthermore, it has been shown[40] that Eq. (103) is exact at $X=1$ for all the combinations of geometries (F_g and F_p). Thus

$$t^*_{X=1}=1+\hat{\sigma}^2 \qquad (104)$$

The above analyses have been success fully applied to the reduction of nickel-oxide pellets with hydrogen[42].

2.2.4 *Further comments*

The effect of external mass transfer has also been studied [40]. The appropriate relationship was determined to be:

$$t^*\simeq g_{F_g}(X)+\hat{\sigma}^2[P_{F_p}(X)+\frac{2X}{Sh^*}] \qquad (105)$$

where $Sh^*\equiv Sh(D_M/D_e)=\frac{k_M}{D_e}\cdot\left(\frac{F_p V_p}{A_p}\right)$

The case where the solid product has different effective diffusivity from that of the initial reactant solid has been studied by Ishida and Wen[48] and Sohn and Szekely[43]. The results for incorporating the Langmuir-Hinshelwood type kinetics, rather than a first-order kinetics, have been reported[41].

All of the above analyses assume that the diffusion through the product layer around each grain offers negligible resistance. When this intragranular diffusion is important, the approximate relationship between X and t^* has been shown to be[51]:

$$t^*\simeq g_{F_g}(X)+\hat{\sigma}_g^2\cdot P_{F_g}(X)\hat{\sigma}+^2\left[P_{F_p}(X)+\frac{2X}{Sh^*}\right] \qquad (106)$$

where

$$\hat{\sigma}_g^2 = \frac{k}{2D_g}\left(\frac{V_g}{A_g}\right)$$

Nonisothermal reaction between a porous solid and a gas is generally very complex, although a few simple asymptotic cases can be solved systematically. For example, the maximum temperature rise in a diffusion-controlled system discussed earlier for nonporous solid applies directly to that for porous solid. The most important behaviors in this group of reactions are instability and multiplicity.

The rigorous formulation of the problem of nonisothermal reaction requires an energy balance equation in addition to the mass balance equation given by Eq. (84). Making use of the pseudo steady-state approximation for heat conduction, the energy equation can be written as

$$\lambda_e \nabla^2 T + (-\Delta H)v_A = 0 \qquad (107)$$

Eliminating v_A from Eqs. (84) and (107), and integrating, we obtain

$$T - T_s = \frac{(-\Delta H)\mathcal{D}_e}{\lambda_e}(C_{As} - C_A) \qquad (108)$$

In obtaining this equation we have made use of boundary conditions given by Eqs. (95) and (96) and corresponding boundary conditions for temperature. Equation (108) gives a relationship between temperature and concentration within the porous solid during the reaction. It is significant to note that this relationship is not affected by radial position and is, furthermore, valid regardless of the pellet geometry.

Equation (108) can now be substituted in to the temperature dependent parameters into Eq. (84) and the resultant equation solved for the concentration profile. The relationship between conversion and time can then be obtained by following the same procedure as for the isothermal system.

Instability and multiple steady-state may occur because there may be more than one solution for a nonisothermal system, that is, there may be more than one concentration profile satisfying

Eq. (84). These effects have been discussed in the literature[5,f2]. A more detailed discussion on this subject is beyond the scope of this review.

2. 3 Concluding remarks

The reaction of a porous solid with a fluid involves chemical reaction and intrapellet diffusion occurring in parallel. Thus, the analysis of such a reaction system is generally more complicated than that of the reaction of nonporous solids. The grain model which was discussed above is a rather recent development in this area, and represents one of the distributed models proposed in the last few years. These distributed models have been tested against experiments and found to describe the reaction of porous solids reasonably well[42, 46, 53~55]. In the text, the grain model was described in terms of dimensionless equations enabling us to establish an important parameter $\hat{\sigma}$ which characterizes the behavior of the reaction system and also gives us numerical criteria for asymptotic regimes. Furthermore, the closed-form approximate solution obtained in the text is very useful, especially when we are confronted with analyzing multiparticle systems. Without such a closed-form solution, both the process within the individual particles and that over the whole system must be solved numerically. Even with the availability of impressive capacities of modern computers, this will present a formidable problem. The application of the approximate solution of Sohn and Szekely to multiparticle systems has been discussed in the literature[56,57].

Nomenclature

A_g, A_p external surface area of an individual grain and the pellet, respectively

b number of moles of solid B reacted

by one mole of fluid reactant A

C molar concentration of fluid species

D_e effective diffusivity in porous solid effective

D_g diffusivity in the product layer around a grain

f roughness factor defined as the ratio of the true external surface area to the apparent surface area

F shape factor ($=$I, 2 and 3 for flat plates, long cylinders, and spheres, respectively

$g(X)$ conversion function defined by Eq. (99)

$(-\varDelta H)$ molar heat of reaction

k reaction-rate constant

k_m external mass transfer coefficient

$p(X)$ conversion function defined by Eq. (26)

r distance from the center of symmetry in a nonporous particle or a grain

R distance from the center of symmetry in a porous pellet

Sh, Sh^* the Sherwood and the modified Sherwood numbers, respectively, defined in Eq. (105)

S_v surface area per unit volume of the pellet

t time

t^* dimensionless time defined by Eq. (89)

T temperature

V volume

x distance coordinate in Eq. (60)

X fractional conversion of the solid

Greek symbols

α fraction of volume of pellet occupied by reactant solid

β dimensionless quantity defined by Eq. (82)

γ dimensionless quantity defined by Eq. (81)

δ dimensionless quantity defined by Eq. (80).

ε porosity

η dimensionless distance defined by Eq. (90)

θ dimensionless temperature defined

λ_e effective thermal conductivity of porous solid

ξ dimensionless position of the reaction front in the grain, defined by Eq. (54) or (88)

ρ molar concentration of solid reactants

ρ_s density of the particle including the inert solid, if any

σ dimensionless parameter defined by Eq. (91)

$\hat{\sigma}$ generalized gas-solid reaction modulus defined by Eq. (102)

$\hat{\sigma}_g$ shrinking-core reaction modulus defined after Eq. (106)

τ_c parameter defined by Eq. (58)

ψ dimensionless concentration defined by Eq. (87)

Subscripts

A fluid A

b bulk property

B solid B

c value at reaction interface

g grain

o original value

p particle or pellet

s value at external surface, or for entire solid including inert solid, if any

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