

Chemical Reaction Engineering in the Chemical Processing of Metals and Inorganic Materials

Part I. Advances in Fluid-Solid Reaction Analysis

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Abstract—The advances made in the field of chemical engineering as applied to the processing of metals and other inorganic materials are reviewed. The reactions involved in this field are heterogeneous in nature, the fluid-solid non-catalytic reactions being the most important group of examples. In these heterogeneous reactions, interfacial chemical reactions are always accompanied by the transfer of mass and heat between the reaction interface and the bulk fluid. The interplay of these steps determines the overall characteristics and analysis of the reaction rate. The review examines the developments in the quantitative rate analysis of various fluid-solid reaction systems. Examples are largely drawn from the work of the author and coworkers, which has led to the formulation of the Law of Additive Reaction Times and its application to a wide range of fluid-solid reactions. The serious effects of thermodynamics on fluid-solid reaction with small equilibrium constants, in terms of the overall rate and the falsification of activation energy, have been examined based on a careful quantitative analysis.

Key words: Chemical Reaction Engineering, Diffusion, Fluid-solid Reactions, Heterogeneous Reactions, Kinetics, Law of Additive Reaction Times, Mass Transfer, Porous Solid

INTRODUCTORY REMARKS

It is an honor to be invited to contribute a review article on the occasion of the 40th Anniversary of the founding of the Korean Institute of Chemical Engineers. As a lifetime member of the Institute, I wish to send my heartfelt congratulations to all the members and those who have worked hard and are working hard to make the Institute what it is today. In 1987, I contributed an invited article on the progress of chemical reaction engineering in a special KICChE publication to commemorate its 25th Anniversary [Sohn, 1987]. It was pointed out there that chemical reaction engineering occupies an important and unique position in chemical engineering in that no other engineering disciplines can claim it as a major part of their fields. In contrast, other components of chemical engineering such as material and energy balances, thermodynamics and transport phenomena are also used extensively in other engineering fields.

In the intervening fifteen years, much has changed in the chemical engineering discipline in general and in the chemical reaction engineering field in particular. As in other disciplines, the most notable changes here have been due to the ready availability of powerful computational capabilities. A consequence of this has been the movement away from the research effort to obtain a general mathematical description of a group of related problems and processes, often by making simplifying assumptions and approximations. As an example of such a mathematical treatment, one needs only to think of the many articles on the problem of catalytic reactions in porous pellets accompanied by mass and heat transfer that were published between the 1960's and 1980's. With the ready availability of incredibly large computing capabilities, the needs for general

solutions, which typically contain approximations, have diminished significantly. Solutions that incorporate factors and conditions specific to individual problems have become much easier. This has also coincided with the changing emphasis of research funding sources toward the solution of specific problems, rather than the enrichment of the science of engineering principles. Thus, we do not nowadays see many articles presenting such elegant mathematical treatments as those by Thiele [1939], Petersen [1965], Aris [1965], Satterfield [1970], Smith [1981], Levenspiel [1999], and Szekely et al. [1976], to name a few.

My own work in reaction engineering has spanned this transitional period. With the wide range of topics in which chemical reaction engineering is applied, it is beyond the scope of this article to present a comprehensive treatise on the subject. Rather, the discussion here will be limited to the application of reaction engineering in the field of the chemical processing of metals and other inorganic materials. Even within this subject, the review will draw heavily from the authors own research work, which has dealt mainly with heterogeneous reactions involving inorganic materials. The problems investigated have come from metal extraction, purification, and refining as well as the chemical synthesis and processing of advanced inorganic materials. It is hoped that this review will provide an example of how chemical reaction engineering principles can be fruitfully applied in various related new areas, in addition to presenting a treatise on fluid-solid reaction analysis.

CHEMICAL REACTION ENGINEERING IN HETEROGENEOUS REACTION SYSTEMS

Heterogeneous reactions occur at phase boundaries, unlike homogeneous reactions that take place over the entire volume of a given phase. Therefore, heterogeneous reactions always accompany

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the transfer of mass and heat between the reaction interface and the bulk phase. For this reason, most heterogeneous reactions involve a rather complex set of steps.

The heterogeneous reaction studied widely during the early stages of chemical reaction engineering was the gas-solid catalytic reaction occurring in a porous pellet [Petersen, 1965; Satterfield, 1970]. Most reactions in inorganic materials processing, however, are between solids and fluids in which the solid participates as a reactant that undergoes chemical changes. Although reactions between immiscible liquid phases and between a gas and a liquid are also heterogeneous in nature, the discussion in this article will largely involve the analysis of fluid-solid reactions. Most gas-liquid and liquid-liquid reactions are rate-controlled by mass transfer, and thus their analysis reduces to a problem of mass transfer combined with chemical equilibrium at the interface.

The overall fluid-solid reaction involves a combination of the following individual steps:

1. Transfer of the fluid reactants and the fluid products between the bulk fluid and the external surface of the solid particle.
2. Diffusion of the fluid reactants and the fluid products within the pores of the solid, if the solid contains open porosity.
3. Chemical reaction between the fluid reactant and the solid at the fluid-solid interface.
4. Transfer of the reaction heat within the solid.
5. Transfer of heat between the external surface of the solid and the surroundings by convection and radiation.
6. Changes in the structure of the solid due to chemical reaction and heat.

The rate-controlling step can change depending on reaction conditions, and thus the rate information obtained under a given set of conditions may not be applicable under another set of conditions. Furthermore, there may not be a single rate-controlling step because several steps may have comparable effects on determining the overall rate. The relative importance of these steps could also change in the course of the reaction. Therefore, understanding how the individual reaction steps interact with each other is important in determining not only the rate-controlling step under given reaction conditions but also whether more than a single step must be considered in expressing the rate over the entire duration of the reaction.

The individual treatments of the above component steps can be found in various related literature sources [Satterfield, 1970; Szekely et al., 1976; Bird et al., 2002; Perry and Green, 1984; Kessler and Greenkom, 1999; Welty et al., 2001], and thus will not be covered in this review.

FLUID-SOLID REACTIONS IN A SINGLE PARTICLE OR PELLET

Books on chemical reaction engineering [Smith, 1981; Levenspiel, 1999] contain only rather brief descriptions of this topic, largely limited to the simple systems of the reaction of an initially nonporous solid producing porous product or ash layer. The first treatise on an extended coverage of the subject, including a much wider range of systems, was a book entitled *Gas-Solid Reactions* [Szekely et al., 1976]. Since this book was published, however, a great deal

of advance has been made in the field. This section presents a brief summary of the earlier work followed by the review of the research results published since then. To the best of the authors knowledge, there has been no monograph published that contains these later results.

Because the transfer of mass and, to a lesser extent, heat constitutes an important aspect of a fluid-solid reaction, the quantitative analysis of the overall rate must necessarily take into account the geometry and structure of the solid before, during, and after the reaction. Although there are other types of fluid-solid reactions, the most important group of reactions in metallurgical and materials processing operations consists of those in which a solid reacts with a fluid to produce a coherent layer of porous products. Therefore, this article will mainly be concerned with this type of reaction. Such reactions may in general be expressed by the following equation:



For the analysis of other types of fluid-solid reactions, the reader is referred to other references [Szekely et al., 1976].

1. Reaction of an Initially Nonporous Solid

The earliest model of fluid-solid reactions of the type under consideration is the shrinking unreacted-core model, which pictures the reaction to progress in a topochemical manner from the outer surface of the solid towards its interior, as depicted in Fig. 1. The reaction forms a coherent porous product (or ash) layer around the unreacted portion of the solid, with chemical reaction taking place at a sharp interface between the two zones. This shrinking-core system has been studied extensively and applied to a wide range of reactions. These early investigations have been summarized and reviewed in the aforementioned book by Szekely et al. [1976]. The authors of this book further generalized the results of many previous investigators on reactions that are isothermal and of first order with respect to the fluid reactant. They formulated the following equation incorporating chemical kinetics, diffusion through porous product layer, and external mass transfer, as well as the three basic geometries of the solid:

$$g_{F_p}(X) + \sigma_s^2 [p_{F_p}(X) + 4X/Sh^*] = t^* \quad (2)$$

where F_p is the shape factor (=1, 2, or 3 for a slab, a long cylinder, or a sphere), and

$$t^* \equiv \left(\frac{bk}{\alpha_B \rho_B} \right) \left(\frac{A_p}{F_p V_p} \right) \left(C_{Ab} - \frac{C_{Cb}}{K} \right) t \quad (3)$$

$$\sigma_s^2 \equiv \left(\frac{k}{2D_{eA}} \right) \left(\frac{V_p}{A_p} \right) \left(1 + \frac{1}{K} \right) \quad (4)$$

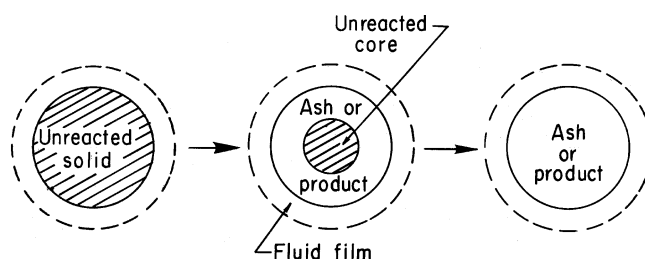


Fig. 1. Reaction of an initially nonporous solid that forms a coherent layer of porous product (the shrinking-core reaction system).

$$\text{Sh}^* \equiv \frac{(D_A/\delta)d_p}{D_{eA}} = \left(\frac{D_A}{D_{eA}}\right) \left(\frac{k_{mA}d_p}{D_A}\right) = \left(\frac{D_A}{D_{eA}}\right) \text{Sh} \quad (5)$$

$$g_{F_p}(X) \equiv 1 - (1-X)^{1/F_p} \quad (6)$$

$$\text{and } p_{F_p}(X) \equiv X^2 \quad \text{for } F_p=1 \quad (7A)$$

$$\equiv X + (1-X)\text{Ln}(1-X) \quad \text{for } F_p=2 \quad (7B)$$

$$\equiv 1 - 3(1-X)^{2/3} + 2(1-X) \quad \text{for } F_p=3 \quad (7C)$$

It has been shown [Szekely, 1976] that chemical reaction controls the overall rate when $\sigma_s^2 < 0.1$ or 0.01 depending on the range of tolerable error (<10% or <1%, respectively). On the other hand, pore diffusion and external mass transfer control the overall rate ($g_{F_p}(X)$ becomes negligible) when $\sigma_s^2 > 10$ or 100.

Individual forms of Eq. (2) were used by McKewan [1960], Themelis and Gauvin [1963], Kawasaki et al. [1963], Lu [1963], Lu and Bitsianes [1968], Seth and Ross [1966], and St. Clair [1965], among others, for various metallurgical reactions. Sohn and Sohn [1980] subsequently showed that the right-hand sides of Eqs. (7A) to (7C) can be derived as a single combined term given by

$$p_{F_p}(X) \equiv 1 - \frac{F_p(1-X)^{2/F_p} - 2(1-X)}{F_p - 2}; \text{ conversion function for pore-diffusion control} \quad (8)$$

$p_2(X)$ for a long cylinder can be obtained by applying L'Hospital's rule to the right-hand side of Eq. (8), resulting in the familiar expression given by Eq. (7B).

The effect of changing particle size due to the difference in the volumes of the reactant and the product solids can be incorporated by redefining $p_{F_p}(X)$ as follows, if one neglects the change in the mass-transfer coefficient with the small change in particle size in the last term of Eq. (2) and [Szekely et al., 1976]:

$$p_{F_p}(X) \equiv Z X^2 \quad \text{for } F_p=1 \quad (9A)$$

$$\equiv \frac{[Z - (Z-1)(1-X)]\text{Ln}[Z - (Z-1)(1-X)]}{Z-1} + (1-X)\text{Ln}(1-X) \quad \text{for } F_p=2 \quad (9B)$$

$$\equiv 3 \left\{ \frac{Z - [Z - (Z-1)(1-X)]^{2/3}}{Z-1} - (1-X)^{2/3} \right\} \quad \text{for } F_p=3 \quad (9C)$$

where Z is the volume of the product solid formed from unit volume of the reactant solid. It can be shown [Sohn] that the right-hand sides of Eqs. (9A) to (9C) (and those of Eqs. (7A) to (7C) as special cases) can be derived as a single term given by

$$p_{F_p}(X) \equiv \frac{F_p}{F_p - 2} \left\{ \frac{Z - [Z - (Z-1)(1-X)]^{2/F_p}}{Z-1} - (1-X)^{2/F_p} \right\} \quad (10)$$

The expressions of $p_{F_p}(X)$ for $Z=1$ and/or $F_p=2$ can again be obtained by applying L'Hospital's rule.

When there is a substantial change in the fluid volume upon reaction, Sohn and Sohn [1980] obtained the following approximate solution to replace Eq. (2):

$$t^* = g_{F_p}(X) + \sigma_s^2 \left(\frac{\theta}{\ln(1+\theta)} p_{F_p}(X) + \frac{4(1+\theta)X}{\text{Sh}^*} \right) \quad (11)$$

$$\text{where } \theta \equiv (v-1)(C_{Ab}/C_T) \quad (12)$$

Natesan and Philbrook [1969] and Haung and Bartlett [1976] used special forms of equations analogous to Eq. (11) for the analysis of just the diffusion-controlled regimes in the roasting of zinc sulfide

and of mixtures of a copper sulfide mineral and lime, respectively.

Sohn and Szekely [1972] analyzed the system in which the reaction order with respect to the fluid reactant is different from unity. In many fluid-solid reactions, substantial enthalpy changes accompany the reactions. Such non-isothermal systems are more difficult to analyze than the isothermal systems discussed above, and may exhibit multiple steady states and thermal instability. These aspects have been reviewed elsewhere [Szekely et al., 1976].

The shrinking-core model is attractive for its conceptual and mathematical simplicity. It should be noted, however, that its validity is limited to the reaction of a nonporous solid occurring at a well-defined sharp reaction interface. In general, the improper application of the shrinking-core model to the reaction of a porous solid results in an erroneous analysis of experimental data. Thus, one may obtain incorrect dependence of the rate on reaction conditions and physical parameters such as temperature, fluid reactant concentration, and particle size. Proper analysis of the reaction of porous solids will be discussed below.

2. Reaction of a Porous Solid

Many solid reactants have some initial porosity, allowing diffusion and chemical reactions to occur simultaneously in a diffuse zone. The progress of reaction in a porous solid is illustrated in Fig. 2. The reaction takes place throughout the particle or pellet volume, and the concentration of the fluid reactant decreases as it diffuses into the interior of the particle while reacting on its path. The reaction given by Eq. (1) taking place in a porous solid can be described mathematically by formulating the conservation equations for the fluid and the solid reactants, and for energy if substantial heat effect is involved.

The conservation of fluid species per unit volume of the pellet (including the pore space) is given by

$$\nabla \cdot \mathbf{N}_i = R_i; i=A \text{ or } C \quad (13)$$

This equation incorporates the pseudo-steady-state approximation, which states that the accumulation term can be neglected for fluid-solid reactions [Bischoff, 1965; Luss, 1968].

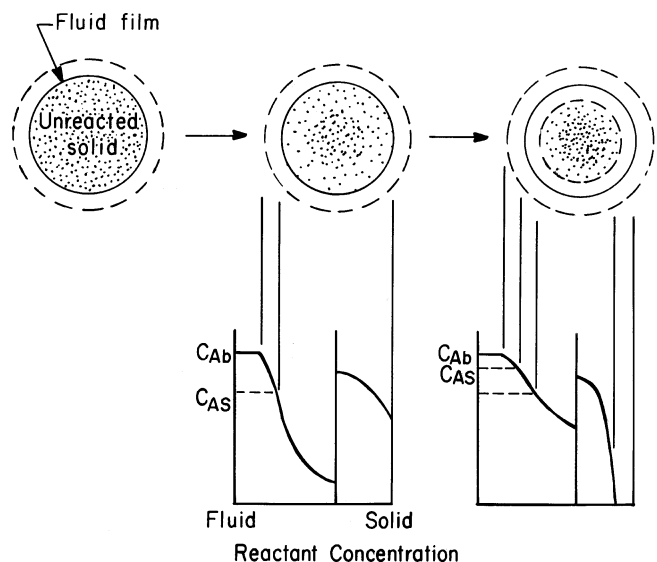


Fig. 2. Reaction of an initially porous solid.

For many heterogeneous reactions, the molar rate of consumption of the fluid reactant per unit area of the reaction interfaces is given by the following Langmuir-Hinshelwood rate equation:

$$(-\dot{m}_A) = \frac{k(C_A^m - C_C^n/K)}{1 + K_1 C_A + K_2 C_C} = \frac{k_p(p_A^m - p_C^n/K_p)}{1 + K_1' p_A + K_2' p_C} \quad (14)$$

For liquid-solid reactions, the molar concentration is used in the rate equation. For gas-solid reactions, either the molar concentration or the partial pressure has been used in the literature. The author prefers the use of the partial pressure for gas-solid reactions because it more accurately represents the activity of a gaseous species and K_p is the thermodynamic equilibrium constant. In this article, however, the molar concentration is used to simultaneously treat both the gas-solid and liquid-solid reaction systems. For a gas-solid reaction at equilibrium, $(-R_A)=0$ and

$$K = \frac{C_C^n}{C_A^m} = \frac{(p_C/RT)^n}{(p_A/RT)^m} = \frac{p_C^n}{p_A^m} (RT)^{m-n} = K_p (RT)^{m-n} \quad (15)$$

where K_p is the thermodynamic equilibrium constant. For a liquid-solid reaction, K is related to the thermodynamic equilibrium constant through the activity coefficients. Many reactions can be described by a simple kinetic expression with $m=n=1$ and $K_1=K_2=0$ in Eq. (14), which represents a first-order reversible reaction.

The molar rate of consumption of the solid reactant per unit volume of the solid is expressed by

$$\rho_B \frac{\partial w}{\partial t} = b(-\dot{m}_A)S_v = b(-\dot{m}_A)S_v^0 f(w) \quad (16)$$

where w is the local fractional conversion of the solid reactant, S_v^0 is the initial surface area per unit volume of the solid, and $f(w)$ represents the relative variation of the specific surface area S_v with solid conversion.

The fluxes of fluid species, N_i , must in general be related to concentrations through the Stefan-Maxwell equations [Szekely and El-Tawil, 1976; Szekely et al., 1977; Eddings and Sohn, 1993]. However, for a binary mixture or by using an effective binary diffusivity, one may use the simpler relationship given below:

$$N_i = -C_T D_{ei} \nabla x_i + x_i \sum_{j=1}^n N_j \quad (17)$$

The rate of production of fluid species, R_i , is related to the rate of reaction of the solid reactant through stoichiometry, as follows:

$$R_A = \frac{\alpha_B \rho_B}{b} \frac{\partial w}{\partial t} = -\alpha_B (\dot{m}_A) S_v^0 f(w) \quad (18A)$$

$$R_C = \frac{c \alpha_B \rho_B}{b} \frac{\partial w}{\partial t} = c \alpha_B (\dot{m}_A) S_v^0 f(w) \quad (18B)$$

When the solid temperature changes during the reaction, the conservation of energy is described by

$$\rho C_p \frac{\partial T}{\partial t} = -\nabla \cdot \underline{q} + (-\Delta H) \cdot (-R_A) \quad (19)$$

The simultaneous solution of Eqs. (13), (16), and (19) with appropriate boundary conditions yields the profiles of the fluid species concentrations as functions of position inside the solid. Using these concentration profiles, the local conversion of solid, w , can be obtained as a function of time by solving Eq. (16) together with Eq.

(14). The overall conversion X is then calculated by integrating the local conversion over the entire solid volume.

Closed-form solutions to the governing equations have been obtained for certain special cases. When the reaction involves a substantial heat effect, these equations must in general be solved using a numerical technique. Even in such a case, the conversion-vs.-time relationship for a diffusion-controlled irreversible reaction ($K \rightarrow \infty$) is given by Eq. (11) without the $g_p(X)$ term. Various models for a reaction between a porous solid and a fluid have been formulated, the differences among which can be interpreted to be those of differences in the dependence of rate on solid conversion, $f(w)$.

2-1. Early Models

Ausman and Watson [1962] proposed a model in which they assumed that the local rate of reaction was independent of solid conversion as long as some solid reactant remains. This is equivalent to assuming the following:

$$\begin{aligned} f(w) &= 1, \text{ when } w < 1 \\ &= 0, \text{ when } w = 1 \end{aligned} \quad (20)$$

They also assumed the equimolar counter diffusion of fluid species. Ishida and Wen [1968] obtained an analytical solution for such a reaction in a porous sphere. In their solution they incorporated the effect of structural changes in the solid by assigning different diffusivities to the completely and the partially reacted zones. Szekely and Sohn [1973] obtained similar solutions for reactions taking place in a slab and a long cylinder. Although an analytical solution is helpful, the equations representing the solution are rather complex and cumbersome to use and not many fluid-solid reactions follow the rate expressions given in Eq. (20). Furthermore, this is equivalent to a special case of the generalized grain model discussed in the next section.

2-2. The Grain Model

This model assumes that the porous solid is made up of small non-porous grains of a uniform size that each react according to the chemical-reaction-controlled shrinking-core scheme discussed above [Szekely et al., 1976; Szekely and Evans, 1970; Sohn and Szekely, 1972]. This picture, illustrated in Fig. 3, although rather

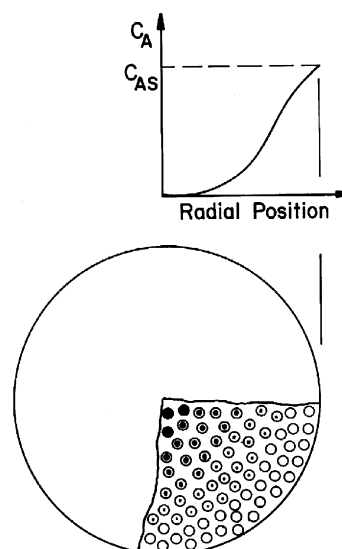


Fig. 3. The grain model of a porous solid.

unrealistic and restrictive, provided an early basis to incorporate the solid structure in analyzing gas-solid reactions. Furthermore, the analysis of this system also provided this author with the foundation for more realistic and less restrictive description of fluid-solid reactions in his subsequent work, as will be discussed later in this article.

The generalized grain model developed by Sohn and Szekeley [1972], which encompasses many other specific models to represent similar configurations [Szekeley and Evans, 1970; Tien and Turkdogan, 1972; Calvelo and Smith, 1972], was formulated for an isothermal, first-order reaction with equimolar counter-diffusion (or diffusion at low concentrations). It was also assumed that the diffusion of the reactant gas through the product layer around the individual grain offers little resistance to the overall rate. This assumption is usually valid for small grains but can readily be relaxed as will be seen subsequently. Sohn and Szekeley [Szekeley et al., 1976; Sohn and Szekeley, 1972] considered porous solids in which the pellet and the grain may each have the shape of a slab, a long cylinder, or a sphere for a total of nine possible combinations. In their development, they used the following equation for the reaction of the grains in lieu of Eq. (16):

$$-\rho_B \frac{\partial r_c}{\partial t} = bk \left(C_A - \frac{C_C}{K} \right) \quad (21)$$

where r_c is the position of the reaction interface within the grain, and ρ_B is the molar density of the solid reactant. It is noted that Eq. (21) is a special form of Eq. (16) for grains reacting according to the chemical-reaction-controlled shrinking-core scheme by considering that

$$w = 1 - (r_c/r_g)^{F_g} \quad (22)$$

The term R_A is now given as

$$R_A = -\alpha_B k \left(\frac{A_g}{V_g} \right) \left(\frac{A_g r_c}{F_g V_g} \right)^{F_g-1} \left(C_A - \frac{C_C}{K} \right) \quad (23)$$

It is noted that

$$F_g V_g / A_g = r_g \quad (24)$$

the initial radius or half thickness of the grain.

The case of flat grains ($F_g = 1$) corresponds to models of Ausman and Watson [1962] and Ishida and Wen [1968] discussed in the previous section. When $F_g \neq 1$, Eqs. (13) and (16) must be solved numerically, even for an isothermal, first-order reaction. For systems in which the effective diffusivity remains unchanged upon reaction, Sohn and Szekeley [1972] obtained the following approximate solution for the conversion-vs.-time relationship:

$$t_g^* \cong g_{F_g}(X) + \hat{\sigma}^2 [p_{F_g}(X) + 4X/\text{Sh}^*] \quad (25)$$

where

$$t_g^* \equiv \left(\frac{bk}{\rho_B} \right) \left(\frac{A_g}{F_g V_g} \right) \left(C_{Ab} - \frac{C_{Cb}}{K_c} \right) t \quad (26)$$

$$\hat{\sigma}^2 = \frac{\alpha_B F_p k}{2D_e} \left(\frac{A_g}{F_g V_g} \right) \left(\frac{V_B}{A_p} \right)^2 \left(1 + \frac{1}{K_c} \right) \quad (27)$$

and $g(X)$ and $p(X)$ have been defined in Eqs. (6) and (8). The results of these analyses were applied to the reduction of nickel oxide

pellets with hydrogen by systematically designed experiments [Szekeley et al., 1973].

Eq. (25) has a number of noteworthy characteristics. The equation is valid for the nine combinations of F_g and F_p over the entire range of $\hat{\sigma}$ approaching zero (chemical reaction control) and infinity (pore diffusion control); it is also exact at the conversion values of zero and unity. In other words, the time for complete conversion is exactly predicted by Eq. (25) even for an intermediate value of $\hat{\sigma}$ for which the equation is valid only approximately for $0 < X < 1$. This property was originally determined by the comparison of Eq. (25) with the exact numerical solution of Eq. (13) together with Eqs. (21) and (23) [Sohn and Szekeley, 1972]. Subsequently, a rigorous mathematical proof of this interesting property has been developed [Sohn et al., 1985].

The above analyses of the grain model have been made for the case of a constant effective diffusivity. In many fluid-solid reactions, the product solid layer has a substantially different effective diffusivity than the reactant. One of the simplified methods of incorporating this structural change is to assign different effective diffusivities to the completely and partially reacted zones. Such a case with flat grains was discussed in the previous section. Szekeley and Sohn [1973] reported the results of computation for this two-diffusivity system made up of grains of other geometries.

2-3. The Law of Additive Reaction Times

Based on the conversion-vs.-time relationships for porous and nonporous solids discussed above, Sohn [1978] developed the "Law of Additive Reaction Times". This law is applicable for an isothermal reaction in which the effective diffusivity of the solid remains constant during the reaction. The law states that

$$\begin{aligned} &\text{Time required to attain a certain conversion} \\ &\equiv \text{Time required to attain the same conversion under} \\ &\quad \text{the conditions of rapid intergrain pore diffusion} \\ &\quad + \text{Time required to attain the same conversion under the rate} \\ &\quad \text{control by intergrain pore diffusion and external mass transfer} \end{aligned} \quad (28A)$$

or

$$t(X) = t|_{\hat{\sigma} \rightarrow 0} + t(X)|_{\hat{\sigma} \rightarrow \infty} \quad (28B)$$

$$= a \cdot g(X) + a \cdot \hat{\sigma}^2 [p_{F_g}(X) + 4X/\text{Sh}^*] \quad (28C)$$

where a is a constant term containing the chemical-reaction-rate constant. In general, the term $t|_{\hat{\sigma} \rightarrow 0}$ is related to $f(w)$ in Eq. (16) by

$$t(X)|_{\hat{\sigma} \rightarrow 0} = \frac{\rho_B}{b(-\dot{m}_A)_b S_v^0} \int_0^X \frac{dw}{f(w)} = \frac{\rho_B}{bk S_v^0 (C_{Ab} - C_{Cb}/K)} \int_0^X \frac{dw}{f(w)} = a \cdot g(X) \quad (29)$$

in which $(-\dot{m}_A)_b$ is $(-\dot{m}_A)$ at bulk conditions. From Eq. (2) or (25), the term $t(X)|_{\hat{\sigma} \rightarrow \infty}$ is given by

$$t(X)|_{\hat{\sigma} \rightarrow \infty} = \left(\frac{V_B}{A_p} \right)^2 \frac{\alpha_B \rho_B F_p}{2b D_e (C_{Ab} - C_{Cb})} \left(1 + \frac{1}{K} \right) [p_{F_g}(X) + 4X/\text{Sh}^*] = a \cdot \hat{\sigma}^2 [p_{F_g}(X) + 4X/\text{Sh}^*] \quad (30)$$

The conversion function $g(X)$ should be chosen in such a way that its magnitude varies between 0 and 1 as X varies from 0 to 1 (not always possible) - typically the entire function containing X in the last term in Eq. (29), leaving all the constant coefficient in a . Note that any constant arising from the integration in Eq. (29) goes into a . Then, $\hat{\sigma}^2$ is defined by dividing by the constant term that

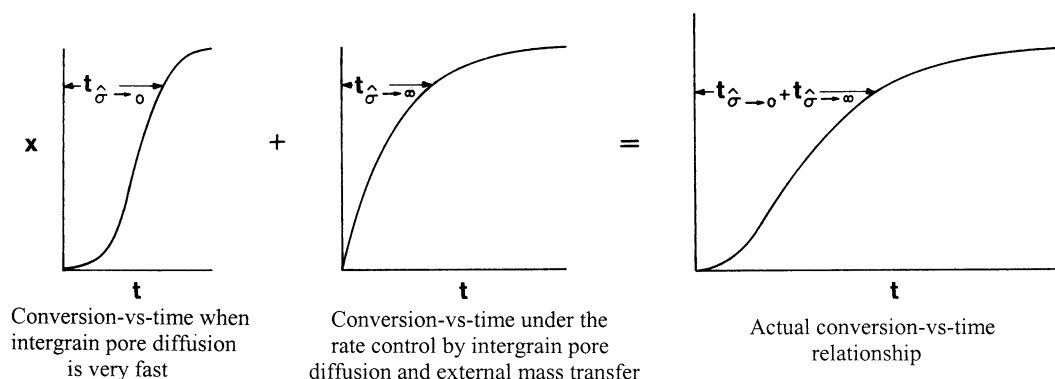


Fig. 4. Graphical representation of the Law of Additive Reaction Times.

multiplies the conversion function $p(X)$ in Eq. (30). A different choice of $g(X)$ does not affect the validity of Eqs (28). The appropriate selection of $g(X)$ and thus the constant a will, however, result in the definition of $\hat{\sigma}^2$ in such a way that the numerical criteria for chemical-reaction control and pore-diffusion control will remain, respectively, $\hat{\sigma}^2 < 0.1$ and $\hat{\sigma}^2 > 10$.

Fig. 4 illustrates how the law of additive reaction times can be applied in general if we have information on the chemical reaction rate in the absence of the resistance due to intra-pellet diffusion and on the rate controlled by intra-pellet diffusion. Eqs. (2), (11), and (25) are examples of the mathematical expressions of this law. This law is exact for the reaction of a nonporous solid following the shrinking-core scheme. It is approximately valid for the reaction of a porous solid with constant effective diffusivity. In the latter case, the exact solution must in general be obtained by numerical solution of the governing second-order differential equations.

The Law of Additive Reaction Times, which results in a closed-form solution, is even more useful in the analysis of multi-particle systems involving various particle sizes and changes in fluid concentration and solid temperature, because the solution is explicit in time. Thus, in a differential form it yields the instantaneous conversion rate dX/dt as a function of solid conversion (X) and other conditions at any time. This allows the application of the approximate solution to systems in which conditions vary with time (and position in the reactor) as long as the temperature within a particular pellet is spatially uniform at any given time [Sohn, 1978]. It has further been shown [Sohn, 1978] that this law is valid regardless of the dependence of rate on solid conversion. The general applicability and usefulness of this law have been verified using a wide variety of fluid-solid reaction systems. Some of these cases will be discussed below.

Structural changes such as sintering, swelling, and softening are very complex and not well understood. If information is available, the effects of such changes on effective diffusivity and chemical reactivity could be incorporated into the governing equations. When there is a substantial heat effect, the analysis becomes much more complex with the possible existence of multiple steady states and instability [Szekely et al., 1976; Calvelo and Smith, 1972]. Many metallurgical systems involve solids with high thermal conductivities. In such cases, temperature within the solid may be sufficiently uniform and resistance to heat transfer may be limited to the external heat transfer between the external surface and the bulk fluid

stream. For such systems, the reaction rate in the form of dX/dt can still be obtained from Eq. (25) by writing it in a dimensional form and expressing the temperature-dependent parameters as functions of temperature. The validity of this approach has been verified [Sohn, 1978], as illustrated in the following Example A.

Example A. Porous solids in which the reaction of the solid follows the nucleation-and-growth

Gas-solid reactions usually involve the adsorption of gaseous reactants at preferred sites on the solid surface and the formation of nuclei of the solid product. For small particles the formation and growth of nuclei are important steps. The conversion-vs-time relationship in this case is given by the nucleation-and-growth kinetics. A frequently used form of such a rate expression, which is attributed to Erofeev [Young, 1966], is

$$[-\ln(1-w)]^{1/n} = kt \quad (31)$$

Sohn [1978] obtained the following equation by applying Eq. (28B) to this system:

$$t_N^* = g_N(X) + \hat{\sigma}_N^2 [p_{F_p}(X) + 4X/Sh^*] \quad (32)$$

$$\text{where } t_N^* \equiv \frac{bkS_p^0}{\rho_B} \left(C_{Ab} - \frac{C_{Cb}}{K} \right) t \quad (33)$$

$$\hat{\sigma}_N^2 \equiv \frac{\alpha_B F_p k S_p^0}{2D_e} \left(\frac{V_p}{A_p} \right)^2 \left(1 + \frac{1}{K} \right) \quad (34)$$

$$g_N(X) \equiv [-\ln(1-X)]^{1/n} \quad (35)$$

A comparison between Eq. (32) and the exact numerical solution of the governing differential equation (13), with the correspond-

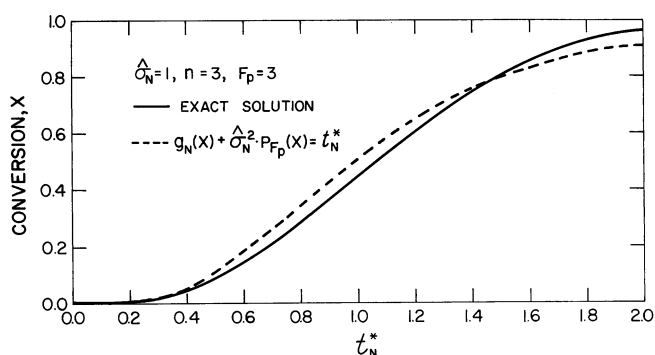


Fig. 5. Comparison of Eq. (32) with the exact solution ($Sh^* = \infty$).

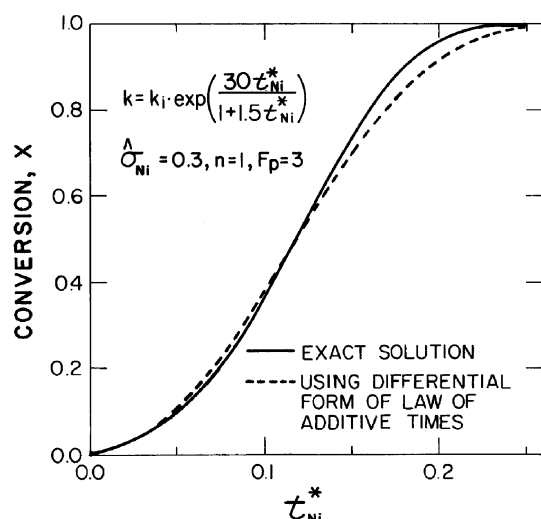


Fig. 6. Comparison of the differential form of the Law of Additive Reaction Times with the exact numerical solution for the case of changing temperature.

ing Eq. (16) obtained from the differential form of Eq. (31), is shown in Fig. 5. This comparison is made for the case of $\hat{\sigma}_N^2=1$, i.e., when chemical kinetics and pore diffusion are equally significant, which represents the severest test of the approximate solution. Other appropriate rate expressions for $f(w)$ in Eq. (16) could be used giving rise to the corresponding forms of $g_s(X)$ according to Eq. (29). Sohn and Kim [1984] applied Eq. (32) to reanalyze the data on the hydrogen reduction of nickel oxide pellets [Szekely et al., 1973] and determined that this equation gave a better overall representation of this reaction system than the original grain model approach.

As discussed above, a major advantage of the approximate solution such as Eq. (32) is that it is time-explicit. This allows the approximate solution to be applied, in a differential form in terms of dX/dt , to the situation in which bulk conditions change with time (as long as the temperature within the solid remains spatially uniform). Fig. 6 shows an example of this in which the uniform solid temperature varies linearly with time, causing the system to shift from chemical control to mixed control to pore diffusion control as the conversion increases from zero to unity. It is seen that the application of the Law of Additive Reaction Times (in the differential form) yields a very satisfactory result.

A special case of the rate expression given by Eq. (31) is the case of $n=1$, which is equivalent to the "first-order" rate dependence on the fraction of the solid reactant remaining unreacted. Among the many fluid-solid reactions treated with this rate expression, the most familiar one is the reaction of carbon dispersed in a matrix of an inert solid, such as the removal of carbonaceous residue from the organic binder used in ceramic forms and the regeneration of coked catalysts. It has been shown for such systems [Sohn and Wall, 1989] that Eq. (32) is not only valid but also superior to other closed-form approximate solutions of the governing differential equations.

Example B. Solids that follow the random-pore model

For many porous solids, the changes in the pore structure accompanying chemical reaction are substantial and are often described by a random-pore model. Bhatia and Perlmutter [Bhatia and Perlmutter, 1980, 1981] obtained a useful analytical relationship between

the solid conversion and time in the absence of intra-pellet diffusion effects. Their solution includes the cases of pore growth or shrinkage due to reaction as well as the diffusion through the solid product forming on the pore wall.

When intra-pellet diffusion and external mass transfer are important, a numerical solution is necessary. The law of additive reaction times has been applied to this situation [Sohn and Chaubal, 1986]. Since the pore size and thus the effective diffusivity changes significantly in this type of a system, the law was applied in a differential form, i.e., from Eq. (28C)

$$\frac{dt}{dX} = ag'(X) + a \cdot \hat{\sigma}^2 \cdot p'_{F_p}(X) + \frac{4a\hat{\sigma}^2}{Sh^*} \quad (36)$$

The change in the effective diffusivity will make $\hat{\sigma}^2$ a function of conversion X , whereas $\hat{\sigma}^2/Sh^*$ is not dependent on effective diffusivity. Reintegration of this equation yields

$$t = ag(X) + a \int_0^X \hat{\sigma}(X) \cdot p'_{F_p}(X) \cdot dX + \frac{4a\hat{\sigma}^2}{Sh^*} X \quad (37)$$

Comparison of the X -vs.- t relationship obtained from this equation with the numerical solution of the governing differential equation including intra-pellet diffusion gave satisfactory agreement for various values of system parameters [Sohn and Chaubal, 1986].

Example C. The grain-pellet system with intragrain diffusion effect

When diffusion through the product layer around each grain (see Fig. 3) presents a substantial resistance, the $t|_{\hat{\sigma} \rightarrow 0}$ term is obtained from Eq. (2) without the last term. Thus, the application of Eq. (28B) yields [Sohn and Szekely, 1974]

$$t_g^* \equiv [g_{F_g}(X) + \hat{\sigma}_g^2 p_{F_g}(X)] + \hat{\sigma}^2 [p_{F_p}(X) + 4X/Sh^*] \quad (38)$$

$$\text{where } \hat{\sigma}_g^2 \equiv \left(\frac{k}{2D_g}\right) \left(\frac{V_g}{A_g}\right) \left(1 + \frac{1}{K}\right) \quad (39)$$

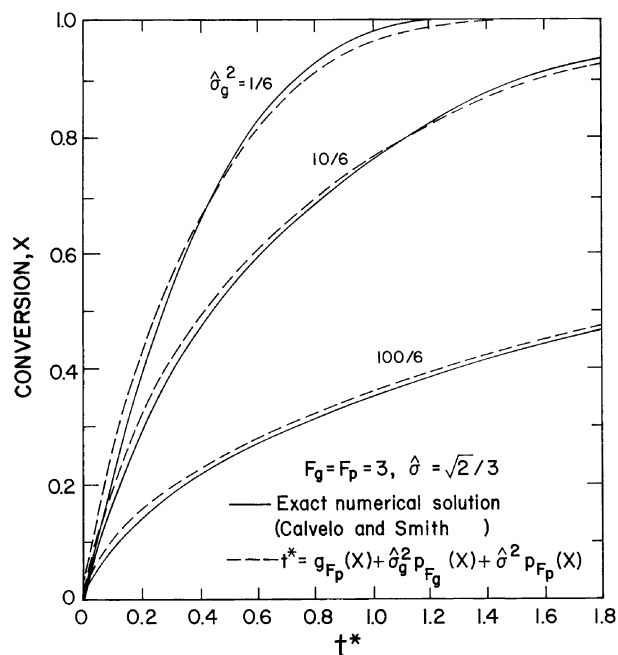


Fig. 7. Comparison of Eq. (38) with the exact numerical solution in Calvelo and Smith, 1972.

For the reaction of a spherical pellet made up of spherical grains, Eq. (38) was found to closely represent the exact numerical solution obtained by Calvelo and Smith [1972], as illustrated in Fig. 7.

Example D. Reactions between one solid and two gaseous reactant

An example of this type of reaction is the reduction of metal oxides by a mixture of hydrogen and carbon monoxide. Wen and Wei [1970, 1971] and Rehmat and Saxena [1977] studied the problem of simultaneous gas-solid reactions in terms of the shrinking-core model for an initially nonporous solid. Szekeley and coworkers [Szekeley and El-Tawil, 1976; Szekeley et al., 1977] have studied the reduction of hematite pellets by hydrogen-carbon monoxide mixture.

The reaction of a porous solid with two reactant gases can be described by writing Eq. (13) for the four gaseous species involved (two if both reactions are irreversible) and modifying Eq. (16) to add the contribution from the second reactant gas. This would involve a substantial amount of computation, especially when analyzing a multi-component system. Sohn and Braun [1980] obtained an approximate but much simpler solution by applying the law of additive reaction times for a system in which there are no reactions between the reactant gases and the product gases. In order to present their result, we write the simultaneous reactions in the following form:



For an isothermal system with a constant effective diffusivity and first-order kinetics, Sohn and Braun [1980] found that the application of the differential form of Eq. (32) to the two reactions gave a result that satisfactorily represented the results of numerical integration of the governing differential equations. Thus, the overall rate of conversion is given by:

$$\frac{dX}{dt} = \frac{\psi_{1b}}{g'(X) + \hat{\sigma}_1^2 \left(p_{F_p}'(X) + \frac{4}{Sh^*} \right)} + \frac{\psi_{2b}}{g'(X) + \hat{\sigma}_2^2 \left(p_{F_p}'(X) + \frac{4}{Sh^*} \right)} \quad (41)$$

where

$$t^* \equiv \left[b_1 k_1 \left(C_{A,b} - \frac{C_{p,b}}{K_1} \right) + b_2 k_2 \left(C_{A,b} - \frac{C_{p,b}}{K_2} \right) \right] \frac{S_v^0}{p_B} t \quad (42)$$

$$\psi_{1b} \equiv \frac{b_1 k_1 \left(C_{A,b} - \frac{C_{p,b}}{K_1} \right)}{b_1 k_1 \left(C_{A,b} - \frac{C_{p,b}}{K_1} \right) + b_2 k_2 \left(C_{A,b} - \frac{C_{p,b}}{K_2} \right)} \quad (43A)$$

$$\psi_{2b} \equiv \frac{b_2 k_2 \left(C_{A,b} - \frac{C_{p,b}}{K_2} \right)}{b_1 k_1 \left(C_{A,b} - \frac{C_{p,b}}{K_1} \right) + b_2 k_2 \left(C_{A,b} - \frac{C_{p,b}}{K_2} \right)} \quad (43B)$$

$$\hat{\sigma}_1^2 \equiv \frac{\alpha_B F_p k_1 S_v^0}{2 D_{eA_1}} \left(\frac{V_p}{A_p} \right)^2 \left(1 + \frac{1}{K_1} \right) \quad (44A)$$

$$\hat{\sigma}_2^2 \equiv \frac{\alpha_B F_p k_2 S_v^0}{2 D_{eA_2}} \left(\frac{V_p}{A_p} \right)^2 \left(1 + \frac{1}{K_2} \right) \quad (44B)$$

In addition to the overall conversion, Sohn and Braun [1980] showed that the rate of conversion of the solid due to each gaseous reductant was well represented by each of the terms on the right-hand side of Eq. (41). The overall conversion and the conversion by each gas can be obtained by numerically integrating the respective deriv-

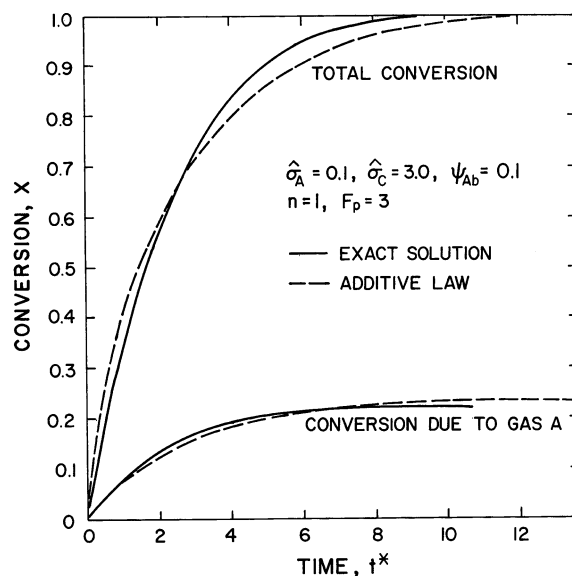


Fig. 8. Comparison of the approximate solution with the exact numerical solution for the reaction of one solid with two fluid reactants.

atives. Fig. 8 illustrates results for a combination of parameters representing the cases that would yield the poorest agreement. As can be seen, even in this case the agreement between the exact numerical solution and the approximate solution described above is quite satisfactory. They also described how to apply this approximate solution to a system in which the bulk concentrations and temperature vary with time. Although $g_N(X)$ with $n=1$ was used in the formulation, Eq. (41) is expected to be valid with any other forms of $g(X)$.

The approximate solution given in Eq. (41) is exact when both reactions are controlled either by chemical reaction or by diffusion. Thus when both $\hat{\sigma}_1$ and $\hat{\sigma}_2$ approach zero (chemical reaction control), we have:

$$g(X) = t^* \quad (45)$$

When both $\hat{\sigma}_1$ and $\hat{\sigma}_2$ approach infinity (diffusion control), the asymptotic solution is:

$$p_{F_p}(X) + \frac{4X}{Sh^*} = \left(\frac{\psi_{1b}}{\hat{\sigma}_1^2} + \frac{\psi_{2b}}{\hat{\sigma}_2^2} \right) t^* \quad (46)$$

Example E. The reaction of a porous solid with a gas accompanied by a volume change in the gas phase

In this case, the application of the law of additive reaction times, expressed by Eq. (25B), yields

$$t(X) \equiv a \cdot g(X) + a \cdot \hat{\sigma}^2 \left[\frac{\theta}{\ln(1+\theta)} p_{F_p}(X) + \frac{4(1+\theta)}{Sh^*} X \right] \quad (47)$$

This equation is the porous solid counterpart of Eq. (11) for an initially nonporous solid. It has been shown [Sohn and Bascur, 1982] that Eq. (47) gives a very satisfactory representation of the exact numerical solution of the governing differential equation that includes the bulk flow effects due to the volume charge in the gas phase upon reaction.

Example F. The reaction of a solid in which the reactant solid is

nonuniformly distributed in a mixture with an inert solid

If the solid is initially nonporous and produces a porous product layer, much like in the shrinking unreacted-core system, discussed earlier, Eq. (28B) has been shown to apply exactly to the case in which the distribution of the solid reactant in a mixture with an inert solid is non-uniform [Sohn and Xia, 1986]. In the case where such a solid is initially porous, Sohn and Xia [1987] have shown that the application of the law of additive reaction times yields an excellent closed-form approximation of the exact solution that is possible only by the numerical solution of the governing differential equations.

Example G. Fluid-solid reactions involving multicomponent diffusion

Eddings and Sohn [1993] have shown how multi-component diffusion can be simplified, which enables the use of the law of additive reaction times to describe fluid-solid reaction systems involving a fluid mixture with a wide range of binary diffusivities. Such a system could only be solved by numerical method before their development of an approximate method.

Example H. Application to liquid-solid reactions

An example of such an application is the ferric chloride leaching of galena (PbS). There were conflicting conclusions drawn for the controlling reaction mechanism depending on the conditions under which the reaction was carried out. By applying the law of additive reaction times, Sohn and Baek [1989] showed that the different behaviors could be included within a unified rate expression encompassing them as special cases of the overall behavior, and Eqs. (28) gave an excellent representation of the experimental data in the region of mixed control.

2-4. Gas-solid Reaction-Rate Enhancement by Pressure Cycling

This topic illustrates an additional example of the application of the systematic analysis of a fluid-solid reaction. Since the chemical kinetics is dependent on temperature by the Arrhenius equation, the intrinsic chemical reaction rate can be greatly increased by a moderate increase in temperature. Thus, many gas-solid reactions are carried out under the conditions in which the pore diffusion controls the overall rate. Unfortunately, pore diffusion rate is weakly dependent on temperature, and thus a further increase of temperature does not result in a substantial increase in the overall rate if it is rate-controlled by pore diffusion.

Diffusion occurs due to the molecular movement of matter under a concentration gradient, which is a slow process. On the other hand, a bulk flow of matter, which is caused by external forces such as pressure, is much faster than a diffusion process. Thus, if a bulk flow can be generated in a porous solid, the transfer of the gaseous species can take place much faster, thus increasing the overall rate of the reaction. Since it is not possible to maintain a fixed pressure gradient across a solid pellet, a possible method to add the bulk flow component is to cycle the pressure of the gas outside the pellet. As the pressure rises, there will be a bulk flow of the gaseous reactant toward the interior of the pellet; as the bulk pressure decreases, there will be an outward bulk flow of the gas rich in the product.

The systematic understanding and incorporation of the various individual steps taking place in the reaction of a porous solid with a gas enable one to examine the effect of pressure cycling on the overall rate even before an experimental test is performed. This recognition led Sohn and Chaubal [1984] to formulate the governing equation and evaluate the effect of pressure cycling. To describe

such a system, Eq. (13) must be modified to include the bulk flow due to pressure cycling and the time-dependent concentration change at any position, as follows:

$$\varepsilon \frac{\partial C_A}{\partial t} + \nabla \cdot (C_A \underline{u}) - \nabla \cdot (D_{eA} C_T \nabla X_A) - R_A = 0 \quad (48)$$

in which the second term represents the bulk flow of the gas. Eq. (16) remains valid.

Using the example of the gaseous reduction of a porous hematite pellet, Sohn and Chaubal [1984] showed that a substantial rate increase could be obtained by applying pressure cycling. Subsequently, Sohn and Aboukheshem [1992] verified this result by an experimental study using the hydrogen reduction of nickel oxide pellets. The effect of pressure cycling by an acoustic pressure on the removal of carbonaceous residue from a multi-layer multi-chip ceramic module for a mainframe computer during the green-sheet processing was also tested experimentally [Sohn, unpublished work]. The results showed a substantial increase in the carbon removal rate.

3. The Effect of Chemical Equilibrium on Fluid-Solid Reaction Kinetics and the Falsification of Activation Energy

An often overlooked aspect of fluid-solid reaction analysis is the importance of thermodynamics, expressed through the equilibrium constant K . With reference to Eqs. (3), (4), (26), (27), (33), (34), and (42)-(44), it is seen that equilibrium consideration is not necessary for an irreversible reaction ($K \rightarrow \infty$) with the K term disappearing from the equations. If the reaction has a small value of K , however, several important consequences appear [Sohn, 2003]:

(1) The overall rate tends to be controlled by mass transfer. This can be seen from the fact that all the σ^2 terms contain the $1/K$ term, which increases to infinity as $K \rightarrow 0$. This results in the mass transfer term (that contains σ^2) in the X -vs.- t relationships becoming dominant over the $g(X)$ term that represents the effect of chemical kinetics. Physically, this means that, as $K \rightarrow 0$, the presence of even a small concentration of the fluid product near the reaction interface tends to lead the conditions there toward equilibrium. Thus, the ability of the system to remove the fluid reactant (mass transfer) becomes the critical step.

(2) The overall rate of a reaction with small K tends to be slow. This can be seen from the fact that the time required to attain a certain conversion level X becomes large as σ^2 becomes large with $K \rightarrow 0$. The required time becomes even larger if the bulk fluid contains the fluid product, as seen from the definitions of t^* . Physically, this follows the reasoning given in (1) above. As $K \rightarrow 0$, the concentration of the fluid product at the interface becomes small even at equilibrium (rapid chemical kinetics), which makes the mass transfer rate correspondingly slow [Conversely, the concentration difference of the fluid reactant, which is related to that of the fluid product by the reaction stoichiometry, becomes small].

(3) The apparent activation energy of the overall rate is falsified. It is usually stated that the temperature dependence of a mass-transfer controlled reaction is weak, i.e., the apparent activation energy is small. It is also usually assumed that large apparent activation energy (larger than a few kilocalories per mol) indicates a rate control by chemical kinetics. These statements are not necessarily correct for systems with small K values, as shown below.

As stated in (1), the term that depends on the rate constant k , $g(X)$, becomes insignificant as $K \rightarrow 0$. Then, k is cancelled out from the

remaining terms t^* and σ^2 , i.e., chemical kinetics do not affect the overall rate. Rather, the overall rate becomes proportional to K when $C_{cb}=0$. Now,

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = \exp\left(-\frac{\Delta H^\circ}{RT}\right) \cdot \exp\left(-\frac{\Delta S^\circ}{R}\right) \quad (49)$$

Considering that ΔS° , ΔH° , and D_e are weak functions of temperature, it is seen that the apparent activation energy of a fluid-solid reaction with small K will be approximately equal to ΔH° . Furthermore, a small K value means a large positive value of ΔG° and thus large ΔH° , leading to large apparent activation energy. This has led some researchers to an erroneous conclusion of rate control by chemical kinetics. The reduction of many a stable metal oxide by reducing gases has a small value of K , and requires a careful examination of rate dependences.

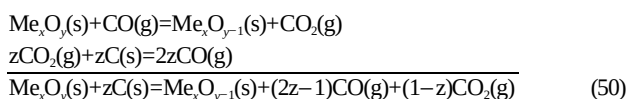
COMPLEX FLUID-SOLID REACTIONS

The ideas and principles discussed in the previous sections have been applied to the quantitative analysis of complex fluid-solid reaction systems. Examples are listed below. The reader is referred to the references given in each case for further detail.

1. Solid-Solid Reactions Proceedings through Gaseous Intermediates with a Net Production of Gases

A number of such reactions are of considerable importance in metallurgical processes. These reactions may be considered as coupled gas-solid reactions, and can thus be analyzed in light of the mathematical analyses developed in the previous parts of this article.

The most important example is the carbothermal reduction of metals oxides. These reactions proceed through the intermediates of CO and CO₂, according to the following mechanism:



The reduction of iron oxides [Otsuka and Kunii, 1969; Rao, 1971], the reaction between ilmenite and carbon [El-Guindy and Davenport, 1970], the reduction of tin oxide [Padilla and Sohn, 1979], and the reaction between chromium oxide and chromium carbide [Maro et al., 1973] are some examples. In all these reactions, there is a net generation of gaseous species CO and CO₂ resulting in a bulk flow of the gas mixture from the reaction zone. These reactions can be expressed by the following general equations:



In order for this reaction to be self-sustaining without requiring an external supply of gaseous reactants and with a net generation of gaseous species, the condition $ac > 1$ must be satisfied.

In the early investigations, the kinetics of solid-solid reactions was analyzed for specific conditions in which one of the gas-solid reactions controls the overall rate. The studies on the carbothermal reduction of hematite [Rao, 1971], the reaction between ilmenite and solid carbon [El-Guindy and Davenport, 1970], the carbothermal reduction of stannic oxide [Padilla and Sohn, 1979], and the reaction between chromium oxide and chromium carbide [Maro et al., 1973] make use of the assumption of such a single controlling

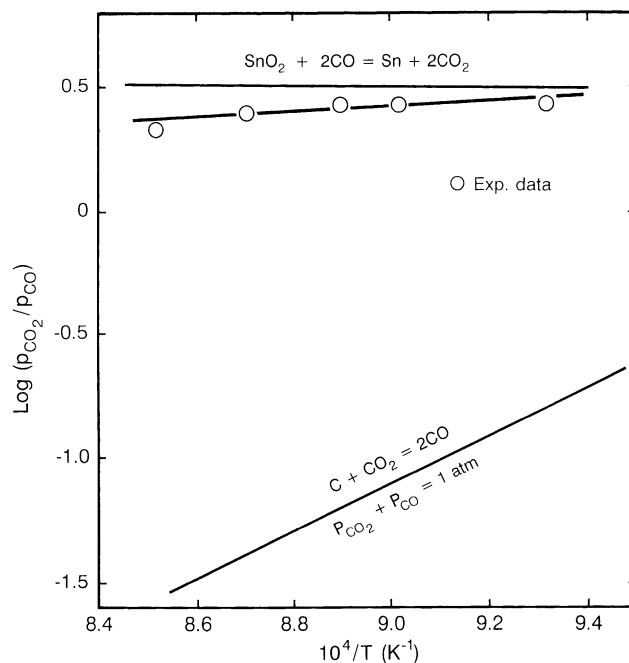


Fig. 9. Observed values of $p_{\text{CO}_2}/p_{\text{CO}}$ ratios compared with the computed equilibrium values for the component reactions in the carbothermal reduction of stannic oxide.

reaction. Padilla and Sohn [1979] showed experimentally that for their experimental conditions this assumption is valid by directly measuring for the first time the partial pressures of the intermediate gases. This experimental evidence is given in Fig. 9, which indicates that the SnO_2 -CO reaction is very fast (near equilibrium), and thus the overall rate of reaction is controlled by the C-CO₂ reaction taking place at the observed p_{CO_2} and p_{CO} .

Sohn and Szekely [1973] developed a theoretical basis for analyzing the general case in which both reactions affect the overall rate and for establishing a criterion for the controlling step. Let us consider a uniform mixture of solids B and D. They may be in the form of small particles or pellets that undergo reactions of the types discussed in Sections 1 and 2. We shall here consider isothermal systems and the case of uniform gas concentrations between the particles or pellets of solids B and D. This latter condition is applicable when the overall reaction, and thus the CO₂/CO production, is reasonably fast. This condition is also valid if the mixture is placed in a container with only a small opening that allows the CO₂/CO gas product to exit but does not allow the back diffusion of any gas from the surroundings. From the mass balances of the gaseous species, the rates of net generation of the gaseous species are given as follows:

$$\frac{dn_A}{dt} = -v_1 + av_2 \quad (52\text{A})$$

$$\frac{dn_C}{dt} = cv_1 + v_2 \quad (52\text{B})$$

where v_1 and v_2 are the net forward rates of reactions (51A) and (51B), respectively, per unit volume of the solid mixture. These terms can be expressed, using Eqs. (18A) and (18B), as follows:

$$v_1 = \left(\frac{\alpha_B \rho_B}{b} \right) \frac{dX_B}{dt} \quad (53\text{A})$$

$$v_2 = \left(\frac{\alpha_D \rho_D}{b} \right) \frac{dX_D}{dt} \quad (53B)$$

The reaction rate terms, dX_i/dt , depend on the reaction mechanism of each solid. It can be given by any of the solutions given earlier for the reaction of a single solid such as the differential form of Eqs. (2), (16), (25), or (28B). It must be noted that the bulk concentration terms in these equations are now the interstitial concentrations, which vary with time as the reaction progresses.

If the total pressure of the system is maintained constant, the following relationships hold:

$$\frac{dn_A}{dt} = \frac{C_A dV}{V_p dt} \quad (54A)$$

$$\frac{dn_C}{dt} = \frac{C_C dV}{V_p dt} \quad (54B)$$

where dV/dt is the rate of volume generation of the gas mixture, and V_p is the volume of the mixture. We have made a pseudo-steady-state assumption that the gas-phase concentrations at any time are at the steady-state values corresponding to the amounts and sizes of the solids at that time, namely, $CdV/dt \gg VdC/dt$.

We also have the condition that

$$C_A + C_C = C_T \quad (55)$$

Eqs. (52) to (55) may be solved for C_A and C_C . Using these values, the rates of reaction of the solids may then be obtained from the appropriate expressions used for dX_B/dt and dX_D/dt . Integration of these rates over dt will yield incremental values of X_B and X_D . Using the new values of X_B and X_D , Eqs. (52) to (55) are solved again to obtain C_A and C_C at the next time step. The procedure is repeated to give conversions as functions of time. In certain simple cases, analytical solutions are possible [Sohn and Szekely, 1973].

2. Solid-Solid Reactions Proceeding through Gaseous Intermediates with No Net Production Gas

This situation arises when $ac=1$ in reactions represented by Eqs. (51A) and (51B). An example is the oxidation of metal sulfides with lime to produce the corresponding oxides [Sohn, 1983; Sohn and Kim, 1984, 1987, 1988; Soepriyanto et al., 1989]. This reaction can in general be expressed by the following:



Using this scheme, selected metal sulfides such as molybdenum disulfide and zinc sulfide can be transformed into the corresponding oxides without producing a sulfur-containing gas. The role of lime in this process is two-fold: (1) It improves the thermodynamics of the reaction between sulfide and steam, which has a very low equilibrium constant due to the positive Gibbs free energy change, by eliminating hydrogen sulfide, and (2) the reaction between hydrogen sulfide and lime fixes sulfur as calcium sulfide which can be further treated to recover sulfur.

Reactions (56) involve no net consumption or generation of the gaseous intermediates, and the gaseous species do not appear in the overall stoichiometry. The gaseous species simply act as carriers of oxygen and sulfur atoms. In this respect, the mechanism for this type of reaction might be termed "catalysis by gases" [Sohn, 1991].

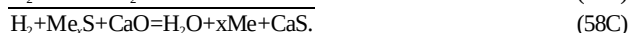
The kinetics of this reaction can be described by Eq. (52). The difference between this case and the reactions with net generation of gases is that, since no gases are formed or consumed,

$$v_1 = av_2 \quad (57)$$

Eqs. (53) and (55) are valid also in this case. The solution of these equations gives the conversion as a function of time. Using this approach, the detailed kinetics of reactions of various sulfide minerals with lime has been described [Sohn and Kim, 1987, 1988; Soepriyanto et al., 1989; Sohn, 1991].

3. Successive Fluid-solid Reactions in Which the Reactant Fluid Reacts with the First Solid, Producing an Intermediate Fluid Which in Turn Reacts with the Second Solid

Two notable examples, in which successive fluid-solid reactions play a major role, utilize lime as a scavenger of sulfur-containing gases. The first is the hydrogen reduction of metal sulfides in the presence of lime [Kay, 1968; Chech and Tiemann, 1969; Habashi and Dugdale, 1973; Habashi and Yostos, 1977; Sohn and Rajamani, 1977; Shah and Ruzzi, 1978; Rajamani and Sohn, 1983; Sohn and Won, 1985; Won and Sohn, 1985], which can be represented by the following general scheme:



In this reaction scheme, lime serves two purposes: (1) It fixes sulfur in the solid, thereby reducing the emission of hydrogen sulfide into the atmosphere, and (2) the presence of lime improves the otherwise unfavorable thermodynamics of reaction (58A) by removing hydrogen sulfide from the gas phase. Reaction (58B) is highly favorable thermodynamically. The second example is the roasting of sulfide minerals in the presence of lime [Haug and Bartlett, 1976; Haver and Wong, 1972; Bartlett and Haug, 1973].

Sohn and coworkers [Sohn and Rajamani, 1977; Rajamani and Sohn, 1983; Sohn and Won, 1985] developed a model for successive fluid-solid reactions in a porous pellet. The model takes into consideration the effects of the relative amounts of the solids, grain sizes, the pellet size and porosity, and the diffusion of gaseous species, as well as the effect of improved thermodynamics in systems represented by the first example. The model describes not only the rate of reaction of the solid reactants but also the fraction of the intermediate gas (the sulfur-containing gases in the above examples) that is captured by the second solid (lime in the above examples).

4. Staged Reaction of a Solid with a Fluid in which the Solid Forms a Series of Thermodynamically Stable Intermediate Phases

A notable example of such a system is the gaseous reduction of hematite (Fe_2O_3) to iron through the successive formation of magnetite (Fe_3O_4) and wustite (FeO) [Sohn and Chaubal, 1984; Sohn, 1981].

5. Simultaneous Reaction of One Solid with Two Gases

This system has been discussed as Example D in Section 2-3 in relation to the application of the law of additive reaction times.

6. Simultaneous Reaction of Several Solid Reactants with One Fluid Reactant

This system is described by including the consumption of the fluid reactant by the different solids in the right-hand side of Eq.

(13) and solving the resulting equation by a numerical method. The reader is referred to the literature for further detail [Sohn and Braun, 1984; Lin and Sohn, 1987; Paul et al., 1992].

MULTIPARTICLE SYSTEMS

In the above sections, the discussion mainly involved the analysis of reactions taking place in a single particle or pellet of solids. The eventual objective for studying single particle systems is, of course, to apply the results to the analysis and design of multi-particle systems of industrial importance. Examples of multi-particle fluid-solid contacting equipment include packed beds, moving beds, fluidized beds, and rotary kilns. The extension of single-particle studies to multi-particle systems will depend on the nature of the particulate assemblages, the mode of fluid-solid contacting, and the spatial variation of the fluid properties within the system. Therefore, a general analysis of these processes will not be made, and the reader is referred to the literature for developments in this area [Szekely et al., 1976; Sohn, 1991; Paul et al., 1992; Ishida and Wen, 1971; Evans and Song, 1974; Sohn, 1976; Herbst, 1979; Bartlett, 1979; Gao et al., 1983; Rhee and Sohn, 1990; Sohn and Lin, 1990; Zhou and Sohn, 1996].

CLOSING REMARKS

In this review, the advances made in the last two decades in the field of chemical reaction engineering as applied to the chemical processing of metals and other inorganic materials have been presented. The scope of the article did not allow the review of the advances made in other fields, such as catalytic reactions. Even within the topics discussed, this review was written with a rather limited scope and time constraint, concentrating mainly on the work done over the years by the author and his coworkers. Regrettably, the large amount of work on the subject published by numerous other researchers could not be discussed in this article. It is hoped, however, that even this limited review shows how chemical reaction engineering principles can be fruitfully applied to areas and topics that are new and different from the traditional domain of chemical engineers.

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NOMENCLATURE

a : constant in Eqs. (28C) and (36)
 A : fluid reactant
 A_g, A_p : external surface area of an individual grain and the pel-

let, respectively
 b : number of moles of solid B reacted per mole of fluid reactant A
 B : solid reactant
 c, d : stoichiometry coefficients
 C : fluid product
 C_i : molar concentration of fluid species i
 C_T : total molar concentration of fluid
 d_p : thickness of a slab or diameter of a cylinder or a sphere
 D : solid product or diffusivity
 D_{ei} : effective diffusivity of fluid species in the porous solid
 D_g : effective diffusivity of fluid species in the product layer around a grain
 F_g, F_p : shape factor for the grain and pellet, respectively (=1, 2, or 3 for flat plates, long cylinders, or spheres, respectively)
 g(X) : conversion function defined by Eq. (6), (29), or (35)
 $(-\Delta H)$: heat of reaction
 k : reaction-rate constant
 k_m : external-mass-transfer coefficient
 K : equilibrium constant
 m : apparent rate constant, Eq. (31)
 $(-\dot{m}_A)$: molar rate of consumption of the fluid reactant A per unit area of solid
 n_i : number of moles of species i per unit volume of the solid mixture including the pore space
 $\underline{N}_i$: molar flux vector for species i
 p_i : partial pressure of species i
 p(X) : conversion function defined by Eq. (7), (8), (9), or (10)
 $\underline{q}$: heat flux vector
 r_c : position of reaction interface in a nonporous particle
 r_g : original radius of the grain
 R_i : rate of production of species i per unit volume of the pellet
 S_s, S_s^0 : surface area per unit volume of the solid (not pellet) at any time and its initial value, respectively
 Sh^* : modified Sherwood number defined by Eq. (5)
 t : time
 t^*, t_g^*, t_p^* : dimensionless times defined by Eqs. (3), (26), and (33), respectively
 T : temperature
 $\underline{u}$: bulk velocity vector
 v_1, v_2 : net forward rates of reactions (51A) and (51B), respectively, per unit volume of the solid mixture including the pore space
 V_g, V_p : volume of a grain or the pellet, respectively
 w : local fraction conversion of solid reactant
 x_i : mole fraction of species i
 X : overall fractional conversion of solid reactant
 Z : volume of product solid formed from unit volume of reactant solid

Greek Letters

α_B, α_D : fractions of pellet volume initially occupied by solid reactants B and D, respectively
 δ : boundary layer thickness
 ε : porosity
 θ : volume change parameter defined by Eq. (12)

- v : number of gaseous products formed from one mole of gaseous reactant
 ρ_B, ρ_D : true molar densities of solids B and D, respectively
 $\hat{\sigma}, \hat{\sigma}_g, \hat{\sigma}_N, \hat{\sigma}_s$: fluid-solid reaction moduli defined by Eqs. (27), (39), (34), and (4), respectively
 ψ_i : dimensionless concentration of fluid species i defined by Eqs. (43A) and (43B)

Subscripts

- A, C : fluid species A and C, respectively
 b : bulk stream value
 B, D : solid species B and D, respectively
 i : species i , or based on initial conditions

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