Approximate Closed-Form Solutions to Various Model Equations for Fluid-Solid Reactions

H. Y. Sohn, P. C. Chaubal
Department of Metallurgy and
Metallurgical Engineering
University of Utah
Salt Lake City, UT 84112

Fluid-solid reactions occupy an important position in the chemical and metallurgical industries. Considerable interest in mathematical modeling of these systems has hence been generated in recent years. Most of the previously described models may be classified into the following three groups:

1. The shrinking unreacted-core model for an initially nonporous solid producing a porous product layer (Szekely et al., 1976).
2. The grain model for an initially porous solid made up of fine particles (grains) producing a porous product layer (Sohn and Szekely, 1972, 1973a, b, 1974).
3. The pore models for an initially porous solid, which consider the porous solid to be made up of pores in a continuous solid phase (Petersen, 1957; Ramachandran and Smith, 1977; Bhatia and Perlmutter, 1980, 1981; Gavalas, 1980).

The unreacted shrinking-core model is the simplest and easiest to solve. Other models generally require a numerical solution to obtain the conversion vs. time relationship. Hence, in dealing with multiparticle systems, the complexity of the solution increases drastically. One of the present authors (Sohn, 1978) has proposed the law of additive reaction times for isothermal fluid-solid reactions, which produces a relatively simple approximate solution to the governing equations, thus greatly reducing the need for numerical solutions.

For an isothermal reaction, the law of additive reaction times states that

$$\begin{array}{l} \text{Time required to} \\ \text{attain certain} \\ \text{conversion} \end{array} \simeq \begin{array}{l} \text{Time required to attain} \\ \text{the } \textit{same} \text{ conversion in the} \\ \text{absence of the resistance} \\ \text{due to intrapellet diffusion} \\ \text{of fluid reactant} \end{array} + \begin{array}{l} \text{Time required to attain} \\ \text{the same conversion} \\ \text{under the control of} \\ \text{intrapellet diffusion} \end{array} \quad (1)$$

This law has been applied to grain models for single fluid-solid reactions with various rate expressions in terms of solid conversion (Sohn and Szekely, 1972, 1973b, 1974; Sohn, 1978, 1981; Sohn and Kim, 1984) as well as simultaneous fluid-solid reactions (Sohn and Braun, 1980, 1984). It was also found to be applicable to gas-solid reactions with volume change in the gas phase (Sohn and Sohn, 1980; Sohn and Bascur, 1982).

It is the purpose of this note to present the results of applying the law to a random-pore model (Bhatia and Perlmutter, 1981) and to compare the same with a collocation solution of the model equations (Ramachandran and Kulkarni, 1980):

$$D_e \nabla^2 C_A - \alpha_B \rho_B (1 - \omega) k_A C_A = 0 \quad (2)$$

$$\frac{\partial \omega}{\partial t} = b k_A C_A (1 - \omega) \quad (3)$$

for the reaction between a fluid and a porous solid represented by the following general equation:

$$A(f) + b \cdot B(s) = C(f) + d \cdot D(s) \quad (4)$$

Application of the Law to the Random-Pore Model

The random-pore model (Bhatia and Perlmutter, 1980, 1981) assumes the solid to be made up of cylindrical pores of various diameters in a solid matrix. The reaction starts at the surface of the pores in the solid. As the reaction proceeds, a layer of product is formed around each pore. For the reaction to proceed, the reactant gas must diffuse through the pores to the surface of the product solid and then through the product layer to the reaction surface. The model also accounts for intersection of neighboring reaction surfaces as the product layer grows.

The authors were able to obtain analytical solutions relating conversion and time for two cases: when chemical reaction kinetics are controlling, and when chemical reaction kinetics and product layer diffusion, but not intrapellet diffusion, are controlling. The relative importance of chemical reaction rate and product layer diffusion is described by β, the modified Biot number. When intrapallet diffusion and/or external mass transfer are important, a numerical solution is necessary.

Mathematically, the law of additive reaction times stated in Eq. 1 is expressed as follows when all parameters remain constant during the reaction (Sohn, 1978):

$$t_N^* \simeq t_N^*|_{\hat{\sigma}_N \to 0} + t_N^*|_{\hat{\sigma}_N \to \infty} \tag{5}$$

where

$$t_N^*|_{\hat{\sigma}_N \to \infty} = \hat{\sigma}_N^2 \left[p_{F_p}(X) + \frac{2X}{Sh^*} \right] \tag{6}$$

$$p_{F_p}(X) = X^2 \qquad F_p = 1 \tag{7}$$

$$= X + (1 - X)\ln(1 - X) \qquad F_p = 2 \tag{8}$$

$$= 1 - 3(1 - X)^{2/3} + 2(1 - X) \qquad F_p = 3 \tag{9}$$

$$\hat{\sigma}_N = \frac{V_p}{A_p} \sqrt{\frac{\alpha_B \rho_B F_p k}{2bD_e}\left(1 + \frac{1}{K}\right)} \tag{10}$$

It is noted that when $\hat{\sigma}_N \to 0$, intrapellet diffusion is extremely rapid, and when $\hat{\sigma}_N \to \infty$, intrapellet diffusion is rate-controlling. When the effect of intrapellet diffusion and external mass transfer is negligible, Bhatia and Perlmutter (1981) obtained the following for the random-pore model:

$$t_N^*|_{\hat{\sigma}_N \to 0} = \left\{ \sqrt{\frac{\beta z}{\psi}\left[\frac{1}{\psi} - \ln(1 - X)\right] + \frac{1}{\sqrt{\beta z}}} - \frac{\sqrt{\beta z}}{\psi} \right\}^2 - \frac{1}{\beta z} \tag{11}$$

In the above expression, β is the modified Biot number, z is the volume of product formed from unit volume of reactant, and ψ is a structural parameter dependent on the initial pore characteristics, namely L_o, the length, and S_o, the surface area of the pores. For common porous solids, Bhatia and Perlmutter (1980) found that $\psi = 1$, which corresponds approximately to the grain model with $m = 2/3$ (Szekely et al., 1976).

Equation 6 has been derived based on the assumption of constant diffusivity. In the random-pore model (Bhatia and Perlmutter, 1981), the effect of pore structure on the diffusivity of the gaseous species is described by the following equation:

$$D_e = D_{eo}\left[1 - \frac{(z - 1)(1 - \epsilon_o)X}{\epsilon_o}\right]^2 \tag{12}$$

In order to incorporate Eq. 12 in the expression for $t_N^*|_{\hat{\sigma}_N \to \infty}$, we used the differential form of Eq. 6:

$$\frac{dt_N^*}{dX} = \hat{\sigma}_N^2 \left[p'_{F_p}(X) + \frac{2}{Sh^*} \right] \tag{13}$$

Combining Eqs. 10, 12, and 13, we have

$$\frac{dt_N^*}{dX} = \hat{\sigma}_N^2 \left\{ \frac{p'_{F_p}(X)}{\left[1 - \frac{(z - 1)(1 - \epsilon_o)X}{\epsilon_o}\right]^2} + \frac{2}{Sh^*} \right\} \tag{14}$$

with D_e in the expression for $\hat{\sigma}_N$ and Sh^* being replaced by D_{eo}.

For the random-pore model, Eq. 6 hence becomes

$$t_N^*|_{\hat{\sigma}_N \to \infty} = \frac{\phi^2}{6(1 - \epsilon_o)} \cdot \left\{ \int_o^X \frac{p'_3(X)dX}{\left[1 - \frac{(z - 1)(1 - \epsilon_o)X}{\epsilon_o}\right]^2} + \frac{2X}{Sh^*} \right\} \tag{15}$$

where ϕ, the Thiele modulus, is related to the gas-solid reaction modulus $\hat{\sigma}_N$ by

$$\phi^2 = 6\hat{\sigma}_N^2 \tag{16}$$

The integral in Eq. 15 was evaluated by Adam's method of stepwise integration (Atkinson, 1978). Although the law of additive reaction times does not provide a closed-form solution to the random-pore model, the numerical evaluation of the integral is much easier than that of the differential equation of the random-pore model, which is necessary when both chemical reaction and mass transport affect the overall rate. Furthermore, $z \simeq 1$ for most practical systems, in which case the integral in Eq. 15 reduces to $p_3(X)$ (Eq. 6), and a closed-form approximation is obtained.

In Figures 1–3, the conversion vs. time relationship obtained from the exact solution of the model equations is compared to that from the approximate solution obtained by substituting Eqs. 11 and 15 in Eq. 5. Figure 1 shows the comparison for various values of the Thiele modulus. Good agreement exists between the approximate and exact solutions, especially for values of ϕ between 3 and 5. The maximum error obtained for $\phi = 1$ is only about 15%.

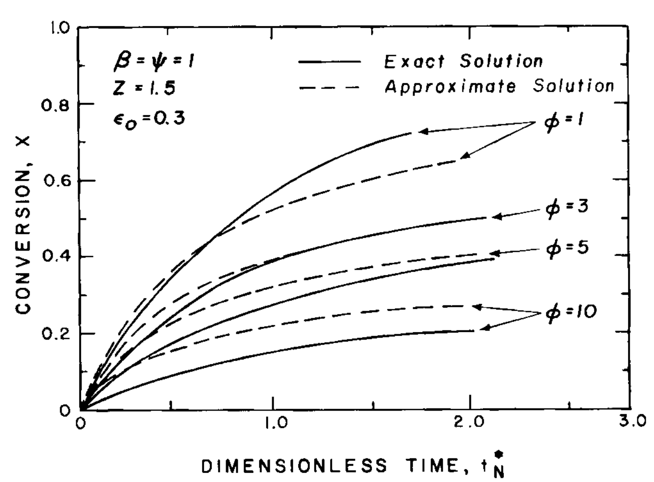

Figure 1. Comparison of exact and approximate solutions for random-pore model.
Effect of the Thiele modulus ($\beta = \psi = 1$).

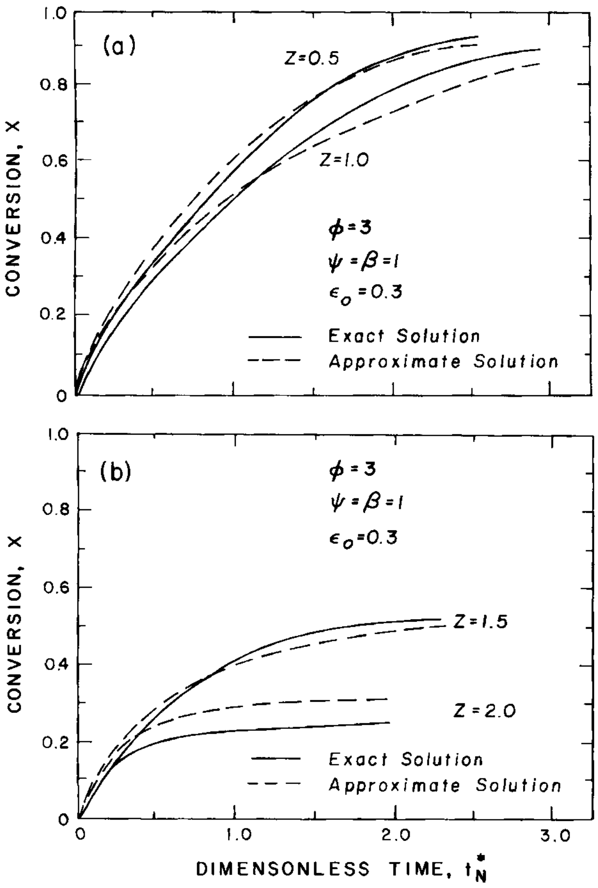

Figure 2. Comparison of exact and approximate solutions for random-pore model.
a. $z = 0.5, 1.0$
b. $z = 1.5, 2.0$ ($\phi = 3.0, \beta = \psi = 1.0$)

Figure 2 shows that the solution based on the law of additive times closely approximates the actual solution, especially for $z < 1.5$. Figure 3 shows the comparison for various values of Sh^*. The approximation represents the exact solution equally well in this case.

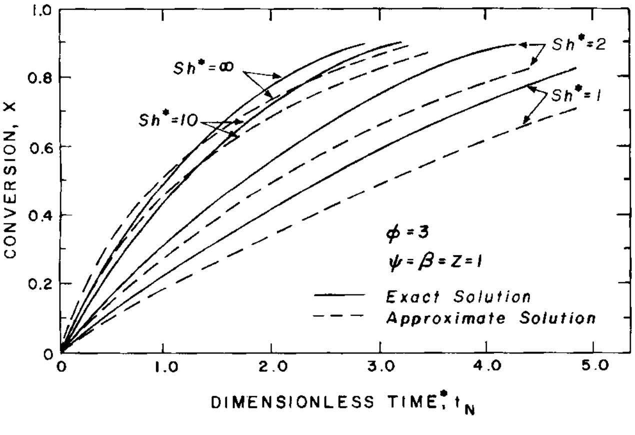

Figure 3. Comparison of exact and approximate solutions for random-pore model for various values of modified Sherwood number.

When $\psi = 1$, the rate of reaction decreases monotonically. The law of additive reaction times has been shown to yield satisfactory approximations for other types of conversion curves (Sohn, 1978, 1981).

Law of Additive Reaction Times vs. Single-Point Collocation Solution

Recently, Ramachandran and Kulkarni (1980) obtained an approximate analytical solution for Eqs. 2 and 3, which describe an isothermal gas-solid reaction that is first-order with respect to the solid as well as gaseous reactant concentrations and in which structural changes and external mass transfer effect are negligible. The authors used single-point collocation on the cumulative gaseous reactant concentration and obtained the following implicit analytical solution relating overall conversion and time:

$$\ln\left[\frac{1-X}{w_1(1+\beta^*)} - \frac{w_2}{w_1}\exp(-t_N^*)\right] + t_N^* = \frac{\phi^2}{B_{12}}\left[1 - \frac{(1-X)}{w_1(1+\beta^*)} + \frac{w_2}{w_1}\exp(-t_N^*)\right] \qquad (17)$$

In the above equation w_1 ($=0.233$) and w_2 ($=0.1$) are the collocation weights, B_{12} ($=10.5$) is a collocation constant, and β^* ($=2$) is the geometry factor for the pellet. The values given in parentheses are for a spherical geometry. In Eq. 17, ϕ is the Thiele modulus and is related to $\hat{\sigma}_N$, the gas-solid reaction modulus, as shown in Eq. 16.

The equivalent solution using the law of additive reaction times is

$$t_N^* = g_N(X) + \hat{\sigma}_N^2 p_3(X) \qquad (18)$$

with

$$g_N(X) = -\ln(1-X) \qquad (19)$$

The approximate solutions by the collocation technique and the law of additive reaction times are compared with the exact solution in Figures 4a and 4b. For small values of $\hat{\sigma}_N$ ($\simeq 0.3$), i.e., in the chemical-control regions, both solutions are almost exact. When intrapellet diffusion becomes dominant ($\hat{\sigma}_N > 10.0$), the law of additive reaction times again approaches the exact solution, whereas the single-point collocation solution deviates considerably. When $\hat{\sigma}_N$ is between 0.3 and 10.0, i.e., in the region of mixed control, the collocation solution is only marginally better. The law of additive reaction times hence gives a superior approximation over the entire range of $\hat{\sigma}_N$ values.

Furthermore, the collocation solution, Eq. 17, is implicit in both conversion and time and hence must be solved numerically. Additionally, unlike Eq. 18, Eq. 17 cannot be rearranged to give the instantaneous rate (dX/dt^*) as a function of solid conversion. The expression of conversion rate as a function of reaction parameters is necessary and useful for describing multiparticle systems in which fluid concentration and temperature vary in time and space (Sohn, 1978, 1981; Sohn and Braun, 1980, 1984). Moreover, it would be difficult to incorporate the effect of external mass transfer into Eq. 17, whereas Eq. 18 has it already built in.

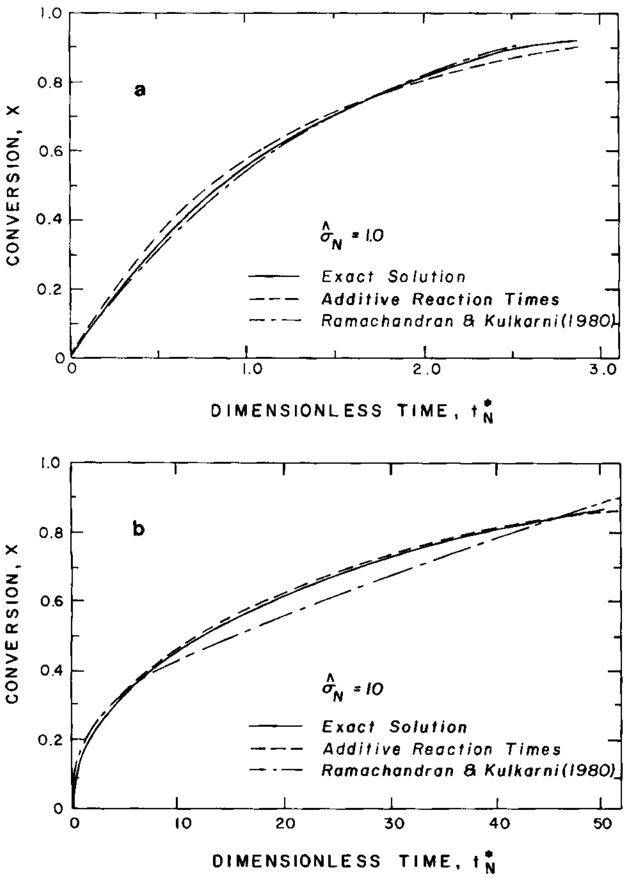

Figure 4. Comparison of exact solution with approximate solution obtained by application of the law of additive reaction times and a collocation solution.

a. $\hat{\sigma}$ = 1.0 b. $\hat{\sigma}$ = 10.0

Additional Remarks

The comparisons shown in this note are mainly for intermediate values of ϕ or $\hat{\sigma}_N$ where both chemical kinetics and pore diffusion play an important role in determining the overall rate. These represent the cases in which the approximate solution gives the largest error. As ϕ or $\hat{\sigma}_N$ becomes smaller or larger, the approximate solution is expected to yield better results.

The law of additive reaction times, previously formulated and tested for the shrinking-core and grain models, has thus been shown to give an approximate solution for the random-pore models. This result enhances the conclusion (Sohn, 1978, 1981) that the approximate solution is applicable regardless of the shape of the conversion curve. For the most common situation, $z = 1$, a closed-form solution is obtained, which is most useful in the analysis of multiparticle systems. The law has also been shown to compare favorably with a recently proposed collocation solution.

In this work, further verification of the usefulness of the law of additive reaction times has thus been made.

Notation

A_p = external surface area of pellet
b = moles of solid reacted per mole of gaseous reactant
C_A = concentration of gaseous reactant
D_e, D_{eo} = effective diffusivity of gaseous species in porous solid and its initial value, respectively
D_p = effective diffusivity in product layer
F_p = shape factor for pellet, = 1, 2, 3 for flat plates, long cylinders, and spheres, respectively
k = reaction rate constant
k_m = external mass transfer coefficient
K = equilibrium constant
L_o = total length of overlapped pore system at $t = 0$
$p(X)$ = conversion function, Eqs. 4–6
S_o = overall reaction surface per unit volume at $t = 0$
Sh^* = modified Sherwood number, $(k_m/D_{eo})(F_pV_p/A_p)$
t = time
t_N^* = dimensionless reaction time, $k\,C^nS_ot/(1-\epsilon_o)$
V_p = volume of the pellet
X = overall fractional conversion of solid reactant
z = volume of product solid formed from unit volume of reactant solid

Greek letters

α_B = fraction of pellet volume initially occupied by solid reactant B
β = modified Biot number, $[2k\rho_B(1-\epsilon_o)]/bD_pS_o$
ϵ_o = porosity at $t = 0$
ρ_B = true molar density of solid reactant B
$\hat{\sigma}_N$ = gas-solid reaction modulus, Eq. 7
ϕ = Thiele modulus
ψ = structural parameter, $4\pi L_o(1-\epsilon_o)/S_o^2$
ω = local fractional conversion

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