Kinetic Invariant Model of Dissolution with Chemical Reaction of Large Particles

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The kinetic invariant model has been reformulated and an approximate analytical form of a kinetic function is obtained for the dissolution accompanied by a chemical reaction of large solid particles. A restriction on the analytical solution is provided in the form of a sufficient condition for the convergence of the series involved. Expressions for the concentration of unreacted, dissolved solid reactant, the time of complete conversion, and the ratio of driving forces available for the reaction and mass transfer steps are presented. Solutions for the rate-limiting regimes are deduced as special cases of the general solution. The small-particle solution is recovered as a special case in the limit of a vanishingly small Reynolds number. Rigorous numerical solution has been obtained to assess the accuracy of the pseudostationary-state solution and to discern the validity of the approximations.

Introduction

Dissolution of solids in liquids is a commonly encountered physical operation in chemical engineering practice. Often, the dissolved solid reactant also undergoes a chemical reaction with either the liquid phase itself or another component dissolved in it. A homogeneous catalyst is frequently incorporated into the liquid phase to enhance the rate of reaction and/or to promote the selective yield of a desired product.

Kinetics of the reactive dissolution of solid particles in liquids is often described by the method of invariant functions (Vidgorchik and Shein, 1971). This method is applied usually to inorganic (Kurtasova et al., 1980) and electrochemical (Gorichev et al., 1981) processes. It has been used recently for description of the kinetics of a complex multiphase process of organic synthesis (Sidorov et al., 1986). Approximate analytical and rigorous numerical solutions of a comparatively more logical kinetic invariant model are available now for the dissolution of very fine monodisperse (Bhaskarwar, 1988) and polydisperse (Bhaskarwar, 1989) solid particles under the conditions of negligible slip velocity between the particles and liquid phase. This article extends the kinetic invariance analysis to the more practical case of large, monodisperse solid particles with their significant characteristic slip velocities.

Background of Fluid-Solid Reactions and Dissolution Kinetics

The diffusion-reaction equations governing the fluid-solid reactions frequently are not amenable to analytical procedures that could lead to general solutions. The pseudosteady-state approximation is, therefore, commonly employed, especially for the gas-solid reactions (Bischoff, 1963; Luss, 1968; Sidorov et al., 1986; Bhaskarwar, 1988, 1989). In general, the afore-stated approximation may be valid for the gas-solid reacting systems, but not always for the liquid-solid systems (e.g., ion exchange). As a consequence of analytical difficulties, numerical solutions have been obtained by Wen (1968) and for the kinetic invariant model by Bhaskarwar (1988).

The common formulation is the one based on the unreacted-core or shell-progressive model. Actually, the particles may either change in size or may not, depending on the nature of the particular chemical system. The situation involving a variable particle size is quite complex from the point of view of analysis, especially when diffusion is the rate-controlling step. The problem is, therefore, approached semiempirically and fairly complex relationships result (Ranz and Marshall, 1952; Carberry, 1976; Froment and Bischoff, 1979; Levenspiel, 1972). LeBlanc and Fogler (1987) described the rate-limiting regimes in the dissolution of polydisperse particulates. Under certain circumstances, different possible controlling steps might be in a concurrent action (Bischoff, 1963; Sidorov et al., 1986; Bhaskarwar, 1988, 1989).

Nonisothermal fluid-solid reactions have also received the attention of some researchers (Carberry, 1976; Luss and Amundson, 1969). Experimental data on fluid-solid reactions have been reported by: Endom and Lehmann (1965) for the reduction of magnetite and Fe_3O_4 by hydrogen; Vandenbussche (1966) for the fluorination of uranium oxide or plutonium oxide; Habashi and Thurston (1967) for the dissolution of UO_2 in sulfuric acid solutions; and Bretsnajder and Piskorski (1967), for the formation of polysulfides in leaching of sulfur from ores with ammonium sulfide. Many of these results have been tabulated in the *Chemical Engineers Handbook* (Perry and Chilton, 1973).

Rice and Jones (1979) presented a theoretical analysis to predict the time required for the complete dissolution of a spherical particle during its free fall in a diffusion-controlled environment. A correction for the transpiration effect has also been proposed by Rice (1982). The theory was compared with the physical dissolution data on urea particles disappearing in water.

Ballesteros et al. (1982) summarized the results of the analysis of mass transfer rates in liquid fluidization of spherical particles. Tournie et al. (1979) published an experimental correlation of a large range of validity and another simplified one implying no influence of Reynolds number on the mass transfer kinetics. Their experimental finding is that for liquid fluidized systems the mass transfer coefficient depends neither on the liquid velocity nor on the particle diameter, but only on the physico-chemical properties of the system. Thus, for a given solid-liquid system at the constant temperature, the mass transfer coefficient remains constant. This characteristic feature of fluidized systems has been confirmed by Riba and Couderc (1980) and by Chhun and Couderc (1980) at high concentration and mass flux, while Panier et al. (1980) corroborated it with partially active spheres.

Yagi et al. (1983) observed that the mass transfer coefficient and its dependence on agitation decreased with increasing specific surface area of the particles, even though variations in the physical properties were negligible. They explained these tendencies by a theoretical model that considered the interaction of adjacent particles impeding the mass transfer. In a rather sharp contrast, Asai et al. (1988) found that the effect of solid particle concentration on the mass transfer was of little importance in the range of specific area up to at least 3,000 m^2/m^3 of liquid. The particle density and vessel diameter too had negligible effects on the mass transfer coefficient. They provided a new correlation for the mass transfer coefficient and claimed the first quantitative support to the postulate that fine particles may stay in and move together with microeddies.

Kinetic Invariance Theory

Concept

Dissolution accompanied by a chemical reaction, under a variety of operating conditions, can be uniquely represented in terms of a kinetic function ($\omega = 1 - X$) and a dimensionless time ($\theta = t/\tau$), provided the hydrodynamic environment is fixed and its relationship with the mass transfer process is characterized in a definite manner. The specific nature of each set of kinetic conditions is reflected merely in the corresponding time of complete conversion of the solid reactant. Critical appraisal and limitations of this approach are discussed by Bhaskarwar (1988).

Idealization of the physical system

The dissolution of large solid particles occurs, as the particles settle in a stagnant suspension or slip partially with respect to the surrounding liquid in an agitated reactor.

The solid-liquid system is idealized making the following assumptions:

- The nonporous particles are spherical in shape and monodisperse with regard to size.
- The particles are large, and consequently a significant slip velocity exists between any particle and the surrounding liquid. The slip velocity remains constant at its initial maximum value.
- The initial loading of solid particles in the slurry is low.
- The reaction of dissolved solid-phase reactant and liquid-phase reactant is irreversible. It is first-order in the solid reactant and the homogeneous catalyst, and zero-order in the liquid reactant that is present in a large excess.

Model

The governing equations in terms of the kinetic function are:

$$d\omega/d\theta = -[6K_{LS}Md_p^2\tau/\rho d_0^3](C^* - C) \tag{1}$$

$$d_p = d_0\omega^{1/3} \tag{2}$$

$$dC/d\theta = -C_0\, d\omega/d\theta - K_r\tau Z_0 C \tag{3}$$

The mass transfer coefficient for the liquid film surrounding a large particle can be obtained from the Frösling equation (Ranz and Marshall, 1952),

$$Sh = 2.0 + 0.6\, Re^{1/2}Sc^{1/3} \tag{4}$$

as

$$K_{LS} = (2.0D/d_p) + 0.6\,(Re^{1/2}Sc^{1/3}D/d_p) \tag{5}$$

Note that the leading coefficient in Eq. 4 equals 2 for small spheres and cubes, $2\sqrt{6}$ for tetrahedrons, and $2\sqrt{2}$ for octahedrons (Ohara and Reid, 1973).

Equations 1, 2 and 5 are combined to obtain

$$d\omega/d\theta = -a'\tau(2D\omega^{1/3} + C'\omega^{1/2})(C^* - C) \tag{6}$$

where

$$a' = 6.0\, M/\rho d_0^2$$

and

$$C' = 0.6\, Re_0^{1/2}Sc^{1/3}D$$

Equations 6 and 3 constitute the system of differential equations governing the dissolution process. The appropriate boundary conditions for this system are:

$$\theta = 0; \quad \omega = 1; \quad C = 0 \tag{7}$$

$$\theta = 1; \quad \omega = 0 \tag{8}$$

Eliminating C between Eqs. 3 and 6, integrating the resulting equation after some rearrangement, and incorporating condition 7, we obtain

$$C=(1-\omega)C_0-K_r\,Z_0\,\tau C^*\theta + [3K_rZ_0/Da']\sum_{n=0}^{\infty}[(-1)^n C''^n/(n+4)](1-\omega^{(n+4)/6}) \tag{9}$$

where

$$C''=C'/2D$$

This is an exact analytical relationship among C, ω, and θ. Further progress toward obtaining the exact forms of $C(\theta)$ and $\omega(\theta)$, is, however, precluded by the nonlinearity of the ordinary differential equations governing their transience.

Pseudostationary-state solution

An approximate analytical solution of Eqs. 6 and 3 subject to conditions 7-8 is, therefore, obtained by making an assumption of a pseudostationary state, $dC/d\theta=0$. Efficacy of this assumption was illustrated in the earlier work (Bhaskarwar, 1988). Elimination of C from Eqs. 6 and 3 in view of the aforestated assumption leads one to

$$d\omega/d\theta+\frac{[a'\tau(2D\omega^{1/3}+C'\omega^{1/2})C^*]}{[1+a'(2D\omega^{1/3}+C'\omega^{1/2})C_0/K_rZ_0]}=0 \tag{10}$$

Equation 10 is a nonlinear, first-order, ordinary differential equation with separable variables. Employing the binomial expansion after separating the variables and a straightforward integration, one obtains

$$\theta=\frac{[(3/D)\sum_{n=0}^{\infty}[(-1)^nC''^n/(n+4)](1-\omega^{(n+4)/6})+a'C_0(1-\omega)/K_rZ_0]}{a'C^*\tau} \tag{11}$$

where

$$\tau=\frac{[(3/D)\sum_{n=0}^{\infty}(-1)^nC''^n/(n+4)+a'C_0/K_rZ_0]}{a'C^*} \tag{12}$$

Equation 12 gives the time of complete conversion of the solid reactant. Convergence of the series, hence applicability of the analytical solution, depends on the values of parameters involved, Re_0 and Sc. Application of the theorem constituting the Leibniz test for real series involving terms with alternating signs (Kreyszig, 1972) leads us to the following condition sufficient for convergence of the series in Eq. 12:

$$Re_0\leq 11.1111\ Sc^{-2/3} \tag{13}$$

Furthermore, the convergence of the series in Eq. 11 is guaranteed by condition 13 because of the presence of an additional factor, involving ω which assumes magnitudes less than unity for all the values of the index n.

The concentration of the dissolved unreacted solid reactant is:

$$C=\frac{a'(2D\omega^{1/3}+C'\omega^{1/2})C^*}{[K_rZ_0/C_0+a'(2D\omega^{1/3}+C'\omega^{1/2})]} \tag{14}$$

The ratio of the driving forces used up by the chemical reaction and mass transfer steps is

$$\lambda=C/(C^*-C) \tag{15}$$

Combination of Eqs. 14 and 15 results in

$$\lambda=a'(2D\omega^{1/3}+C'\omega^{1/2})/\alpha \tag{16}$$

where

$$\alpha=K_rZ_0/C_0$$

Unilateral reductions to rate-limiting regimes

Diffusion-Controlled Regime. Under conditions of this regime, $C\ll(C^*-C)$. This implies that

$$\lambda\to 0 \tag{17}$$

Equation 16 in the limit (Eq. 17) indicates that

$$\alpha\to\infty \tag{18}$$

Simplifying Eqs. 11-12 in view of the limit (Eq. 18), we obtain

$$\theta=\frac{\sum_{n=0}^{\infty}[(-1)^nC''^n/(n+4)](1-\omega^{(n+4)/6})}{\sum_{n=0}^{\infty}[(-1)^nC''^n/(n+4)]} \tag{19}$$

Kinetically Controlled Regime. In this regime, we have $(C^*-C)\ll C$. This in turn implies the following limits:

$$\lambda\to\infty \tag{20}$$

and

$$\alpha\to 0 \tag{21}$$

Limit (Eq. 21) of Eqs. 11-12 yields

$$\theta=1-\omega \tag{22}$$

Notably, the form of the kinetic function in the kinetically controlled regime is the same as that obtained in the previous works (Sidorov et al., 1986; Bhaskarwar, 1988).

Special Case of Very Small Particles. For very fine solid particles, the slip velocity is negligible and therefore

$$C'' \to 0 \tag{23}$$

Equations 11 and 12 in conjunction with the limit (Eq. 23) show that

$$\theta = E\,(1-\omega^{2/3}) + B(1-\omega) \tag{24}$$

where

$$E = \alpha'/(1+\alpha') \tag{25}$$

$$B = 1 - E \tag{26}$$

and

$$\alpha' = (K_r Z_0 \rho d_0^2)/(8C_0 MD) \tag{27}$$

Equations 24-27 coincide with the results obtained earlier (Bhaskarwar, 1988) and inductively imply the correctness of the more general expressions developed in this work.

Rigorous numerical solution

A rigorous numerical solution has been obtained to provide a standard, against which the approximate solution may be compared. It also provides the information contained in the actual governing equations, such as the rigorous features of their true solution if it does exist.

A shooting method described earlier by Bhaskarwar (1988) has been used for solving the nonlinear, two-point boundary value problem, posed by the primitive equations (Eqs. 6 and 3) and conditions 7-8, employing a fourth-order Runge-Kutta algorithm with modification due to Gill (the system subroutine: DRKGS from SSP Library on DEC-1090). For the sake of computational convenience, the following transformation has been used.

$$\eta = \omega^{1/6} \tag{28}$$

Table 1. Basic Set of Parameters Used in Computing Kinetic Invariant Plots

Sl No.	Parameter	Value
1	Equiv. conc. of solid reactant at initial loading, C_0	10 kmol/m^3
2	Specific reaction velocity constant, K_r	1 m^3/kmol·s
3	Conc. of homogeneous catalyst in liquid phase, Z_0	10 kmol/m^3
4	Equilib. conc. at solid-liquid interface, C^*	1 kmol/m^3
5	Molec. wt. of solid, M	100
6	Density of solid, ρ	5,000 kg/m^3
7	Initial dia. of solid particles, d_0	0.01 m

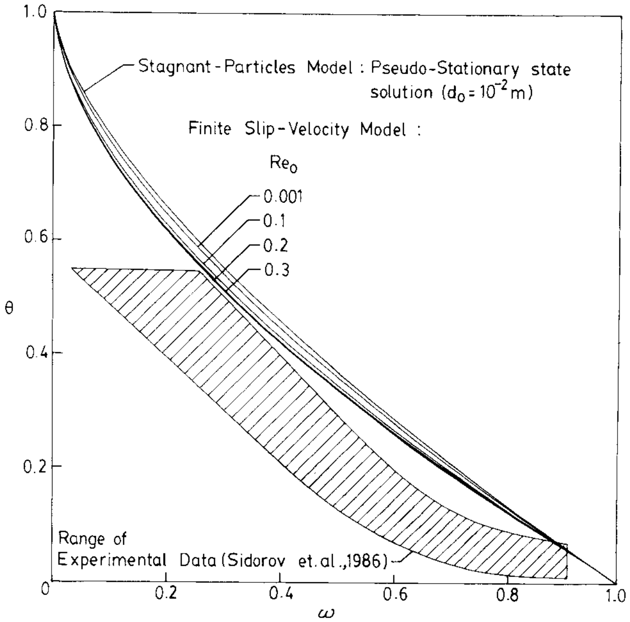

Figure 1. Kinetic invariant plots vs. experimental dissolution data.

The governing system of transformed equations is

$$d\eta/d\theta = -(a'\tau/6)[(2D + C'\eta)/\eta^3](C^* - C) \tag{29}$$

$$dC/d\theta = -6C_0\,\eta^5(d\eta/d\theta) - K_r\tau Z_0 C \tag{30}$$

$$\theta = 0;\ \eta = 1;\ C = 0 \tag{31}$$

$$\theta = 1;\ \eta = 0 \tag{32}$$

The required values of the kinetic function ω are easily recovered from the numerical solution obtained in terms of the transformed variable η using Eq. 28.

Phase plane analysis

The autonomous system of two first-order ordinary differential equations (Eqs. 1 with 2) and Eq. 3 subject to the initial condition (Eq. 7) has been solved in the phase plane using PHASER (Kocak, 1985) which is an animator/simulator for dynamical systems.

Results and Discussion

Computations of θ vs. ω profiles have been carried out for a number of values of Schmidt number in the range (1,200). The Reynolds number based on the initial particle size is chosen as a parameter. It is varied in the ranges restricted by the convergence-limited critical values given by Eq. 13. The values of other parameters are shown in Table 1. A typical set of kinetic invariant plots, θ vs. ω, is presented in Figure 1.

The predictions of the present theory are in an improved agreement with the experimental data of Sidorov et al. (1986) in comparison to those of the previous model (Bhaskarwar, 1988), which had completely neglected the slip velocity existing between the particulate and liquid phases. The increase in the rate of mass transfer with the initial Reynolds number is indicated in this case by the downward shift of the $\theta\omega$ curves. A rigorous numerical solution could not be obtained for $d_0 = 10^{-2}$ m due to a failure in achieving an iterative convergence in the integration. Under the chosen conditions, however, the effect of particle size on the solution is expected to be weak, because these conditions indicate a predominantly diffusion-controlled mass transfer and Eq. 19 implies the independence of the kinetic function with respect to d_0 at a fixed value of the initial Reynolds number. Regarding this observation as a working hypothesis, the numerical solution has been obtained for $d_0 = 10^{-4}$ m. It coincides with the coincident pseudostationary-state solutions (corresponding to $Re_0 = 0.3$) in Figure 1 for both $d_0 = 10^{-2}$ m and 10^{-4} m. This agreement, therefore, confirms the validity of the pseudostationary-state solution.

A comparison of the ratio of the driving forces, λ, predicted by the two models—the stagnant-particles model and finite slip-velocity model—is presented in Figure 2. It shows that the assumption of pseudostationary-state is reflected much stronger in the predictions of the finite slip-velocity model than in those of the former. Another interesting feature worth noting here is the maximum in the $\lambda\theta$ plane that is brought out by the rigorous numerical solution. This peak is absent in the approximate pseudostationary-state solution. The presence of the maximum in the $\lambda\theta$ plane can be explained easily by considering the trends of variations of the individual driving forces for the reaction and mass transfer steps (Bhaskarwar, 1988).

Figure 3 illustrates the phase portrait of the kinetic invariant model with C on the ordinate and ω on the abscissa axis, respectively. As ω decreases continuously (and monotonically), C undergoes an excursion from the initial zero value showing a sharp maximum very near $\omega = 1.0$. As ω tends to be zero, C continues to decrease from its instantaneous nonzero value corresponding to $\theta = 1.0$. This first-order decay of concentration of the unreacted dissolved solid beyond the moment of disappearance of particles is represented by the vertical fall at $\omega = 0.0$. The origin ($\omega = 0.0$, $C = 0.0$) is a stable node, and any phase plane trajectory necessarily gets attracted to it in an asymptotically linear fashion. The trajectory after entering the node remains trapped motionless in this singularity for an infinite time (corresponding to the situation of complete reaction of the dissolved solid reactant).

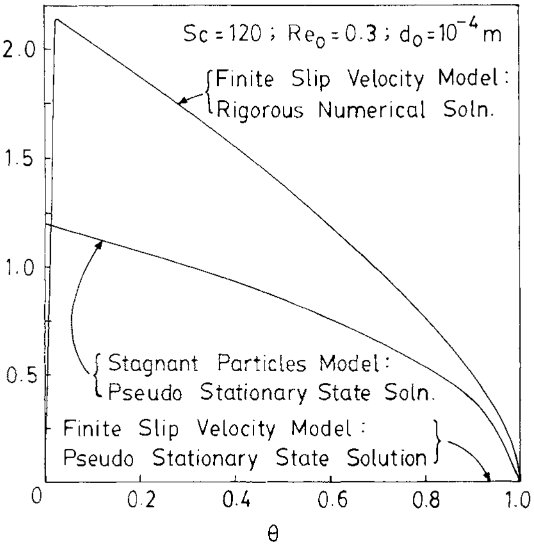

Figure 2. Pseudostationary-state solutions vs. rigorous numerical solution of the finite slip velocity model.

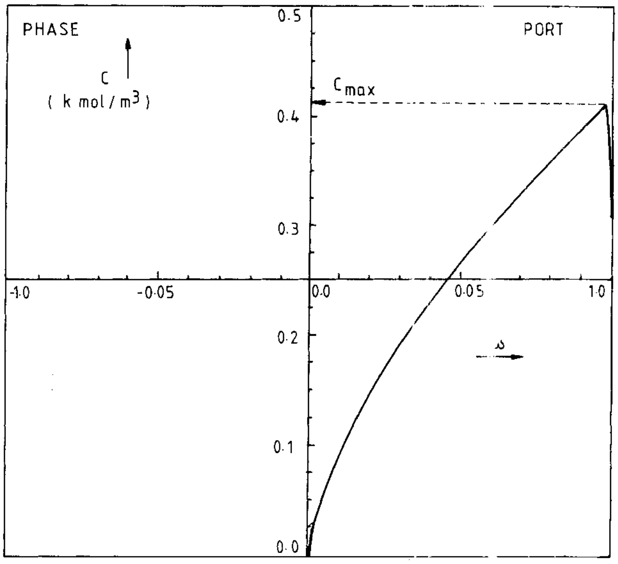

Figure 3. Phase portrait of the kinetic invariant model.

In certain cases, the restriction on Re_0 (Eq. 13) may become a serious limitation on the use of this pseudostationary-state solution. Nonexistence of the expressions for integrals in terms of the elementary functions or standard special functions, such as that encountered in this investigation, suggests the use of restricted analytical solutions with their validity confirmed by the numerical technique, as one of the judicious choices left in the endeavor to save the analytical insight and the computational time.

Conclusions

The general approach of kinetic invariant description of dissolution which accounts for the slip velocity of particles, improved its agreement with the comprehensive experimental data by Sidorov et al. (1986). Although the logical consistency of the theory was preserved it is still not possible to predict the data accurately (Sidorov-Gluzman-Ivanova-Vulakh paradox). Perhaps, the key to this riddle lies in the appropriate theoretical analysis of diffusion from particles suspended in turbulent fluids, notably as has been attempted by Levich (1962).

This kind of investigation may settle the two issues simultaneously: 1. the kinetic invariant model could be refined further through a more rigorous consideration of the flow field under turbulent conditions; and 2. Levich's (or similar) approach could also be confirmed in its essentially quantitative features.

Notation

a' = constant defined in Eq. 6
B = constant defined in Eq. 26
C = concentration of dissolved solid reactant in the bulk liquid, kmol/m³
C' = constant defined in Eq. 6
C'' = constant defined in Eq. 9

C^* = equilibrium concentration at solid-liquid interface, kmol/m^3
C_0 = equivalent concentration of solid reactant at initial loading, kmol/m^3
d_p = instantaneous diameter of a solid particle, m
d_0 = initial diameter of a solid particle, m
D = diffusion coefficient of solid reactant dissolved in liquid, m^2/s
E = constant defined in Eq. 25
K_{LS} = mass transfer coefficient for liquid film at the particle surface, m/s
K_r = specific reaction velocity constant, m^3/kmol·s
M = molecular weight of reactant solid
n = index in series
Re = instantaneous Reynolds number
Re_0 = Reynolds number based on initial diameter of a solid particle
Sc = Schmidt number
Sh = Sherwood number
t = time, s
X = fractional conversion
Z_0 = concentration of the homogeneous catalyst dissolved in liquid, kmol/m^3

Greek letters

α = constant defined in Eq. 16
α' = constant defined in Eq. 27
η = transformation defined in Eq. 28
θ = dimensionless time ($=t/\tau$)
λ = ratio of driving forces available for reaction and mass transfer steps
ρ = density of solid, kg/m^3
τ = time of complete conversion of solid reactant, s
ω = kinetic function ($=1-X$)

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Appendix

The kinetic invariance analysis can be generalized further in view of the fact that most of the mass transfer correlations available in the literature relevant to a solid-liquid system can be expressed in the following generalized form:

$$Sh = s + p\ \mathrm{Re}^q\ Sc^r \qquad \text{(A1)}$$

Equation 6 would be replaced by the equivalent general equation for the kinetic function.

$$d\omega/d\theta = -a'\tau(sD\omega^{1/3} + C'\omega^{(q+1)/3})(C^* - C) \qquad \text{(A2)}$$

where

$$a' = 6M/\rho d_0 \qquad \text{(A3)}$$

and

$$C' = pRe_0^q Sc^r D \qquad \text{(A3)}$$

The pseudostationary-state solution of Eqs. A2 and A3, subject to the boundary conditions (Eqs. 7 and 8), is

$$\theta = [1/(a'\tau C^*)][(3/sD)\sum_{n=0}^{\infty}(-1)^n C''^n/(qn+2)(1-\omega^{(qn+2)/3})$$

$$+(a'C_0/K_rZ_0)\ (1-\omega)] \tag{A4}$$

where

$$C'' = C'/sD \tag{A5}$$

and

$$\tau = (1/a'C^*)\ [(3/sD)\sum_{n=0}^{\infty}(-1)^n C''^n/(qn+2)$$

$$+a'C_0/K_rZ_0] \tag{A6}$$

The concentration of unreacted dissolved solid in liquid is

$$C = \frac{a'(sD\omega^{1/3} + C'\omega^{(q+1)/3})C^*}{[K_rZ_0/C_0 + a'(sD\omega^{1/3} + C'\omega^{(q+1)/3})]} \tag{A7}$$

The ratio of driving forces available for the reaction and mass transfer is

$$\lambda = (a'/\alpha)\ [sD\omega^{1/3} + C'\omega^{(q+1)/3}] \tag{A8}$$

where

$$\alpha = K_rZ_0/C_0$$

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