velocity and capacity (void space) but not of intraparticle transport rate coefficients.

In contrast, the second central moment does become function of D_{ei}, as in the fixed-bed case. This can be shown by writing μ'_2 as

$$\mu'_2 = \frac{m_2}{m_o} - \left(\frac{m_1}{m_o}\right)^2 \tag{8}$$

where m_1 and m_o are given by Equations (5) and (6), and

$$m_2 = \lim_{s\to 0} \frac{d^2\overline{C}(L,s)}{ds^2} \tag{9}$$

Evaluating m_2 from the solution in the Laplace domain and using the previously obtained results for m_o and m_1, we get

$$\mu'_2 = \left\{\frac{L^2}{6D_e}[\alpha + (1-\alpha)\beta]\right\}^2 \frac{\left(3\dfrac{AD_e}{L} + F\right)^2}{\left(\dfrac{AD_e}{L} + F\right)^2}$$

$$- \frac{L^2}{90D_e}\left(\frac{r_o^2}{D_{ei}}\right)(1-\alpha)\beta^2 \frac{3\dfrac{AD_e}{L} + F}{\dfrac{AD_e}{L} + F}$$

$$- \frac{1}{60}\left\{\frac{L^2}{D_e}[\alpha + (1-\alpha)\beta]\right\}^2 \frac{5\dfrac{AD_e}{L} + F}{\dfrac{AD_e}{L} + F} \tag{10}$$

The second term of Equation (10) gives the contribution of intraparticle diffusion to μ'_2. When the particles are nonporous, $\beta = 0$, Equation (10) becomes identical to that given by Dogu and Smith (1976).

In principle, first moment data could be used with Equation (7) to obtain D_e, and then this result along with data for μ'_2 could be used with Equation (10) to obtain D_{ei}. An accurate result would depend on the second term of Equation (10) being relatively large with respect to the first and third terms. Use of a short pellet (small L) and large particles (large r_o) would favor this situation.

For a linear rate of adsorption on the intraparticle pore surface, the previous development can be readily extended to gases that adsorb as well as diffuse. The rate of adsorption is written

$$\frac{\partial n}{\partial t} = k\left(C_i - \frac{1}{K}n\right) \tag{11}$$

Equation (2) must be modified by adding to the right side the term $\rho(\partial n/\partial t)$. Then the solution of Equations (1) and (2) and Equation (11) gives for the first moment

$$\mu_1 = \frac{L^2}{6D_e}[\alpha + (1-\alpha)(\beta + \rho K)] \frac{3\dfrac{AD_e}{L} + F}{\dfrac{AD_e}{L} + F} \tag{12}$$

As in Equation (7), the bracketed term is a measure of the total capacity of the pellet for the adsorbable gas.

NOTATION

A = area of end face of cylindrical pellet, cm^2
C = concentration of diffusing gas in interparticle region; C_i = concentration in intraparticle region, mole/cm^3
$\overline{C}$ = Laplace transform of $C(x, t)$
D_e = effective diffusivity in macropores, cm^2/s
D_{ei} = effective diffusivity in micropores (intraparticle region), cm^2/s
F = volumetric flow rate through lower chamber of pellet holder, cm^3/s
K = adsorption equilibrium constant, cm^3/g
k = first-order adsorption rate constant, cm^3/(s) (g cat)
L = pellet length, cm
m_o, m_1, m_2 = elements of zero, first and second moments defined as $m_{n'} = \int_o^\infty Ct^{n'}\,dt$
n = concentration of diffusing gas adsorbed on micropores, mole/(g cat)
r = radial coordinate in spherical particle; r_o = radius of particle, cm
s = Laplace variable, s^{-1}
t = time, s
x = coordinate in diffusion direction (axial direction) in cylindrical pellet, cm

Greek Letters

α = interparticle porosity in pellet
β = intraparticle porosity in pellet
μ_1 = first absolute in cylindrical pellet, s
ρ = particle density, g/cm^3
μ'_2 = second, central moment, s^2

LITERATURE CITED

Dogu, Gulsen, and J. M. Smith, "A Dynamic Method for Catalyst Diffusivities," *AIChE J.*, **21**, 58 (1975).

———, "Rate Parameters from Dynamic Experiments with Single Catalyst Pellets," *Chem. Eng. Sci.*, **31**, 123 (1976).

Schneider, Peter, and J. M. Smith, "Adsorption Rate Constants from Chromatography," *ibid.*, **14**, 762 (1968).

Manuscript received June 21, 1976; revision received July 6, and accepted July 7, 1976.

A Note on Gas Solid Noncatalytic Reactions

M. P. DUDUKOVIĆ

Chemical Reaction Engineering Laboratory
Department of Chemical Engineering
Washington University
St. Louis, Missouri 63130

Heterogeneous reactions between gases and solids play an important role in chemical and metallurgical industry. Mathematical modeling of these processes begins with the description of reaction of a single solid pellet. A

number of models can be used for this purpose; among them the simultaneous diffusion with reaction model (SDRM) has received considerable attention. The model is useful in describing gas solid reactions (Lacey et al., 1965; Wen, 1968, Pigford and Sliger, 1973) and the related problem of parallel catalyst deactivation (Masamune and Smith, 1966; Murakami et al., 1968; Khang and Levenspiel, 1973).

The major obstacle to a wide use of the SDRM has been in computational difficulties and costs. This was caused by lengthy Crank-Nicholson and other implicit and explicit finite difference schemes which were employed and which often required extremely fine grid structures.

The objective of this note is to present a mathematical transformation which enables us to calculate all the relevant qualities of the model at two order of magnitude lower costs. This novel transformation reduces the boundary value problem for two coupled nonlinear partial differential equations to a two point boundary value problem for an ordinary differential equation which is ultimately reduced to an initial value problem.

For a typical reaction

$$\alpha A(g) + \beta S(s) = \gamma P(s) + \delta G(g) \tag{1}$$

the dimensionless form of the governing equations based on the SDRM and with first-order reaction assumed with respect to the gas and solid reactant is:

$$\frac{1}{\xi^\nu}\frac{\partial}{\partial\xi}\left(\xi^\nu\frac{\partial y}{\partial\xi}\right) - \phi^2 yz = \begin{cases} \epsilon\dfrac{C_{A_o}}{C_{S_o}}\phi^2\dfrac{\partial y}{\partial\theta} & (2a) \\ \epsilon\dfrac{C_{A_o}}{C_{S_o}}\dfrac{r}{r+1}\phi^2\dfrac{\partial y}{\partial\theta} & (2b) \end{cases}$$

$$\frac{\partial z}{\partial\theta} = -yz \tag{3}$$

with initial and boundary conditions

$$\theta = 0, \quad y = 0, \quad z = 1 \tag{4a}$$

$$\xi = 0, \quad \frac{\partial y}{\partial\xi} = 0 \tag{4b}$$

$$\xi = 1, \quad \frac{\partial y}{\partial\xi} = Bi_m(1-y) \tag{4c}$$

Parameter $\nu = 0, 1, 2$ for the slab, cylinder, and sphere, respectively. Equation (2a) is for gas solid reactions, and Equation (2b) applies to parallel catalyst deactivation. However, when the pseudo steady state assumption (PSSA) is invoked, the right-hand side of Equations (2a) and (2b) is zero. PSSA, the validity of which has been demonstrated for gas-solid systems, is used in this work.

In many engineering applications it is not necessary to know the profiles of the solid and gas reactant concentration within the pellet. The only quantities of interest are solid conversion or catalyst effectiveness factor as functions of time

$$X(\theta) = 1 - (\nu+1)\int_o^1 \xi^\nu z(\xi,\theta)\,d\xi \tag{5}$$

$$\eta(\theta) = \frac{\nu+1}{r+1}\frac{1}{\phi^2}\frac{\partial y}{\partial\xi}\bigg|_{\substack{\xi=1\\\theta=\theta}} \approx \frac{\nu+1}{\phi^2}\frac{\partial y}{\partial\xi}\bigg|_{\substack{\xi=1\\\theta=\theta}} \tag{6}$$

since $r << 1$.

Convenient integral transformations are the average solid concentration $Z(\theta)$

$$Z(\theta) = (\nu+1)\int_o^1 \xi^\nu z(\xi,\theta)\,d\xi \tag{7}$$

and cumulative point gas concentration $Y(\xi,\theta)$:

$$Y(\xi,\theta) = \int_o^\theta y(\xi,\theta')\,d\theta' \tag{8}$$

With the use of PSSA, the above two integral transformation and the following transformation of the space coordinate

$$\xi' = \phi\xi \tag{9}$$

the original problem [Equations (2) to (4)] is reduced to the boundary value problem:

$$\frac{1}{\xi'^\nu}\frac{\partial}{\partial\xi'}\left(\xi'^\nu\frac{\partial Y}{\partial\xi'}\right) + e^{-Y} - 1 = 0 \tag{10}$$

$$\xi' = 0, \quad \frac{\partial Y}{\partial\xi'} = 0 \tag{11a}$$

$$\xi' = \phi, \quad \frac{\partial Y}{\partial\xi'} + \frac{Bi_m}{\phi}Y = \frac{Bi_m}{\phi}\theta \tag{11b}$$

Conversion and the effectiveness factor are now given by

$$X(\theta) = \frac{\nu+1}{\phi}\left(\frac{\partial Y}{\partial\xi'}\right)_{\xi'=\phi} \tag{12}$$

$$\eta(\theta) = \frac{dX}{d\theta} \tag{13}$$

This problem, however, can be solved as an initial value problem, and the computational algorithm is extremely simple. Let

$$\frac{\partial Y}{\partial\xi'} = W \tag{14a}$$

$$\frac{\partial W}{\partial\xi'} = \begin{cases} 1 - e^{-Y} - \dfrac{\nu}{\xi'}W; & \text{all } \xi', \quad \nu = 0 \\ & \xi' \neq 0, \quad \nu = 1, 2 \\ \dfrac{1-e^{-Y}}{1+\nu}; & \xi' = 0, \quad \nu = 1, 2 \end{cases} \tag{14b}$$

The initial conditions are

$$\xi' = 0 \quad W = 0 \quad Y = Y_o^i \quad (i = 1, 2, 3, \ldots) \tag{15}$$

where Y_o^i are a set of guessed values for the cumulative gas concentration in the center of the solid particle. The system of Equations (14) can readily be solved by fourth-order Runge Kutta or any standard integration procedure allowing for the term e^{-Y} to become zero at the point of underflow.

Integration of Equations (14) with different initial conditions Y_o^i provides a complete set of solutions for conversion vs. time relationships for all values of parameters ϕ and Bi_m which are of interest. For any chosen value of Y_o when integrating Equations (14) forward, one can obtain solid conversion and time at any desired value of the modulus ϕ from

$$\theta = \frac{\xi'}{Bi_m}\left[W(\xi') + \frac{Bi_m}{\xi'}Y(\xi')\right] \tag{16}$$

$$X = \frac{\nu+1}{\xi'}W(\xi') \tag{17}$$

where $\xi' = \phi$. Clearly, for every set of values $W(\xi')$, $Y(\xi')$ the relationship can be obtained for various Biot numbers.

The effectiveness factor can be obtained by either interpolating through successive X vs. θ points and differentiating or by a simple averaging procedure:

$$\eta = \frac{(\nu + 1)[W(\xi', \theta_2) - W(\xi', \theta_1)]}{\xi'(\theta_2 - \theta_1)} = \frac{X(\theta_2) - X(\theta_1)}{\theta_2 - \theta_1} \tag{18}$$

Owing to the smoothness of the curves involved, it was found that interpolation is necessary only through three successive points and that Equation (18) provides an answer accurate at worst to two significant figures.

In this note we have shown how to find conversion and effectiveness factors efficiently from the SDRM when model parameters are known. Complete X vs. θ and η vs. θ plots can be formed at all values of ϕ and Bi_m at very low costs which are several orders of magnitude lower than when a finite-difference scheme is employed. In addition, it has also been shown that solid- and gas-point concentrations can be determined by the integral transformation method (Dudukovic, 1975). The use of the method in problems of parameter identification and other applications will be described in the near future (Dudukovic and Lamba, 1976).

It has come to the author's attention that a similar transformation has in the meantime been independently discovered by Professor Bischoff, Cornell University, and his co-workers.

ACKNOWLEDGMENT

The author is grateful to the National Science Foundation for financial support of the studies on gas solid noncatalytic reactions (Grant No. ENG76-00700).

NOTATION

$Bi_m = k_m L/D_e$ = Biot number for mass transfer, dimensionless
C_A = concentration of reactant A in the pellet, moles cm^{-3}
C_{A_o} = concentration of reactant A in the bulk of the gas phase, moles cm^{-3}
C_S = concentration of solid reactant S, moles cm^{-3}
C_{S_o} = initial concentration of reactant S, moles cm^{-3}
D_e = effective diffusivity of gaseous reactant A through the pores of the solid pellet, cm^2 s^{-1}
k = apparent rate constant, moles^{-1} cm^3 s^{-1}
k_d = deactivation rate constant, moles^{-1} cm^3 s^{-1}
k_m = mass transfer coefficient, cm s^{-1}
L = characteristic dimension of solid pellets slab half thickness, radius of the cylinder or sphere, cm
$r = k_d/k$ = ratio of deactivation and main reaction rate constant assumed much less than one, dimensionless
t = time, s
W = dependent variable defined by Equation (14a), dimensionless
X = conversion of the solid reactant S, dimensionless
Y = cumulative gas reactant concentration as defined by Equation (8), dimensionless
Y_o = cumulative gas reactant concentration in the center of the pellet, dimensionless
$y = C_A/C_{A_o}$ = gas reactant concentration, dimensionless
Z = average solid reactant concentration as defined by Equation (5), dimensionless
$z = C_S/C_{S_o}$ = solid reactant concentration, dimensionless

Greek Letters

$\alpha, \beta, \gamma, \delta$ = stoichiometric coefficients, dimensionless
ϵ = pellet porosity, dimensionless
η = catalyst effectiveness factor, dimensionless
$\theta = k(\beta/\alpha)C_{A_o}t$ = time for gas solid noncatalytic reactions
$\theta = k_d(\beta/\alpha)C_{A_o}t$ = dimensionless time for parallel catalyst deactivation
$\xi = \xi_a/L$ = dimensionless space coordinate
ξ_a = dimensional space coordinate, cm
ξ' = dimensionless coordinate defined by Equation (9)
ν = parameter
$\phi = \left(\frac{kC_{S_o}}{D_e}\right)^{1/2} L$ = modulus for gas solid noncatalytic reaction, dimensionless
$\phi = \left(\frac{kC_{S_o}(1 + r)}{D_e}\right)^{1/2} L$ = modulus for parallel catalyst deactivation, dimensionless

LITERATURE CITED

Dudukovic, M. P., "Analysis of Gas-Solid Noncatalytic or Catalyst Deactivation Reactions," paper presented at 68th Annual AIChE Meeting, Los Angeles, Calif. (Nov., 1975).

———, and H. Lamba, "Models for Gas Solid Reactions" (1976).

Khang, S. J., and O. Levenspiel, "The Suitability of nth-Order Rate Form to Represent Deactivating Catalyst Pellets," *Ind. Eng. Chem. Fundamentals*, **12**, No. 2, 185 (1973).

Lacey, D. T., J. H. Bowen, and K. S. Basden, "Theory of Noncatalytic Gas-Solid Reactions," *ibid.*, **4**, No. 3, 275 (1965).

Masamune, S., and J. M. Smith, "Performance of Fouled Catalyst Pellets," *AIChE J.*, **12**, No. 2, 384 (1966).

Murakami, Y., R. Kobayashi, T. Hattori, and M. Masuda, "Effect of Intraparticle Diffusion on Catalyst Fouling," *Ind. Eng. Chem. Fundamentals*, **7**, No. 4, 599 (1968).

Pigford, R. L., and G. Sliger, "Rate of Diffusion Controlled Reaction Between a Gas and a Porous Solid Sphere," *Ind. Eng. Chem. Process Design Develop.*, **12**, No. 1, 85 (1973).

Wen, C. Y., "Noncatalytic Heterogeneous Solid Fluid Reaction Models," *Ind. Eng. Chem.*, **60**, No. 9, 34 (1968).

Manuscript received May 25, 1976; revision received June 21, and accepted June 22, 1976.

Vortex Inhibition: Velocity Profile Measurements

C. S. CHIOU
and
R. J. GORDON

Department of Chemical Engineering
University of Florida
Gainesville, Florida 32611

In 1971, we reported a new dilute polymer solution phenomenon termed vortex inhibition (VI) (Balakrishnan and Gordon, 1971; Gordon and Balakrishnan, 1972). VI refers to the disappearance of the air core or vortex which