An Integral Equation Method for Evaluating the Effects of Film and Pore Diffusion of Heat and Mass on Reaction Rates in Porous Catalyst Particles

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The effective design of catalytic reactors requires accurate procedures to predict the rates of chemical reaction on the catalyst surfaces. If the catalyst material is impregnated on the interior and exterior surfaces of porous particles, the diffusion of reactants into the porous structure can greatly influence the overall reaction rate. In addition, the conduction of heat within the porous particles can affect the rate since the chemical reactions are accompanied by an evolution or absorption of heat. The rate of reaction can also be limited by the rate of heat and mass transfer from the bulk fluid, through a stagnant film surrounding the catalyst particles, to the outside surface of the particles.

The effects of film and pore diffusion of heat and mass on reaction rates in porous infinitely long cylindrical catalyst particles, have been considered for simple reaction kinetics by Miller and Deans (*1*) and the effects of pore diffusion alone have been considered by Weisz and Hicks (*2*) for spherical catalyst particles. In both of these cases, however, the pertinent differential equations were expressed in finite difference form and integrated numerically to determine concentration and temperature profiles within the catalyst particles. This procedure can be quite time consuming even with the use of a high-speed digital computer, particularly if the procedure is to be used repeatedly as in the analysis of a packed-bed catalytic reactor where bulk fluid temperature and composition varies with position in the reactor. The appropriate differential equations can be converted to Fredholm integral equations which are much easier to solve numerically, particularly for cases in which film diffusion of heat and mass *significantly influence* the reaction rate. An integral equation method is presented here for evaluating the effects of film and pore diffusion of heat and mass on reaction rates in porous catalyst particles. The method permits the computation of temperature and concentration distributions within the particles for any reaction kinetics.

MATHEMATICAL MODEL

The system under consideration is a spherical porous catalyst pellet which is surrounded by a stagnant film of fluid. Reactant molecules must diffuse through this film and into the interstices of the porous particle before reacting on the catalytic surfaces. In describing the diffusion of mass within a porous pellet, it is assumed that Fick's law applies and that changes in the mass density of fluid within the particle are negligible in relation to changes in concentrations of the reacting species. Fourier's law is used to describe heat conduction within the catalyst pellet. Pressure changes within the particle resulting from nonequimolar diffusion are neglected as is heat transported by pore diffusion of mass. Heat and mass transfer coefficients are used to describe film diffusion of heat and mass. By assuming constant diffusion coefficients, D_p, and effective thermal conductivities, K_p, within the porous structure, the equations describing heat and mass transfer of a single reactant in a catalyst particle may be written as

$$D_p \nabla^2 \rho_p - r_{\text{het}} = 0 \tag{1}$$

$$K_p \nabla^2 T_p - H r_{\text{het}} = 0 \tag{2}$$

where the concentration, ρ_p, and rate of reaction, r_{het}, are expressed in mass units. The boundary conditions which consider diffusion of heat and mass through a film surrounding a spherical particle are

$$D_p \left(\frac{d\rho_p}{dx} \right)_s = k_c[\rho_i - (\rho_p)_s] \tag{3}$$

and

$$H\, D_p \left(\frac{d\rho_p}{dx} \right)_s = h_c[T_i - (T_p)_s] \tag{4}$$

In a subsequent section of this paper Equations (1) through (4) are further generalized to describe multiple reactant systems and to include simultaneous catalytic reactions which are film diffusion controlled.

By using Equations (1) and (2), Prater (*3*) has pointed out that temperature and concentration are related quite simply by

$$T_p - (T_p)_s = - \frac{H\, D_p}{K_p} [(\rho_p)_s - \rho_p] \tag{5}$$

The use of this relationship enables the reaction rate, r_{het}, to be written, for given surface conditions, as a function of concentration alone instead of concentration and temperature. It is only necessary then to solve Equation (1) with $r_{\text{het}} = r_{\text{het}}(\rho_p)$, subject to boundary conditions (3) and (4).

DEVELOPMENT OF INTEGRAL METHOD

If the radius of the spherical catalyst particle is α, and if concentration ρ_p^* is defined such that $\rho_p^* = \rho_p - \rho_i$, Equation (1) can be written as

$$D_p \left[\frac{1}{x^2} \frac{d}{dx} \left(x^2 \frac{d\rho_p^*}{dx} \right) \right] - r_{\text{het}} = 0 \tag{6}$$

where x is the radial distance from the center of a sphere. The boundary conditions associated with Equation (6) are

$$\frac{d\rho_p^*}{dx} = 0 \text{ at } x = 0 \qquad \frac{d\rho_p^*}{dx} = - \frac{k_c}{D_p} \rho_p^* \text{ at } x = \alpha \tag{7}$$

Equation (6) can be rearranged to get

$$\frac{d}{dx} \left(x^2 \frac{d\rho_p^*}{dx} \right) = \frac{r_{\text{het}}\, x^2}{D_p} = \phi(x, \rho_p^*) \tag{8}$$

The solution to Equation (8) is most easily obtained by converting it into a Fredholm integral equation of the form (*4*)

$$\rho_p^*(x) = \frac{1}{x^2[u(x)v'(x) - u'(x)v(x)]} \int_0^\alpha G(x,\xi)\phi(\xi,\rho_p^*)\,d\xi \tag{9}$$

where $u(x)$ is a solution of

$$\frac{d}{dx} \left(x^2 \frac{du}{dx} \right) = 0 \tag{10}$$

subject to the condition that

$$\left[u \frac{d\rho_p^*}{dx} - \frac{du}{dx} \rho_p^* \right]_{x=0} = 0 \tag{11}$$

and $v(x)$ is a solution of

$$\frac{d}{dx} \left(x^2 \frac{dv}{dx} \right) = 0 \tag{12}$$

subject to the condition that

$$\left[v \frac{d\rho_p^*}{dx} - \frac{dv}{dx} \rho_p^* \right]_{x=\alpha} = 0 \tag{13}$$

The Green's function, $G(x,\xi)$ is given by

$$G(x,\xi) = \begin{cases} u(\xi)v(x) & \text{for } 0 \leqq \xi \leqq x \\ u(x)v(\xi) & \text{for } x \leqq \xi \leqq \alpha \end{cases} \tag{14}$$

The function $u(x)$ can be determined by first integrating Equation (10) to get

$$u = -\frac{A_1}{x} + B_1 \tag{15}$$

If we apply Equation (11) together with the first of boundary conditions (7) to Equation (15), we find that $A_1 = 0$ and

$$u = B_1 \tag{16}$$

The function $v(x)$ can be determined in a similar manner by first integrating Equation (12) to get

$$v = -\frac{A_2}{x} + B_2 \tag{17}$$

and then applying Equation (13) and the second of boundary conditions (7) to Equation (17) to get

$$v = A_2 \left[\frac{\alpha k_c - D_p}{\alpha^2 k_c} - \frac{1}{x} \right] \tag{18}$$

Equations (14), (16), and (18) can now be combined to get

$$G(x,\xi) = \begin{cases} A_2 B_1 \left[\dfrac{\alpha k_c - D_p}{\alpha^2 k_c} - \dfrac{1}{x} \right] & \text{for } 0 \leqq \xi \leqq x \\ A_2 B_1 \left[\dfrac{\alpha k_c - D_p}{\alpha^2 k_c} - \dfrac{1}{\xi} \right] & \text{for } x \leqq \xi \leqq \alpha \end{cases} \tag{19}$$

In addition,

$$x^2[u(x)\, v'(x) - u'(x)\, v(x)] = A_2 B_1 \tag{20}$$

Equations (19) and (20) can now be substituted into Equation (9) to get

$$\rho_p^*(x) = \left[\frac{\alpha k_c - D_p}{\alpha^2 k_c} - \frac{1}{x} \right] \int_o^x \phi(\xi,\rho_p^*) d\xi + \int_x^\alpha \left[\frac{\alpha k_c - D_p}{\alpha^2 k_c} - \frac{1}{\xi} \right] \phi(\xi,\rho_p^*) d\xi \tag{21}$$

or

$$\rho_p(x) = \rho_i - \left[\frac{1}{x} - \frac{\alpha k_c - D_p}{\alpha^2 k_c} \right] \int_o^x \xi^2 \frac{r_{\text{het}}(\rho_p)}{D_p} d\xi - \int_x^\alpha \left[\frac{1}{\xi} - \frac{\alpha k_c - D_p}{\alpha^2 k_c} \right] \xi^2 \frac{r_{\text{het}}(\rho_p)}{D_p} d\xi \tag{22}$$

Equation (22) is an implicit integral equation which can be solved numerically to determine the concentration at any point in a porous particle in terms of ρ_i, the concentration in the bulk fluid. Because of the dependence of the reaction rate, r_{het}, on particle surface temperature, $(T_p)_s$, and reactant concentration, $(\rho_p)_s$, it is necessary to solve Equation (22) simultaneously with Equations (3) and (4) to determine the concentration profile within the particle. Numerical methods have been developed to accomplish this and these have been programmed for digital computation. Typical computation time to generate concentration and temperature profiles by using a UNIVAC 1108 computer is 0.25 sec. This is at least an order of magnitude faster than the time required, with the same computer, to calculate these profiles by employing finite difference methods to solve the original differential equations with the pertinent boundary conditions.

In the special case of negligible film resistance to mass transfer (that is $k_c >> D_p/\alpha$) Equation (22) reduces to

$$\rho_p(x) = \rho_i - \left[\frac{1}{x} - \frac{1}{\alpha} \right] \int_o^x \xi^2 \frac{r_{\text{het}}(\rho_p)}{D_p} d\xi - \int_x^\alpha \left[\frac{1}{\xi} - \frac{1}{\alpha} \right] \xi^2 \frac{r_{\text{het}}(\rho_p)}{D_p} d\xi \tag{23}$$

Since the reactant concentration at the particle surface is equal to the concentration in the bulk fluid in this case, the concentration profile within the particle can be determined from the simultaneous solution of Equations (23) and (4) only. If film resistance to heat transfer is negligible also, $(T_p)_s = T_i$ and Equation (23) can be solved alone for the concentration profile. For this special case the integral method has been used in analyses of the behavior of catalytic reactors for hydrazine decomposition (5) and for the dehydrogenation of methylcyclohexane (6).

SAMPLE CALCULATIONS

This integral method has been used to compute concentration and temperature profiles in a porous catalyst particle used for the decomposition of ammonia in a gaseous mixture of ammonia, nitrogen, and hydrogen. The calculations pertain to a Shell 405 catalyst particle (7) for which estimates have been made of the kinetics of the catalytic dissociation of ammonia (8). The reaction rate can be approximated by

$$r_{\text{het}}^{NH_3} = 0.3 \times 10^{11} \frac{\rho_p^{NH_3}}{(\rho_i^{H_2})^{1.6}} e^{-50{,}000/T_p} \tag{24}$$

where T_p is in °R. and the concentrations are expressed in lb/cu.ft. An illustrative example is considered for which the parameters are

$T_i = 2{,}024$ °R.
$P = 100$ lb./sq.in.abs.
Mole Fractions in Bulk Fluid $\begin{cases} NH_3 = 0.19 \\ H_2 = 0.51 \\ N_2 = 0.30 \end{cases}$
$D_p^{NH_3} = 0.35 \times 10^{-4}$ sq.ft./sec.
$H^{NH_3} = 1{,}405$ B.t.u./lb.
$k_c^{NH_3} = 5.0$ ft./sec.
$h_c = 0.29$ B.t.u./sq.ft.-sec.-°R.
$K_p = 0.40 \times 10^{-4}$ B.t.u./ft.-sec.-°R.
$\alpha = 10^{-3}$ ft.

The temperature and ammonia concentration profiles within the catalyst particle are plotted for this case in Figure 1. These profiles were computed by the simultaneous solution of Equations (3), (4), and (22). As pointed out previously, for cases like this one in which $k_c^{NH_3} >> D_p^{NH_3}/\alpha$, concentration and temperature distributions could be obtained by simultaneous solution of Equations (4) and (23) only.

In catalytic reactor systems interest is centered primarily on the flux of reactant material into the catalyst particles. This flux at the particle surface, $D_p(d\rho_p/dx)_s$ or $k_c[\rho_i - (\rho_p)_s]$, is easily calculated once the concentration profile is known. For the ammonia dissociation case discussed above, the mass flux of ammonia into the catalyst particle, normalized by dividing by $(k_c\rho_i)^{\mathrm{NH_3}}$, is plotted as a function of bulk fluid temperature in Figure 2. The reactant concentration profile and then the mass flux at the particle surface were obtained for temperatures between 1,700 and 2,700 °R.; all other parameters were fixed at the same values used in computing the profiles shown in Figure 1. The normalizing factor, $k_c\rho_i$, is the mass flux which would be obtained if the reaction were controlled by the film diffusion of heat and mass. For comparison purposes, normalized fluxes are also plotted in Figure 2 for the case in which film resistance to heat and mass transfer is negligible [that is $(\rho_p)_s = \rho_i$ and $(T_p)_s = T_i$] and for the case where film and pore diffusion are sufficiently rapid so that the system is controlled by the rate of chemical reaction on the catalytic surfaces [that is $\rho_p(x) = \rho_i$ and $T_p(x) = T_i$]. For the case of negligible film resistance to heat and mass transfer, Equation (23) was used to determine the ammonia concentration distribution within the particle and then the flux at the particle surface. For the chemical reaction controlled system, the rate of reaction was calculated from Equation (24) and the flux was then computed as $(\alpha/3)\ r_{\mathrm{het}}^{\mathrm{NH_3}}(\rho_i,T_i)$. As shown in Figure 2, these two cases represent low-temperature asymptotes for the general case where the effects of film and pore diffusion on catalytic reaction rates are considered. At high temperature this flux asymptotically approaches the flux which would be obtained if the reaction were controlled by the film diffusion of heat and mass.

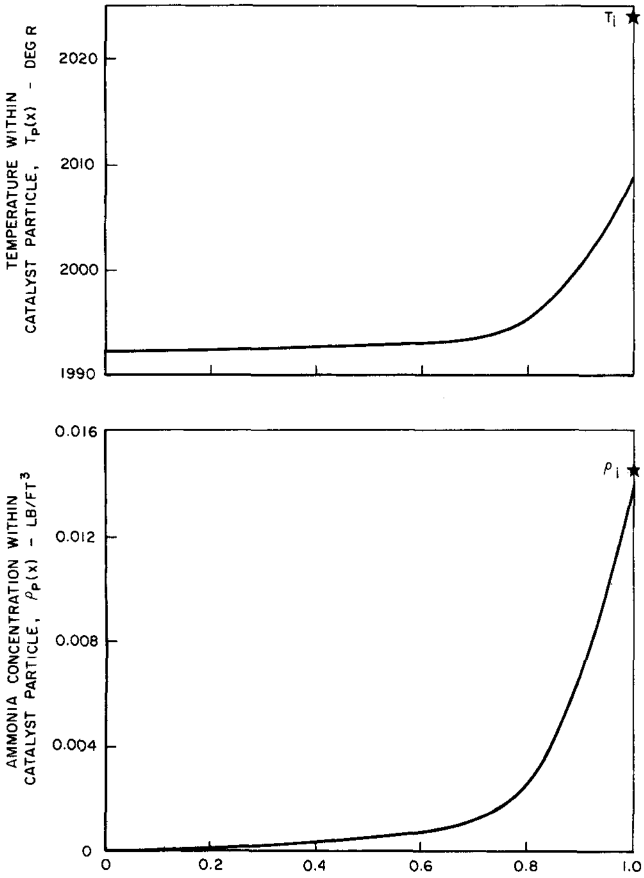

Fig. 1. Temperature and ammonia concentration profiles within catalyst particle. No hydrazine present in bulk fluid. (see text for values of parameters required for numerical solution).

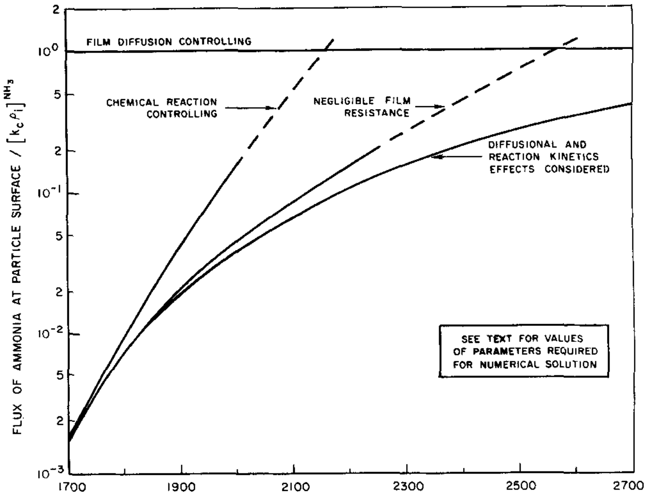

Fig. 2. Effect of bulk fluid temperature on mass flux of ammonia at surface of catalyst particle. No hydrazine present in bulk fluid.

GENERALIZATION OF INTEGRAL METHOD

The integral method described thus far can easily be adapted to include a treatment of simultaneous catalytic reactions, which are film diffusion controlled by simply modifying boundary condition (4) to include the heat generated by these reactions. This can best be illustrated by considering the example of ammonia dissociation again, this time with hydrazine present in the bulk fluid surrounding the catalyst particle. At elevated temperatures hydrazine decomposes catalytically at a rate so rapid that the decomposition is controlled by the rate of transport of hydrazine from the bulk fluid to the surface of a catalyst pellet [that is $(\rho_p)_s^{\mathrm{N_2H_4}} \cong 0$]. The integral expression for the ammonia concentration at any point in the porous catalyst is still Equation (22). The boundary condition which considers diffusion of ammonia through a film surrounding the spherical particle remains as Equation (3), where the concentrations ρ_i and $(\rho_p)_s$ refer to ammonia. The boundary condition which considers heat transfer through the film becomes

$$(Hk_c\rho_i)^{\mathrm{N_2H_4}} + H^{\mathrm{NH_3}}D_p^{\mathrm{NH_3}}\left(\frac{d\rho_p}{dx}\right)_s^{\mathrm{NH_3}} = h_c[T_i - (T_p)_s] \tag{4a}$$

where the first term on the left side of Equation (4a) represents minus the rate of heat generation by the film diffusion-controlled catalytic decomposition of hydrazine. Equations (3), (4a), and (22) have been solved simultaneously for the temperature and ammonia concentration profiles in a porous catalyst particle for a case in which

$$\begin{aligned}
T_i &= 2{,}000\ ^\circ\mathrm{R.}\\
P &= 100\ \mathrm{lb./sq.in.abs.}\\
\text{Mole Fractions in Bulk Fluid}\ \begin{cases}\mathrm{NH_3}\\ \mathrm{N_2H_4}\\ \mathrm{H_2}\\ \mathrm{N_2}\end{cases} &\begin{aligned}&= 0.43\\ &= 0.11\\ &= 0.23\\ &= 0.23\end{aligned}\\
D_p^{\mathrm{NH_3}} &= 0.34 \times 10^{-4}\ \mathrm{sq.ft./sec.}\\
H^{\mathrm{NH_3}} &= 1{,}404\ \mathrm{B.t.u./lb.}\\
H^{\mathrm{N_2H_4}} &= -1{,}928\ \mathrm{B.t.u./lb.}\\
k_c^{\mathrm{NH_3}} &= 4.4\ \mathrm{ft./sec.}\\
k_c^{\mathrm{N_2H_4}} &= 3.0\ \mathrm{ft./sec.}\\
h_c &= 0.29\ \mathrm{B.t.u./sq.ft.\text{-}sec.\text{-}^\circ R.}\\
K_p &= 0.40 \times 10^{-4}\ \mathrm{B.t.u./ft.\text{-}sec.\text{-}^\circ R.}\\
\alpha &= 10^{-3}\ \mathrm{ft.}
\end{aligned}$$

Both the temperature and the ammonia concentration distributions are plotted for this case in Figure 3. Similar concentration profiles were calculated for bulk fluid temperatures between 1,700 and 2,700 °R.; all other param-

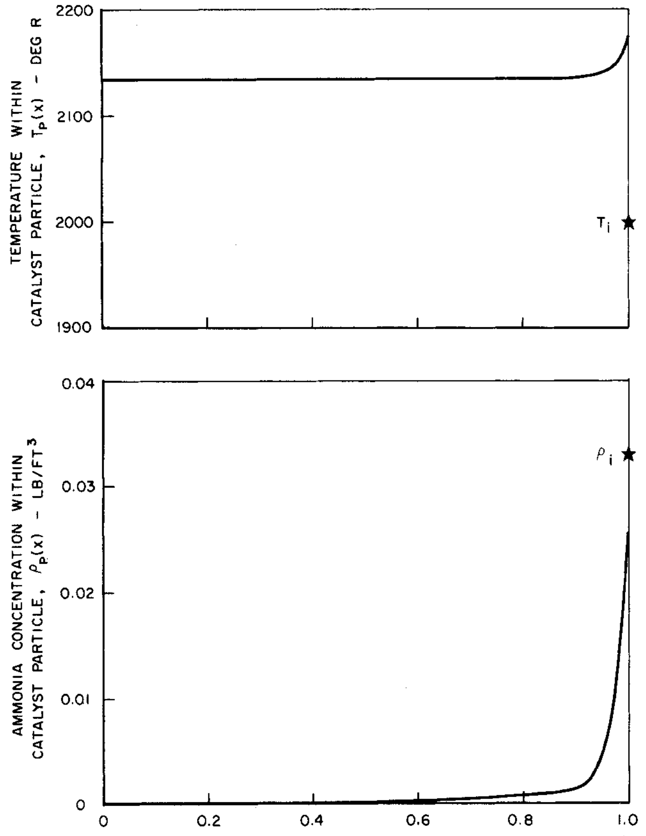

Fig. 3. Temperature and ammonia concentration profiles within catalyst particle. Hydrazine present in bulk fluid. (see text for values of parameters required for numerical solution).

eters were fixed at the same values used in computing the profiles shown in Figure 3. The flux of ammonia at the particle surface was then calculated, normalized by dividing by $(k_c\rho_i)^{NH_3}$, and plotted as a function of bulk fluid temperature in Figure 4. Here again, at high temperature, the flux asymptotically approaches the values which would be obtained if the reaction were controlled by the film diffusion of heat and mass. At low temperature, in this case, film resistance to heat transfer remains important because of the heat generated at the particle surface by the decomposition of hydrazine.

A second, perhaps more important generalization of the integral method presented here involves a description of multiple reactant systems. Consider a reacting system where

$$aA + bB + \ldots \rightarrow tT + \ldots .$$

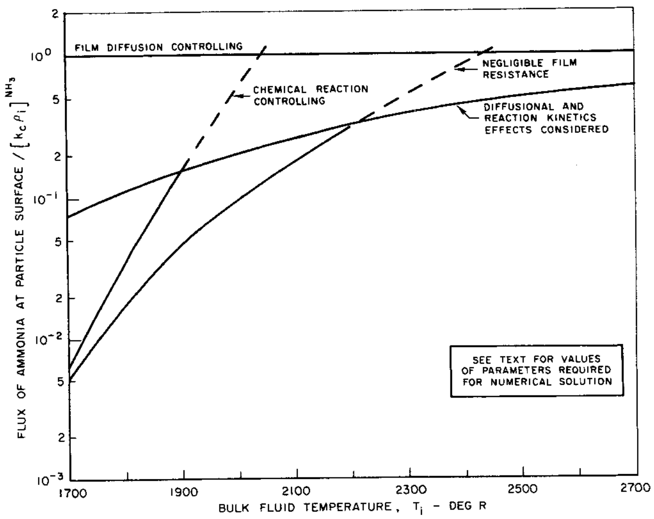

Fig. 4. Effect of bulk fluid temperature on mass flux of ammonia at surface of catalyst particle. Hydrazine present in bulk fluid.

It is apparent that the rate of the reaction can be expressed in terms of any of the reactants or products; however the rate may be a function of the concentration of any or all of those species. The same procedure used in (3) can be employed to relate all reactant and product concentrations at any point within the porous catalyst particle to the concentration of reactant A at the same point. In addition, surface concentrations, $(\rho_p)_s$, of all reactants and products can be written in terms of the surface concentration of reactant A and the known concentrations in the bulk fluid. Thus, as in the case of a single reactant, integral Equation (22) (with concentrations referring to reactant A) may be solved simultaneously with the pertinent boundary conditions to fully determine the concentration and temperature profiles within the porous catalyst particle.

NOTATION

a = coefficient defined by general chemical reaction
b = coefficient defined by general chemical reaction
D_p = diffusion coefficient of reactant gas in the porous particle, sq.ft./sec.
h_c = heat transfer coefficient, B.t.u./sq.ft.-sec.-°R.
H = heat of reaction per unit mass (negative for exothermic reaction) B.t.u./lb.
k_c = mass transfer coefficient, ft./sec.
K_p = effective thermal conductivity of the porous catalyst particle, B.t.u./ft.-sec.-°R.
P = pressure, lb./sq.in.abs.
r_{het} = mass rate of (heterogeneous) chemical reaction on the catalyst surfaces, lb./cu.ft.-sec.
t = coefficient defined by general chemical reaction
T = temperature, °R.
u = mathematical function
v = mathematical function
x = radial distance from the center of the spherical catalyst particle, ft.

Greek Letters

α = radius of spherical particle, ft.
ξ = dummy variable in integral equations
ρ_i = reactant mass concentration in bulk fluid, lb./cu.ft.
ρ_p = reactant mass concentration in gas phase within the porous particle, lb./cu.ft.
ρ_p^* = equals $\rho_p - \rho_i$, lb./cu.ft.
ϕ = mathematical function

Subscripts

i = refers to bulk fluid phase
p = refers to gas within the porous catalyst particle
s = refers to surface of catalyst particle

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