Diffusion-Controlled Rate Mechanisms in Gas-Solid Reaction Systems

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The reaction of solids with gases is normally carried out in a fixed or fluidized bed, such that the solid geometry is approximated by a collection of spheres. The rate at which fresh gas can be transported by diffusion to the reacting solid surface often establishes the overall reaction rate, a situation described as *diffusion-controlling*. No mathematical model has been presented to describe concentration vs. time in such particulate systems.

In this paper we will consider (a) the case where the overall reaction rate equals the diffusion rate, and (b) the case where the intrinsic diffusion and reaction rates both influence the overall rate.

The problem has been considered for the semi-infinite solid by Lacey et al. (*1*), for a reaction

$$\underset{\text{(gas)}}{A} + \underset{\text{(solid)}}{\nu B} \rightarrow \underset{\text{(solid)}}{C}$$

under conditions described by case (a). Then the concentration of A in the solid is given by

$$\frac{\partial C_A}{\partial t} = D\frac{\partial^2 C_A}{\partial x^2} \tag{1}$$

with boundary conditions

$$C_A(0, t) = C_{A0}$$
$$C_A(\infty, t) = 0$$
$$C_A(x, 0) = 0$$

The gas-solid reaction interface is nonstationary, and therefore the situation is a moving-boundary problem. Danckwerts (*2*), and Sherwood and Pigford (*3*) have independently shown that x', the coordinate of the moving boundary in a semi-infinite medium, must be described by

$$x' = \sqrt{4\alpha t} \tag{2}$$

This leads to the solution of Equation (1) as

$$\frac{C_A}{C_{A0}} = \left\{1 - \frac{\text{erf}\,(x/\sqrt{4Dt})}{\text{erf}\,(x'/\sqrt{4Dt})}\right\} = \left\{1 - \frac{\text{erf}\,(x/\sqrt{4Dt})}{\text{erf}\,\sqrt{\alpha/D}}\right\} \tag{3}$$

The constant α is found from the continuity requirement

$$-D\left\{\frac{\partial A}{\partial x}\right\}_{x=x'} = \frac{C_{B0}}{\nu}\frac{dx'}{dt} \tag{4}$$

which yields the following implicit relation for α:

$$\frac{C_{A0}}{C_{B0}} \cdot \sqrt{\frac{D}{\pi\alpha}} = e^{\alpha/D} \cdot \text{erf}\,\sqrt{\alpha/D} \tag{5}$$

The uptake of gaseous A is then found from

$$M = -\int_0^t D\left\{\frac{\partial C_A}{\partial x}\right\}_{x=0} dt = \frac{2C_{A0}}{\text{erf}\sqrt{\dfrac{\alpha}{D}}}\left\{\frac{Dt}{\pi}\right\}^{1/2} \tag{6}$$

For the spherical solid, the rate equation for the diffusion-controlling case is

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial \rho^2} \tag{7}$$

where $u = C_A r$ and $\rho = R - r$, and boundary conditions similar to the semi-infinite medium case. The identity of the form of Equations (1) and (7) suggests that the moving boundary coordinate in a sphere may be described analogous to Equation (2):

$$R - r' = \sqrt{4\alpha t}$$

Then a solution of Equation (7) analogous to Equation (3) is given by

$$\frac{r}{R} \cdot \frac{C_A}{C_{A0}} = \left\{1 - \frac{\text{erf}}{\text{erf}}\left[\frac{(R-r)/\sqrt{4Dt}}{(R-r')/\sqrt{4Dt}}\right]\right\}$$
$$= \left\{1 - \frac{\text{erf}[(R-r)/\sqrt{4Dt}]}{\text{erf}\sqrt{\alpha/D}}\right\} \tag{9}$$

The constant α is again found from Equation (5). Now the uptake per particle of gaseous A is given by

$$M = -\int_0^t D\left\{\frac{\partial C_A}{\partial r}\right\}_{r=R} dt$$
$$= \sqrt{\frac{4Dt}{\pi}}\,\frac{C_{A0}}{\text{erf}\sqrt{\alpha/D}} - \frac{DC_{A0}t}{R} \tag{10}$$

or

$$\frac{M}{C_{A0}R} = \sqrt{\frac{4\tau}{\pi}} \cdot \frac{1}{\text{erf}\sqrt{\alpha/D}} - \tau$$

Comparison with Equation (6) is interesting; as $R \rightarrow \infty$, we approach the semi-infinite case again, and Equation (10) reduces to Equation (6) as required. Figure 1 is a plot of Equation (10). For the semi-infinite solid, all lines

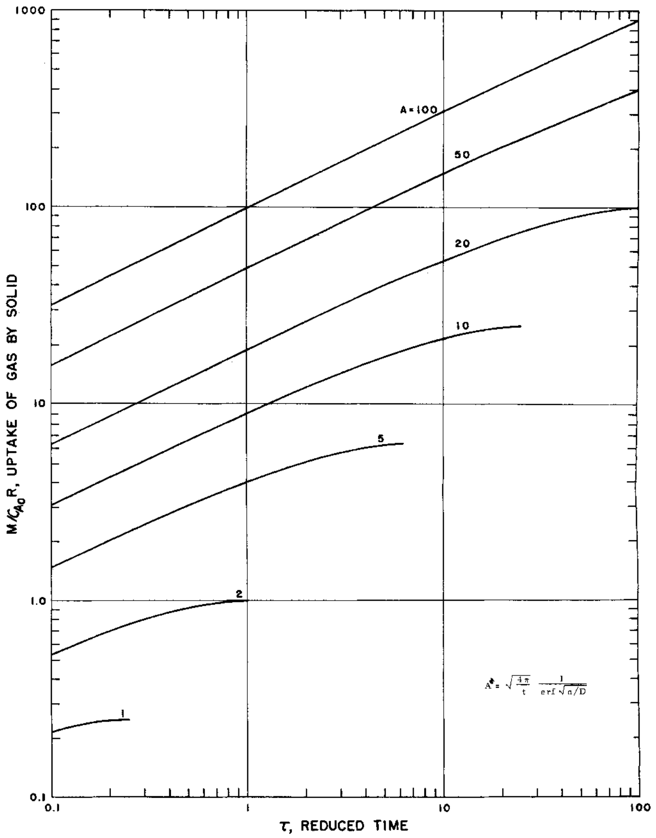

Fig. 1. Uptake of gas as a function of time, with diffusion controlling the reaction rate.

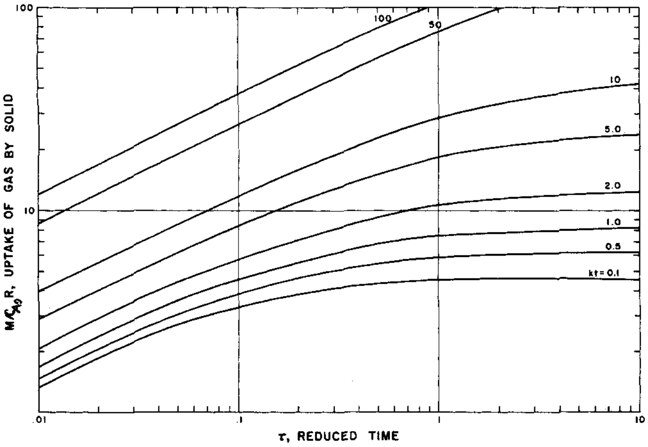

Fig. 2. Uptake of gas in a solid sphere as a function of time, with diffusion and kinetics influencing reaction rate.

on this plot would be parallel, with the slope being ½.

When the intrinsic diffusion and reaction rates are of comparable magnitude, we have a pseudo first-order reaction, and the concentration of A is described by

$$\frac{\partial C_A}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 C_A) - kt \tag{11}$$

if we assume the gas concentration is constant at the sphere surface. The solution of Equation (11) is easily obtained from results derived by Danckwerts (*4*); the uptake per particle of gaseous A is

$$M = 8\pi \frac{DC_{A_0}}{R} \sum_{n=1}^{\infty} \left\{ \frac{kt}{k + Dn^2\pi^2/R^2} + \frac{Dn^2\pi^2/R^2}{(k + Dn^2\pi^2/R^2)^2} [1 - \exp(-t(k + Dn^2\pi^2/R^2))] \right\} \tag{12}$$

or

$$\frac{M}{C_{A_0}R} = 8\pi \sum_{n=1}^{\infty} \left\{ \frac{\tau(kt)}{kt + n^2\pi^2\tau} + \frac{n^2\pi^2\tau}{(kt + n^2\pi^2\tau)^2} [1 - \exp(-kt - n^2\pi^2\tau)] \right\}$$

This result is shown in Figure 2.

When the spheres are of different sizes, the uptake of gas must be summed over all particles. If the size distribution is logarithmiconormal, this summation may be achieved by employing arbitrary segments of the distribution. The process of summation in this fashion has been illustrated by Gallagher (*5*).

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NOTATION

A^* = constant, equal to $\sqrt{4/\pi}\,/\mathrm{erf}\sqrt{\alpha/D}$
C_A = concentration of species A in solid
C_{A_0} = concentration of species A in gas
C_{B_0} = concentration of species B in unreacted solid phase
D = diffusion coefficient of species A in solid medium
k = reaction rate constant
M = uptake of species A by particle
r = radial coordinate in spherical particle
r' = radial position of moving boundary in spherical particle
R = radius of spherical particle
t = time
u = combined variable, equal to $C_A r$
x = linear distance coordinate in semi-infinite medium
x' = position of moving boundary in semi-infinite medium
α = constant of integration, defined by Equations (2) and (8)
ρ = radius difference, equal to $R - r$
τ = dimensionless time, Dt/R^2

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Flow Behavior of a Dilute Polymer Solution in Circular Tubes at Low Reynolds Numbers

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Dilute polymer solutions are of interest due to their drag reducing properties at high rates of flow. At lower flow rates in pipes these solutions exhibit apparent Newtonian behavior when pressure drop vs. flow rate data are exam-