

# A First Course on Kinetics and Reaction Engineering

## Example 40.1

### Problem Purpose

This example illustrates the formulation of a model for a gas-solid reaction in a spherical solid particle using the shrinking core model.

### Problem Statement

Suppose that pure gas phase A reacts with a solid, non-porous, spherical particle of B, yielding porous solid product Z, as in equation (1). Further assume that the porosity of Z and the effective diffusion coefficient for diffusion of A through Z are constants. Show how to calculate the radius of the unreacted core of B as a function of time if the reaction is effectively instantaneous.



### Problem Answer

If the reaction is effectively instantaneous, the shrinking core model can be used. Since the gas phase is pure A and no gas products are generated, no concentration gradient will exist in the gas phase near the particle surface. A mole balance can be written for A within the fully reacted shell of porous solid Z, as given in equation (2). Notice that there is no reaction term because no B is present in the fully reacted shell and that the concentration of A varies with both radial position and time, i. e.  $C_A = C_A(r,t)$ . Three boundary conditions are needed in order to solve equation (2). The first boundary condition, equation (3), stipulates that at the gas-particle interface ( $r = R_p$ ) the concentration of A in the gas phase must equal the concentration of A in the porous Z phase. Since there is no gas film, the concentration of A at the interface is equal to the bulk gas concentration,  $C_{A, gas}$ . The second boundary condition stipulates that A reacts instantaneously with the solid, so the concentration of A at the interface between the porous shell of Z and the core of unreacted B ( $r = R_c$ ) is equal to zero. It is important to note that  $R_c$  will change over time. The initial condition needed to solve equation (2) is that there is no A anywhere within the non-porous solid B at the start of the process, equation (5).

$$\frac{\partial}{\partial t}(\epsilon_s C_A) = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_{eA} r^2 \frac{\partial C_A}{\partial r} \right) \quad (2)$$

$$C_A(R_p, t) = C_{A, gas} \quad (3)$$

$$C_A(R_c, t) = 0 \quad (4)$$

$$C_A(r, 0) = 0 \quad (5)$$

Equation (2) cannot be solved independently because we do not know  $R_c$  as a function of time. We only know that at the start of the process,  $R_c = R_p$ . We could write a mole balance on B within the

unreacted core, but since no reaction takes place there and since B is immobile, that mole balance would simply show that the concentration of B within the unreacted core is constant. The key here is to first note that the moles of B remaining in the core at any instant of time is related to the core radius, equation (6). Since the concentration of B within the core is constant, the instantaneous rate of change of the moles of B is then given by equation (7). The instantaneous rate of consumption of B must equal the instantaneous flux of A at the core-shell interface, equation (8). Combining equations (7) and (8) gives equation (9). In order to solve equation (9), the initial condition in equation (10) can be used. Equation (10) simply requires that at the start of the process no unreacted shell has yet formed.

$$n_{B,core} = \frac{4\pi}{3} R_c^3 C_B \quad (6)$$

$$\frac{dn_{B,core}}{dt} = 4\pi R_c^2 C_B \frac{dR_c}{dt} \quad (7)$$

$$\frac{dn_{B,core}}{dt} = 4\pi R_c^2 \left( D_A \frac{\partial C_A}{\partial r} \Big|_{r=R_c} \right) \quad (8)$$

$$\frac{dR_c}{dt} = \frac{D_A}{C_B} \frac{\partial C_A}{\partial r} \Big|_{r=R_c} \quad (9)$$

$$R_c(t=0) = R_p \quad (10)$$

Equation (9) cannot be solved independently, either, because the instantaneous concentration gradient is needed. In other words, equations (2) and (9) are coupled, and they must be solved simultaneously. Doing so will yield the radius of the unreacted core,  $R_c$ , as a function of time, as requested in the problem statement.