A First Course on Kinetics and Reaction Engineering
Unit 40. Gas-Solid Reactions

Overview

Reactions between a gas and a solid involve the same issues of interfacial gradients as those encountered in heterogeneous catalysis. There is one significant additional issue with gas-solid reactions. Specifically, the solid is being consumed over time. Unit 40 provides an overview of models that can be used to simultaneously capture the effect of interfacial gradients and that of a changing solid size and pore structure.

Learning Objectives

Upon completion of this unit, you should be able to perform the following specific tasks and be able to recognize when they are needed and apply them correctly in the course of a more complex analysis:

- Describe the shrinking core model for gas-solid reactions
- Describe the general isothermal model for gas-solid reactions
- Formulate a general isothermal model for a gas-solid reaction including the specification of the boundary and initial conditions

Information

Gas-solid reactions are similar to heterogeneous catalytic reactions except that the solid changes over time in gas-solid reactions. As a result, the pore structure of the solid changes with time. It is common to start the reaction with a solid that has a low porosity. As the solid is consumed by reaction, the porosity can increase. In addition, some gas solid reactions, for example coal combustion, leave behind a porous ash layer. In order to model isothermal gas solid reactions, it is generally necessary to write mole or mass balances on the gas phase reactant and on the solid reactant. The resulting equations are partial differential equations, and most commonly they are coupled. That is, they must be solved simultaneously not sequentially. With the added complexity introduced by a pore structure that changes over time, models for gas-solid reactions are most often solved numerically. The numerical methods employed are beyond the scope of this course. Therefore, this unit provides a simple introduction to the formulation of models for gas-solid reactions, but more advanced treatments will need to be consulted when one wishes to perform the modeling.

As with gas-liquid reactions, there are a few limiting cases for gas-solid reactions. The first is the case of a reaction with a very fast reaction rate relative to the diffusion rate. In this situation, the reaction takes place in a very narrow zone of the solid. This zone is initially located at the outer surface of the solid particle. As the reaction proceeds, the solid at the outer surface becomes completely consumed, leaving behind an ash layer, and so the narrow reaction zone moves inward toward the center of the solid particle. This limiting case is commonly referred to as the shrinking core model because the unreacted solid forms a core at the center of the particle that shrinks over time. The shrinking core model involves diffusion of the gas phase reactant in two different diffusion layers. First it must diffuse through the

stagnant gas film surrounding the solid particle, and then it must diffuse through the ash layer to reach the reaction zone. Because the solid is completely removed as the core shrinks, the pore structure that the gas must diffuse through does not change over time, but the distance it must diffuse does change.

When the reaction rate is comparable to the diffusion rate, the situation can become quite similar to heterogeneous catalysis, but with a time- and position-varying porosity. The reaction can take place throughout the solid particle because some gas diffuses to the center of the particle before the outermost solid has been completely consumed. Assuming spherical particles, a general isothermal model can be formulated by performing mole balances on a differential spherical shell of the solid. The balance on the gas phase reactant A is given by equation (40.1) where the rate is normalized per unit mass of solid. While its concentration is changing over time, the solid is not diffusing. Consequently the corresponding mole balance on the solid does not include a diffusion term as can be seen in equation (40.2).

$$\frac{\partial}{\partial t}\left(\varepsilon_s C_{As}\right) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_{eA}r^2\frac{\partial C_{As}}{\partial r}\right) - r_A \rho_s \tag{40.1}$$

$$\frac{\partial}{\partial t}\left(C_S\right) = -r_S \rho_s \tag{40.2}$$

In order to solve these equations, two boundary conditions and one initial condition are needed for the gas phase reactant while only an initial condition is needed for the solid. For the gas phase reactant, the boundary conditions are that there can't be a flux through the center of the particle, equation (40.3) and the flux entering the particle must equal the flux through the stagnant gas film surrounding the particles. The latter is given by equation (40.4) where the flux through the gas film is described using a mass transfer coefficient. The initial conditions are simply the initial concentration profiles as expressed in equations (40.5) and (40.6).

$$\left.\frac{\partial C_A}{\partial r}\right|_{r=0} = 0 \tag{40.3}$$

$$\left. D_{eA}\frac{\partial C_A}{\partial r}\right|_{r=R} = k_g\left(C_{Ag} - C_A\big|_{r=R}\right) \tag{40.4}$$

$$C_A\big|_{t=0} = C_A^0\left(r\right) \tag{40.5}$$

$$C_S\big|_{t=0} = C_S^0\left(r\right) \tag{40.6}$$

As already noted, these equations must be solved simultaneously, and usually this will necessitate numerical solution. Before doing so, the effective diffusivity must be related to time and possibly to radial position, as well. This can be done explicitly if the pore model being used permits it. Alternatively, one can try to find an empirical relationship that is convenient to use and that yields accurate results. In some cases, the pseudo-steady state assumption can also be used. When the pseudo-steady state assumption applies, the time derivatives in the mole balances are set equal to zero. In effect, this is equivalent to

assuming that the transient portion of the diffusion process is so rapid that the concentration profiles in the solid are always characteristic of a steady state process with a pore structure corresponding to the actual pore structure at that instant. In other words, the removed solid volume is instantaneously filled with gas A.

Finally it should be noted that the equations given above only apply as long as reactive solid remains throughout the particle. At some point in time, all the reactive solid will have been removed from the outermost radial shell of the original solid. At that point, the mole balances must split into two parts. One part models the outer shell of the solid, and since the reactive solid is all gone in this shell, the mole balance only includes diffusion, and not reaction. The equations above then apply to the remainder of the particle. The necessary boundary condition comes from the requirement that the flux through the non-reactive shell must equal the flux entering the reactive core of the particle. Clearly, once the depleted zone appears, its boundary will continually move inward until it finally reaches the center of the particle.