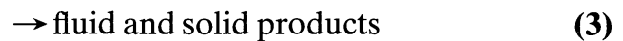# Chapter 25

Fluid–Particle Reactions: Kinetics

This chapter treats the class of heterogeneous reactions in which a gas or liquid contacts a solid, reacts with it, and transforms it into product. Such reactions may be represented by

$$A(fluid) + bB(solid) \rightarrow fluid\ products \tag{1}$$

$$\rightarrow solid\ products \tag{2}$$

$$\rightarrow fluid\ and\ solid\ products \tag{3}$$

As shown in Fig. 25.1, solid particles remain unchanged in size during reaction when they contain large amounts of impurities which remain as a nonflaking ash or if they form a firm product material by the reactions of Eq. 2 or Eq. 3. Particles shrink in size during reaction when a flaking ash or product material is formed or when pure B is used in the reaction of Eq. 1.

Fluid–solid reactions are numerous and of great industrial importance. Those in which the solid does not appreciably change in size during reaction are as follows.

1. The roasting (or oxidation) of sulfide ores to yield the metal oxides. For example, in the preparation of zinc oxide the sulfide ore is mined, crushed, separated from the gangue by flotation, and then roasted in a reactor to form hard white zinc oxide particles according to the reaction

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$
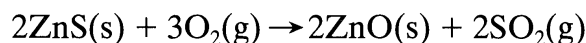
Similarly, iron pyrites react as follows:

$$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$$
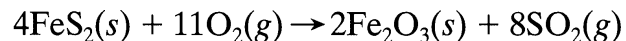
2. The preparation of metals from their oxides by reaction in reducing atmospheres. For example, iron is prepared from crushed and sized magnetite
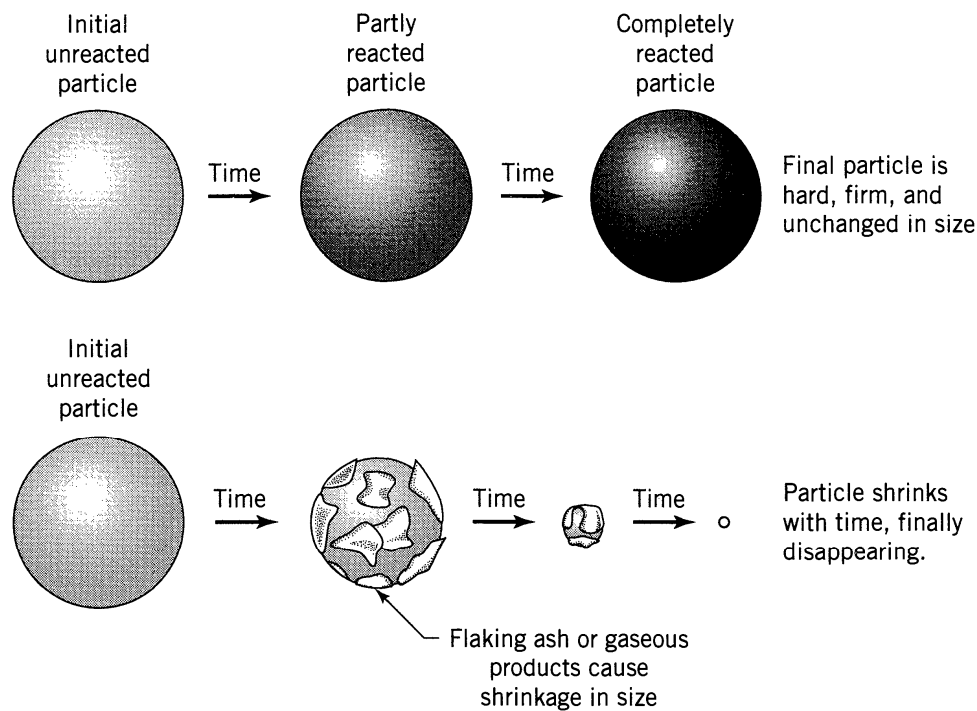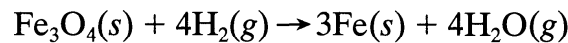
Figure 25.1 Different sorts of behavior of reacting solid particles.

ore in continuous-countercurrent, three-stage, fluidized-bed reactors according to the reaction

$$Fe_3O_4(s) + 4H_2(g) \rightarrow 3Fe(s) + 4H_2O(g)$$

3. The nitrogenation of calcium carbide to produce cyanamide

$$CaC_2(s) + N_2(g) \rightarrow CaCH_2(s) + C(amorphous)$$

4. The protective surface treatment of solids such as the plating of metals.

The most common examples of fluid–solid reactions in which the size of solid changes are the reactions of carbonaceous materials such as coal briquettes, wood, etc. with low ash content to produce heat or heating fuels. For example, with an insufficient amount of air, producer gas is formed by the reactions

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

$$C(s) + CO_2(g) \rightarrow 2CO(g)$$
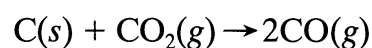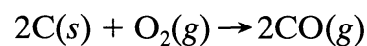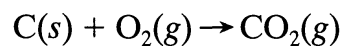
With steam, water gas is obtained by the reactions

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$

$$C(s) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2(g)$$
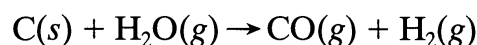
Other examples of reactions in which solids change in size are as follows.

1. The manufacture of carbon disulfide from the elements

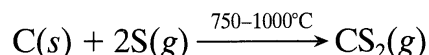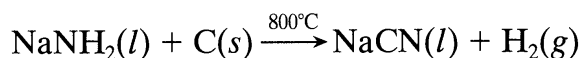$$C(s) + 2S(g) \xrightarrow{750-1000°C} CS_2(g)$$

2. The manufacture of sodium cyanide from sodium amide

$$NaNH_2(l) + C(s) \xrightarrow{800°C} NaCN(l) + H_2(g)$$

3. The manufacture of sodium thiosulfate from sulfur and sodium sulfite

$$Na_2SO_3(\text{solution}) + S(s) \rightarrow Na_2S_2O_3(\text{solution})$$
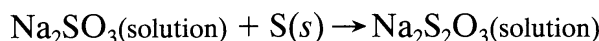
Still other examples are the dissolution reactions, the attack of metal chips by acids, and the rusting of iron.

In Chapter 17 we pointed out that the treatment of heterogeneous reaction required the consideration of two factors in addition to those normally encountered in homogeneous reactions: the modification of the kinetic expressions resulting from the mass transfer between phases and the contacting patterns of the reacting phases.

In this chapter we develop the rate expressions for fluid–solid reactions. The next chapter will then use this information in design.

25.1 SELECTION OF A MODEL

We should clearly understand that every conceptual picture or model for the progress of reaction comes with its mathematical representation, its rate equation. Consequently, if we choose a model we must accept its rate equation, and vice versa. If a model corresponds closely to what really takes place, then its rate expression will closely predict and describe the actual kinetics; if a model differs widely from reality, then its kinetic expressions will be useless. We must remember that the most elegant and high-powered mathematical analysis based on a model which does not match reality is worthless for the engineer who must make design predictions. What we say here about a model holds not only in deriving kinetic expressions but in all areas of engineering.

The requirement for a good engineering model is that it be the closest representation of reality which can be treated without too many mathematical complexities. It is of little use to select a model which very closely mirrors reality but which is so complicated that we cannot do anything with it. Unfortunately, in today's age of computers, this all too often happens.

For the noncatalytic reaction of particles with surrounding fluid, we consider two simple idealized models, the *progressive-conversion* model and the *shrinking unreacted-core* model.

Progressive-Conversion Model (PCM). Here we visualize that reactant gas enters and reacts throughout the particle at all times, most likely at different rates at different locations within the particle. Thus, solid reactant is converted continuously and progressively throughout the particle as shown in Fig. 25.2.
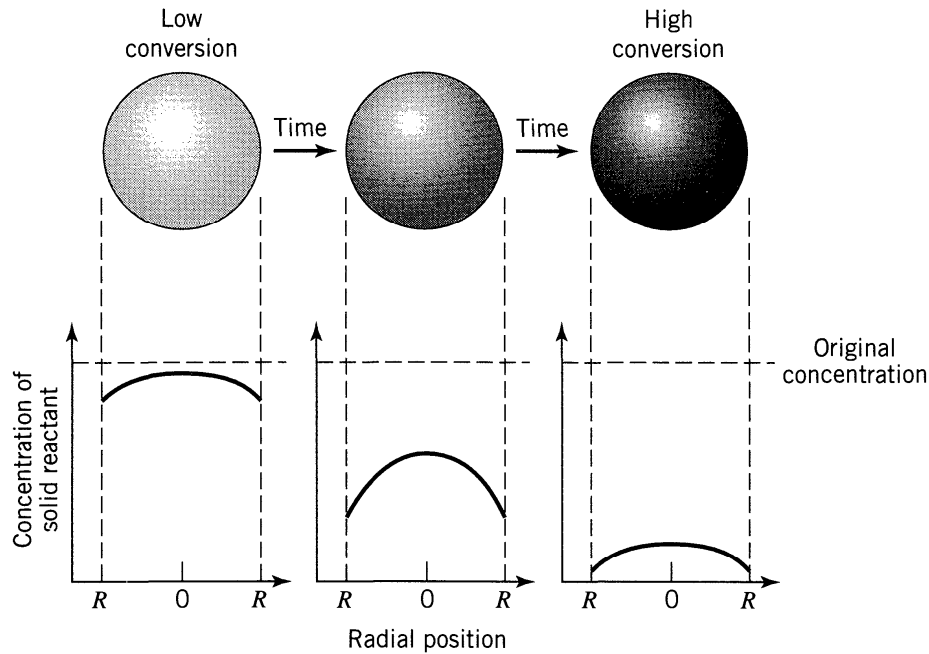
Figure 25.2 According to the progressive-conversion model, reaction proceeds continuously throughout the solid particle.

Shrinking-Core Model (SCM).   Here we visualize that reaction occurs first at the outer skin of the particle. The zone of reaction then moves into the solid, leaving behind completely converted material and inert solid. We refer to these as "ash." Thus, at any time there exists an unreacted core of material which shrinks in size during reaction, as shown in Fig. 25.3.

Comparison of Models with Real Situations.   In slicing and examining the cross section of partly reacted solid particles, we usually find unreacted solid material surrounded by a layer of ash. The boundary of this unreacted core may not
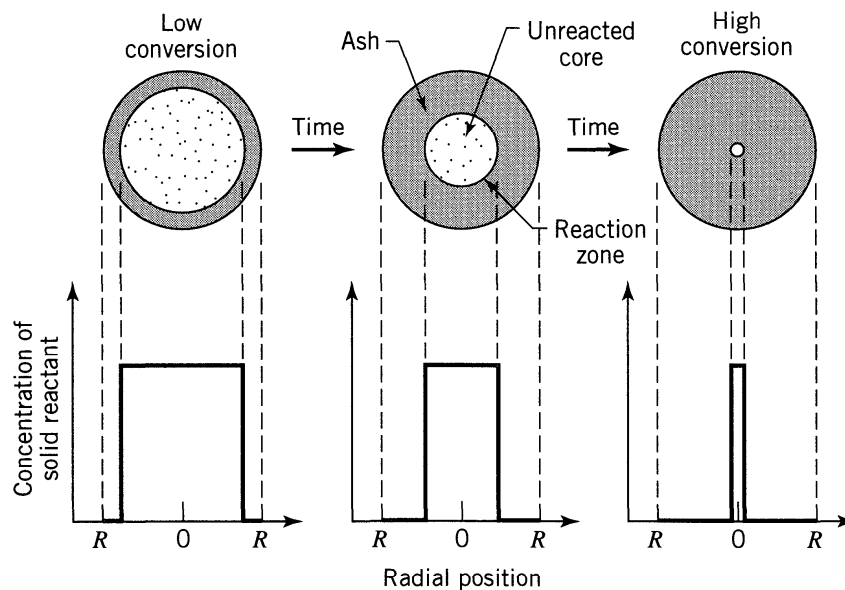

Figure 25.3 According to the shrinking-core model, reaction proceeds at a narrow front which moves into the solid particle. Reactant is completely converted as the front passes by.

always be as sharply defined as the model pictures it; nevertheless, evidence from a wide variety of situations indicates that in most cases the shrinking-core model (SCM) approximates real particles more closely than does the progressive-conversion model (PCM). Observations with burning coal, wood, briquettes, and tightly wrapped newspapers also favor the shrinking-core model. For further discussion on the many other models used (at least ten), see Chapter 55 in Levenspiel (1996).

Since the SCM seems to reasonably represent reality in a wide variety of situations, we develop its kinetic equations in the following section. In doing this we consider the surrounding fluid to be a gas. However, this is done only for convenience since the analysis applies equally well to liquids.

25.2 SHRINKING-CORE MODEL FOR SPHERICAL PARTICLES OF UNCHANGING SIZE

This model was first developed by Yagi and Kunii (1955, 1961), who visualized five steps occurring in succession during reaction (see Fig. 25.4).

Step 1. Diffusion of gaseous reactant A through the film surrounding the particle to the surface of the solid.

Step 2. Penetration and diffusion of A through the blanket of ash to the surface of the unreacted core.

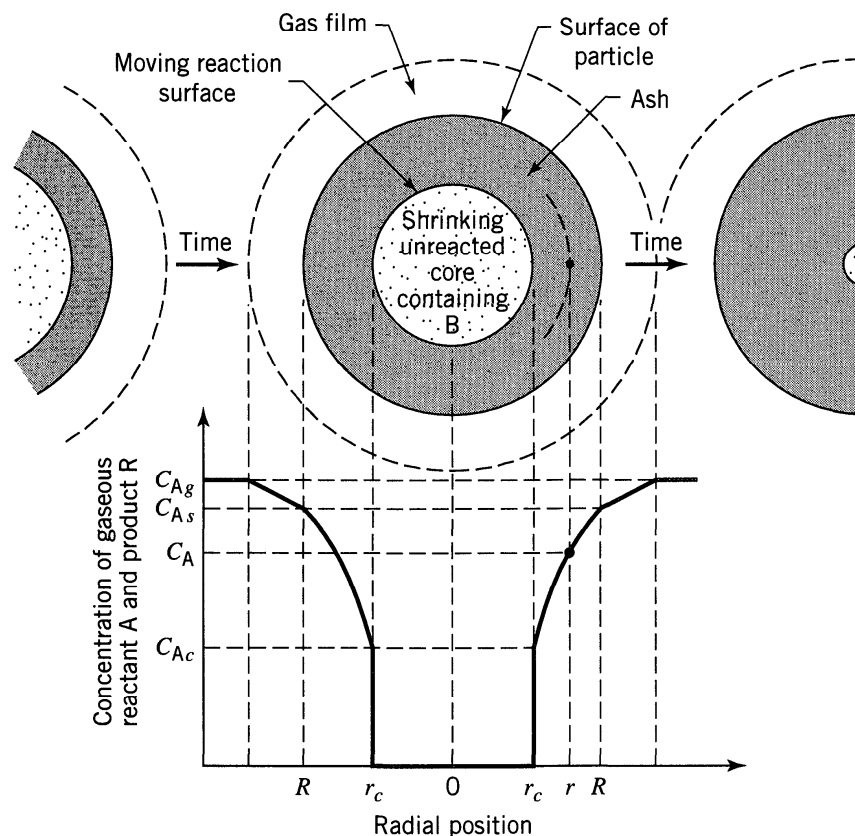*Step 3.* Reaction of gaseous A with solid at this reaction surface.

Figure 25.4 Representation of concentrations of reactants and products for the reaction $A(g) + bB(s) \rightarrow$ solid product for a particle of unchanging size.

Step 4. Diffusion of gaseous products through the ash back to the exterior surface of the solid.

Step 5. Diffusion of gaseous products through the gas film back into the main body of fluid.

In some situations some of these steps do not exist. For example, if no gaseous products are formed, steps 4 and 5 do not contribute directly to the resistance to reaction. Also, the resistances of the different steps usually vary greatly one from the other. In such cases we may consider that step with the highest resistance to be rate-controlling.

In this treatment we develop the conversion equations for spherical particles in which steps 1, 2, and 3, in turn, are rate-controlling. We then extend the analysis to nonspherical particles and to situations where the combined effect of these three resistances must be considered.

Diffusion Through Gas Film Controls

Whenever the resistance of the gas film controls, the concentration profile for gaseous reactant A will be shown as in Fig. 25.5. From this figure we see that no gaseous reactant is present at the particle surface; hence, the concentration driving force, $C_{Ag} - C_{As}$ becomes C_{Ag} and is constant at all times during reaction of the particle. Now since it is convenient to derive the kinetic equations based on available surface, we focus attention on the unchanging exterior surface of a particle S_{ex}. Noting from the stoichiometry of Eqs. 1, 2, and 3 that $dN_B = b\,dN_A$, we write

$$-\frac{1}{S_{ex}}\frac{dN_B}{dt} = -\frac{1}{4\pi R^2}\frac{dN_B}{dt} = -\frac{b}{4\pi R^2}\frac{dN_A}{dt} = bk_g(C_{Ag} - C_{As}) = bk_gC_{Ag} = \text{constant} \quad (4)$$
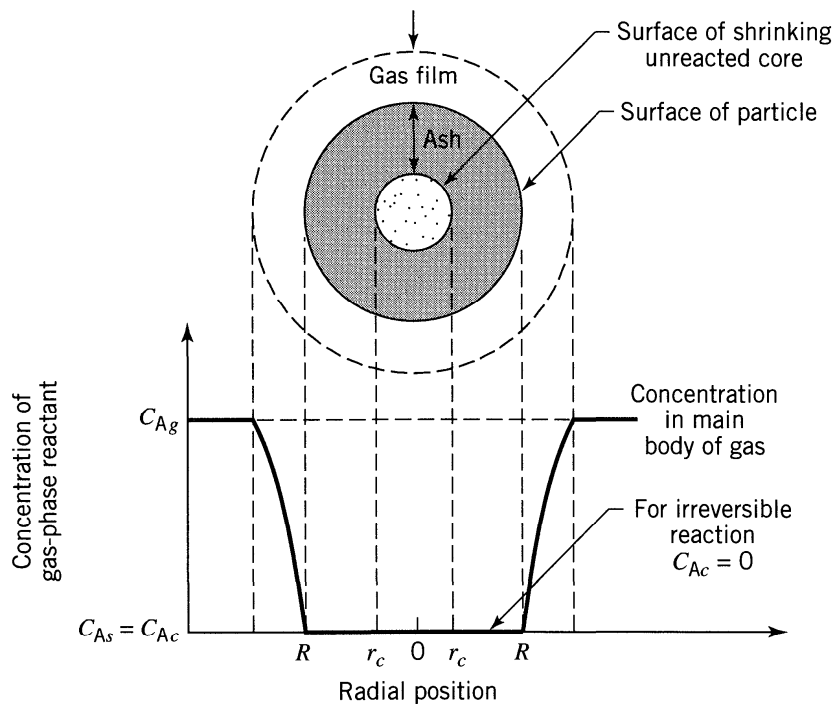
Figure 25.5 Representation of a reacting particle when diffusion through the gas film is the controlling resistance.

If we let ρ_B be the molar density of B in the solid and V be the volume of a particle, the amount of B present in a particle is

$$N_B = \rho_B V = \left(\frac{\text{moles B}}{\text{m}^3 \text{ solid}}\right) (\text{m}^3 \text{ solid}) \tag{5}$$

The decrease in volume or radius of unreacted core accompanying the disappearance of dN_B moles of solid reactant is then given by

$$-dN_B = -b \, dN_A = -\rho_B \, dV = -\rho_B \, d\left(\frac{4}{3} \pi r_c^3\right) = -4\pi \rho_B r_c^2 \, dr_c \tag{6}$$

Replacing Eq. 6 in 4 gives the rate of reaction in terms of the shrinking radius of unreacted core, or

$$-\frac{1}{S_{ex}} \frac{dN_B}{dt} = -\frac{\rho_B r_c^2}{R^2} \frac{dr_c}{dt} = b k_g C_{Ag} \tag{7}$$

where k_g is the mass transfer coefficient between fluid and particle; see the discussion leading up to Eq. 24. Rearranging and integrating, we find how the unreacted core shrinks with time. Thus,

$$-\frac{\rho_B}{R^2} \int_R^{r_c} r_c^2 \, dr_c = b k_g C_{Ag} \int_0^t dt \tag{8}$$

$$t = \frac{\rho_B R}{3 b k_g C_{Ag}} \left[1 - \left(\frac{r_c}{R}\right)^3\right]$$

Let the time for complete conversion of a particle be τ. Then by taking $r_c = 0$ in Eq. 8, we find

$$\boxed{\tau = \frac{\rho_B R}{3 b k_g C_{Ag}}} \tag{9}$$

The radius of unreacted core in terms of fractional time for complete conversion is obtained by combining Eqs. 8 and 9, or

$$\frac{t}{\tau} = 1 - \left(\frac{r_c}{R}\right)^3$$

This can be written in terms of fractional conversion by noting that

$$1 - X_B = \left(\frac{\text{volume of unreacted core}}{\text{total volume of particle}}\right) = \frac{\frac{4}{3} \pi r_c^3}{\frac{4}{3} \pi R^3} = \left(\frac{r_c}{R}\right)^3 \tag{10}$$

Therefore

$$\frac{t}{\tau} = 1 - \left(\frac{r_c}{R}\right)^3 = X_B$$

(11)

Thus we obtain the relationship of time with radius and with conversion, which is shown graphically in Figs. 25.9 and 25.10, pp. 582 and 583.

Diffusion through Ash Layer Controls

Figure 25.6 illustrates the situation in which the resistance to diffusion through the ash controls the rate of reaction. To develop an expression between time and radius, such as Eq. 8 for film resistance, requires a two-step analysis. First examine a typical partially reacted particle, writing the flux relationships for this condition. Then apply this relationship for all values of r_c; in other words, integrate r_c between R and 0.

Consider a partially reacted particle as shown in Fig. 25.6. Both reactant A and the boundary of the unreacted core move inward toward the center of the particle. But for G/S systems the shrinkage of the unreacted core is slower than the flow rate of A toward the unreacted core by a factor of about 1000, which is roughly the ratio of densities of solid to gas. Because of this it is reasonable for us to assume, in considering the concentration gradient of A in the ash layer at any time, that the unreacted core is stationary.
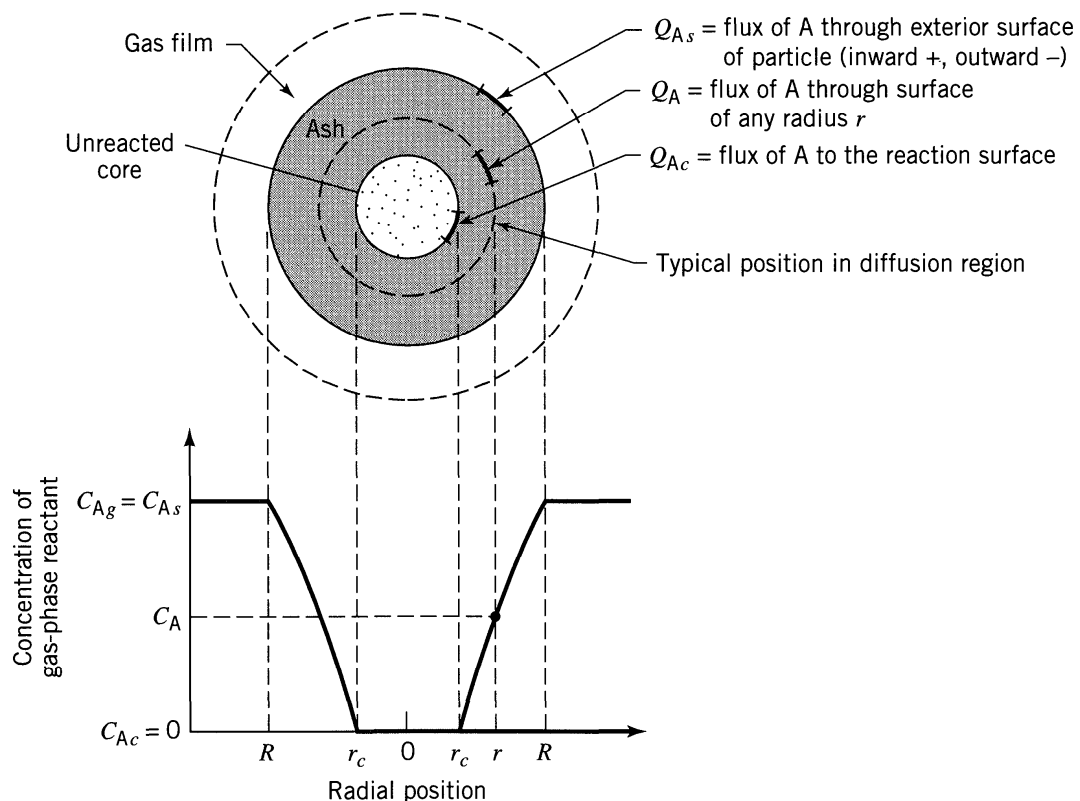

Figure 25.6 Representation of a reacting particle when diffusion through the ash layer is the controlling resistance.

With L/S systems we have a problem because the velocity ratio is closer to unity than to 1000. Yoshida et al. (1975) consider a relaxation of the above assumption.

For G/S systems the use of the steady-state assumption allows great simplification in the mathematics which follows. Thus the rate of reaction of A at any instant is given by its rate of diffusion to the reaction surface, or

$$-\frac{dN_A}{dt} = 4\pi r^2 Q_A = 4\pi R^2 Q_{As} = 4\pi r_c^2 Q_{Ac} = \text{constant} \tag{12}$$

For convenience, let the flux of A within the ash layer be expressed by Fick's law for equimolar counterdiffusion, though other forms of this diffusion equation will give the same result. Then, noting that both Q_A and dC_A/dr are positive, we have

$$Q_A = \mathscr{D}_e \frac{dC_A}{dr} \tag{13}$$

where $\mathscr{D}_e$ is the effective diffusion coefficient of gaseous reactant in the ash layer. Often it is difficult to assign a value beforehand to this quantity because the property of the ash (its sintering qualities, for example) can be very sensitive to small amounts of impurities in the solid and to small variations in the particle's environment. Combining Eqs. 12 and 13, we obtain for any r

$$-\frac{dN_A}{dt} = 4\pi r^2 \mathscr{D}_e \frac{dC_A}{dr} = \text{constant} \tag{14}$$

Integrating across the ash layer form R to r_c, we obtain

$$-\frac{dN_A}{dt} \int_R^{r_c} \frac{dr}{r^2} = 4\pi \mathscr{D}_e \int_{C_{Ag}=C_{As}}^{C_{Ac}=0} dC_A$$

or

$$-\frac{dN_A}{dt} \left(\frac{1}{r_c} - \frac{1}{R} \right) = 4\pi \mathscr{D}_e C_{Ag} \tag{15}$$

This expression represents the conditions of a reacting particle at any time.

In the second part of the analysis we let the size of unreacted core change with time. For a given size of unreacted core, dN_A/dt is constant; however, as the core shrinks the ash layer becomes thicker, lowering the rate of diffusion of A. Consequently, integration of Eq. 15 with respect to time and other variables should yield the required relationship. But we note that this equation contains three variables, t, N_A, and r_c, one of which must be eliminated or written in terms of the other variables before integration can be performed. As with film diffusion, let us eliminate N_A by writing it in terms of r_c. This relationship is given by Eq. 6; hence, replacing in Eq. 15, separating variables, and integrating,

we obtain

$$-\rho_B \int_{r_c=R}^{r_c} \left(\frac{1}{r_c} - \frac{1}{R}\right) r_c^2 \, dr_c = b\mathscr{D}_e C_{Ag} \int_0^t dt$$

or

$$t = \frac{\rho_B R^2}{6b\mathscr{D}_e C_{Ag}} \left[1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3\right] \qquad (16)$$

For the complete conversion of a particle, $r_c = 0$, and the time required is

$$\boxed{\tau = \frac{\rho_B R^2}{6b\mathscr{D}_e C_{Ag}}} \qquad (17)$$

The progression of reaction in terms of the time required for complete conversion is found by dividing Eq. 16 by Eq. 17, or

$$\frac{t}{\tau} = 1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3 \qquad (18a)$$

which in terms of fractional conversion, as given in Eq. 10, becomes

$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \qquad (18b)$$

These results are presented graphically in Figs. 25.9 and 25.10, pp. 582 and 583.

Chemical Reaction Controls

Figure 25.7 illustrates concentration gradients within a particle when chemical reaction controls. Since the progress of the reaction is unaffected by the presence of any ash layer, the rate is proportional to the available surface of unreacted core. Thus, based on unit surface of unreacted core, r_c, the rate of reaction for the stoichiometry of Eqs. 1, 2, and 3 is

$$-\frac{1}{4\pi r_c^2} \frac{dN_A}{dt} = -\frac{b}{4\pi r_c^2} \frac{dN_A}{dt} = bk'' C_{Ag} \qquad (19)$$

where k'' is the first-order rate constant for the surface reaction. Writing N_B in terms of the shrinking radius, as given in Eq. 6, we obtain

$$-\frac{1}{4\pi r_c^2} \rho_B 4\pi r_c^2 \frac{dr_c}{dt} = -\rho_B \frac{dr_c}{dt} = bk'' C_{Ag} \qquad (20)$$
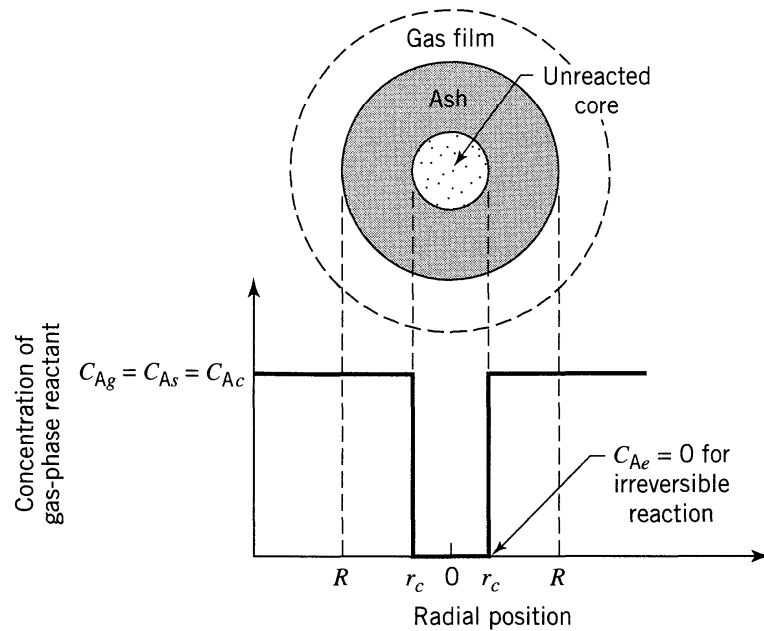
Figure 25.7 Representation of a reacting particle when chemical reaction is the controlling resistance, the reaction being $A(g) + bB(s) \rightarrow$ products.

which on integration becomes

$$-\rho_B \int_R^{r_c} dr_c = bk'' C_{Ag} \int_0^t dt$$

or

$$t = \frac{\rho_B}{bk'' C_{Ag}} (R - r_c) \qquad (21)$$

The time τ required for complete conversion is given when $r_c = 0$, or

$$\boxed{\tau = \frac{\rho_B R}{bk'' C_{Ag}}} \qquad (22)$$

The decrease in radius or increase in fractional conversion of the particle in terms of τ is found by combining Eqs. 21 and 22. Thus,

$$\boxed{\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_B)^{1/3}} \qquad (23)$$

This result is plotted in Figs. 25.9 and 25.10, pp. 582 and 583.

25.3 RATE OF REACTION FOR SHRINKING SPHERICAL PARTICLES

When no ash forms, as in the burning of pure carbon in air, the reacting particle shrinks during reaction, finally disappearing. This process is illustrated in Fig. 25.8. For a reaction of this kind we visualize the following three steps occurring in succession.

Step 1. Diffusion of reactant A from the main body of gas through the gas film to the surface of the solid.

Step 2. Reaction on the surface between reactant A and solid.

Step 3. Diffusion of reaction products from the surface of the solid through the gas film back into the main body of gas. Note that the ash layer is absent and does not contribute any resistance.

As with particles of constant size, let us see what rate expressions result when one or the other of the resistances controls.

Chemical Reaction Controls

When chemical reaction controls, the behavior is identical to that of particles of unchanging size; therefore, Fig. 25.7 and Eq. 21 or 23 will represent the conversion-time behavior of single particles, both shrinking and of constant size.

Gas Film Diffusion Controls

Film resistance at the surface of a particle is dependent on numerous factors, such as the relative velocity between particle and fluid, size of particle, and fluid properties. These have been correlated for various ways of contacting fluid with
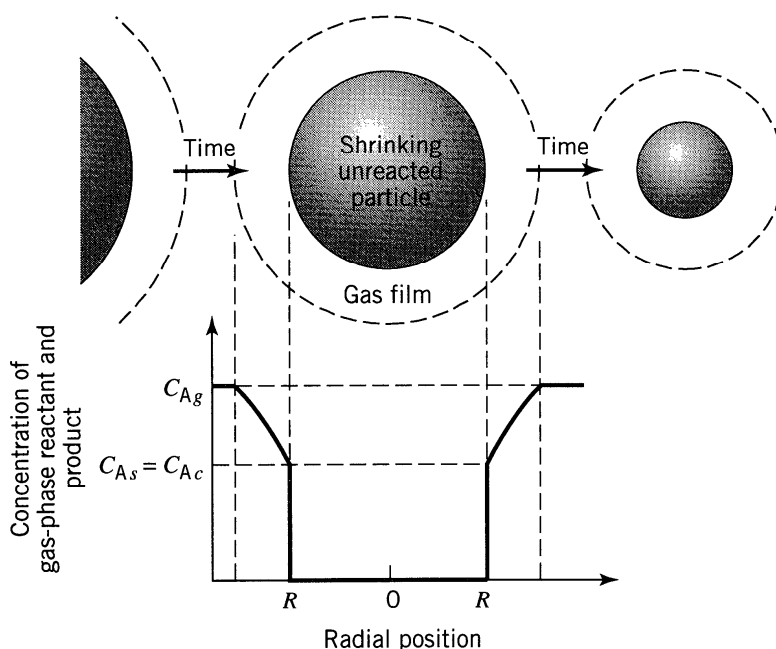

Figure 25.8 Representation of concentration of reactants and products for the reaction $A(g) + bB(s) \rightarrow rR(g)$ between a shrinking solid particle and gas.

solid, such as packed beds, fluidized beds, and solids in free fall. As an example, for mass transfer of a component of mole fraction y in a fluid to free-falling solids Froessling (1938) gives

$$\frac{k_g d_p y}{\mathscr{D}} = 2 + 0.6(\text{Sc})^{1/3}(\text{Re})^{1/2} = 2 + 0.6 \left(\frac{\mu}{\rho \mathscr{D}}\right)^{1/3} \left(\frac{d_p u \rho}{\mu}\right)^{1/2} \qquad \textbf{(24)}$$

During reaction a particle changes in size; hence k_g also varies. In general k_g rises for an increase in gas velocity and for smaller particles. As an example, Fig. 12 and Eq. 24 show that

$$k_g \sim \frac{1}{d_p} \qquad \text{for small } d_p \text{ and } u \qquad \textbf{(25)}$$

$$k_g \sim \frac{u^{1/2}}{d_p^{1/2}} \qquad \text{for large } d_p \text{ and } u \qquad \textbf{(26)}$$

Equation 25 represents particles in the Stokes law regime. Let us develop conversion-time expressions for such particles.

Stokes Regime (Small Particles).   At the time when a particle, originally of size R_0, has shrunk to size R, we may write

$$dN_B = \rho_B \, dV = 4\pi \rho_B R^2 \, dR$$

Thus, analogous to Eq. 7, we have

$$-\frac{1}{S_{ex}} \frac{dN_B}{dt} = \frac{\rho_B 4\pi R^2}{4\pi R^2} \frac{dR}{dt} = -\rho_B \frac{dR}{dt} = b k_g C_{Ag} \qquad \textbf{(27)}$$

Since in the Stokes regime Eq. 24 reduces to

$$k_g = \frac{2\mathscr{D}}{d_p} = \frac{\mathscr{D}}{R} \qquad \textbf{(28)}$$

we have on combining and integrating

$$\int_{R_0}^{R} R \, dR = \frac{b C_{Ag} \mathscr{D}}{\rho_B} \int_{0}^{t} dt$$

or

$$t = \frac{\rho_B R_0^2}{2 b C_{Ag} \mathscr{D}} \left[1 - \left(\frac{R}{R_0}\right)^2 \right]$$

The time for complete disappearance of a particle is thus

$$\tau = \frac{\rho_B R_0^2}{2bC_{Ag}\mathscr{D}}$$

(29)

and on combining we obtain

$$\frac{t}{\tau} = 1 - \left(\frac{R}{R_0}\right)^2 = 1 - (1 - X_B)^{2/3}$$

(30)

This relationship of size versus time for shrinking particles in the Stokes regime is shown in Figs. 25.9 and 25.10, pp. 582 and 583, and it well represents small burning solid particles and small burning liquid droplets.

25.4 EXTENSIONS

Particles of Different Shape. Conversion-time equations similar to those developed above can be obtained for various-shaped particles, and Table 25.1 summarizes these expressions.

Combination of Resistances. The above conversion-time expressions assume that a single resistance controls throughout reaction of the particle. However, the relative importance of the gas film, ash layer, and reaction steps will vary as particle conversion progresses. For example, for a constant size particle the gas film resistance remains unchanged, the resistance to reaction increases as the surface of unreacted core decreases, while the ash layer resistance is nonexistent at the start because no ash is present, but becomes progressively more and more important as the ash layer builds up. In general, then, it may not be reasonable to consider that just one step controls throughout reaction.

To account for the simultaneous action of these resistances is straightforward since they act in series and are all linear in concentration. Thus on combining Eqs. 7, 15, and 20 with their individual driving forces and eliminating intermediate concentrations we can show that the time to reach any stage of conversion is the sum of the times needed if each resistance acted alone, or

$$t_{\text{total}} = t_{\text{film alone}} + t_{\text{ash alone}} + t_{\text{reaction alone}}$$

(32a)

Similarly, for complete conversion

$$\tau_{\text{total}} = \tau_{\text{film alone}} + \tau_{\text{ash alone}} + \tau_{\text{reaction alone}}$$

(32b)

In an alternative approach, the individual resistances can be combined directly to give, at any particular stage of conversion,

$$-\frac{1}{S_{ex}}\frac{dN_B}{dt} = \frac{bC_A}{\dfrac{1}{k_g} + \dfrac{R(R - r_c)}{r_c \mathscr{D}_e} + \dfrac{R^2}{r_c^2 k''}}$$

(33a)

Table 25.1 Conversion-Time Expressions for Various Shapes of Particles, Shrinking-Core Model

	Film Diffusion Controls	Ash Diffusion Controls	Reaction Controls
Constant Size Particles			
Flat plate $X_B = 1 - \frac{1}{L}$, L = half thickness	$\frac{t}{\tau} = X_B$ $\tau = \frac{\rho_B L}{b k_g C_{Ag}}$	$\frac{t}{\tau} = X_B^2$ $\tau = \frac{\rho_B L^2}{2 b \mathscr{D}_e C_{Ag}}$	$\frac{t}{\tau} = X_B$ $\tau = \frac{\rho_B L}{b k'' C_{Ag}}$
Cylinder $X_B = 1 - \left(\frac{r_c}{R}\right)^2$	$\frac{t}{\tau} = X_B$ $\tau = \frac{\rho_B R}{2 b k_g C_{Ag}}$	$\frac{t}{\tau} = X_B + (1 - X_B)\ln(1 - X_B)$ $\tau = \frac{\rho_B R^2}{4 b \mathscr{D}_e C_{Ag}}$	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/2}$ $\tau = \frac{\rho_B R}{b k'' C_{Ag}}$
Sphere $X_B = 1 - \left(\frac{r_c}{R}\right)^3$	$\frac{t}{\tau} = X_B$ **(11)** $\tau = \frac{\rho_B R}{3 b k_g C_{Ag}}$ **(10)**	$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$ **(18)** $\tau = \frac{\rho_B R^2}{6 b \mathscr{D}_e C_{Ag}}$ **(17)**	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$ **(23)** $\tau = \frac{\rho_B R}{b k'' C_{Ag}}$ **(22)**
Shrinking Sphere			
Small particle Stokes regime	$\frac{t}{\tau} = 1 - (1 - X_B)^{2/3}$ **(30)** $\tau = \frac{\rho_B R_0^2}{2 b \mathscr{D} C_{Ag}}$ **(29)**	Not applicable	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$ $\tau = \frac{\rho_B R_0}{b k'' C_{Ag}}$
Large particle (u = constant)	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/2}$ **(31)** $\tau = (\text{const}) \frac{R_0^{3/2}}{C_{Ag}}$	Not applicable	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$ $\tau = \frac{\rho_B R}{b k'' C_{Ag}}$

or

$$-\frac{dr_c}{dt} = \frac{bC_A/\rho_B}{\underbrace{\frac{r_c^2}{R^2 k_g}}_{\text{film}} + \underbrace{\frac{(R - r_c)r_c}{R\mathscr{D}_e}}_{\text{ash}} + \underbrace{\frac{1}{k''}}_{\text{reaction}}} \tag{33b}$$

As may be seen, the relative importance of the three individual resistances varies as conversion progresses, or as r_c decreases.

On considering the whole progression from fresh to completely converted constant size particle, we find on the average that the relative roles of these three resistances is given by

$$-\frac{1}{S_{ex}}\frac{\overline{dN_A}}{dt} = \overline{k''}C_A = \frac{C_A}{\frac{1}{k_g} + \frac{R}{2\mathscr{D}_e} + \frac{3}{k''}} \tag{34}$$

For ash-free particles which shrink with reaction, only two resistances, gas film and surface reaction, need to be considered. Because these are both based on the changing exterior surface of particles, we may combine them to give at any instant

$$-\frac{1}{S_{ex}}\frac{dN_A}{dt} = \frac{1}{\frac{1}{k_g} + \frac{1}{k''}} C_A \tag{35}$$

Various forms of these expressions have been derived by Yagi and Kunii (1955), Shen and Smith (1965), and White and Carberry (1965).

Limitations of the Shrinking Core Model. The assumptions of this model may not match reality precisely. For example, reaction may occur along a diffuse front rather than along a sharp interface between ash and fresh solid, thus giving behavior intermediate between the shrinking core and the continuous reaction models. This problem is considered by Wen (1968), and Ishida and Wen (1971).

Also, for fast reaction the rate of heat release may be high enough to cause significant temperature gradients within the particles or between particle and the bulk fluid. This problem is treated in detail by Wen and Wang (1970).

Despite these complications Wen (1968) and Ishida et al. (1971), on the basis of studies of numerous systems, conclude that the shrinking core model is the best simple representation for the majority of reacting gas-solid systems.

There are, however, two broad classes of exceptions to this conclusion. The first comes with the slow reaction of a gas with a very porous solid. Here reaction can occur throughout the solid, in which situation the continuous reaction model may be expected to better fit reality. An example of this is the slow poisoning of a catalyst pellet, a situation treated in Chapter 21.

The second exception occurs when solid is converted by the action of heat, and without needing contact with gas. Baking bread, boiling missionaries, and

roasting puppies are mouthwatering examples of such reactions. Here again the continuous reaction model is a better representation of reality. Wen (1968) and Kunii and Levenspiel (1991) treat these kinetics.

25.5 DETERMINATION OF THE RATE-CONTROLLING STEP

The kinetics and rate-controlling steps of a fluid–solid reaction are deduced by noting how the progressive conversion of particles is influenced by particle size and operating temperature. This information can be obtained in various ways, depending on the facilities available and the materials at hand. The following observations are a guide to experimentation and to the interpretation of experimental data.

Temperature. The chemical step is usually much more temperature-sensitive than the physical steps; hence, experiments at different temperatures should easily distinguish between ash or film diffusion on the one hand and chemical reaction on the other hand as the controlling step.

Time. Figures 25.9 and 25.10 show the progressive conversion of spherical solids when chemical reaction, film diffusion, and ash diffusion in turn control. Results of kinetic runs compared with these predicted curves should indicate the rate-controlling step. Unfortunately, the difference between ash diffusion and chemical reaction as controlling steps is not great and may be masked by the scatter in experimental data.
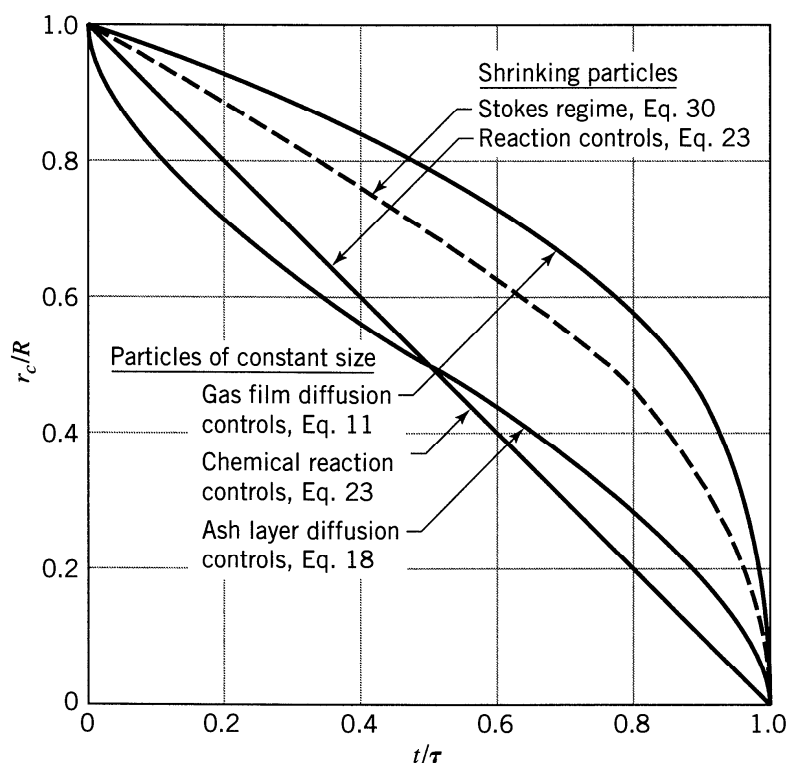

Figure 25.9 Progress of reaction of a single spherical particle with surrounding fluid measured in terms of time for complete reaction.
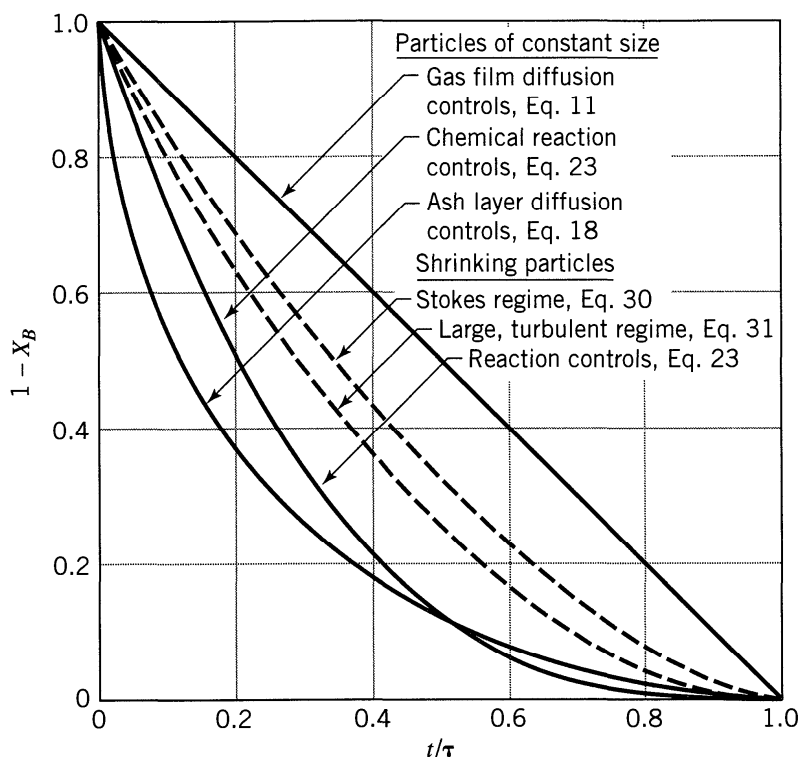
Figure 25.10 Progress of reaction of a single spherical particle with surrounding fluid measured in terms of time for complete conversion.

Conversion-time curves analogous to those in Figs. 25.9 and 25.10 can be prepared for other solid shapes by using the equations of Table 25.1.

Particle Size. Equations 16, 21, and 8 with Eq. 24 or 25 show that the time needed to achieve the same fractional conversion for particles of different but unchanging sizes is given by

$t \propto R^{1.5 \text{ to } 2.0}$	for film diffusion controlling (the exponent drops as Reynolds number rises)	**(36)**
$t \propto R^2$	for ash diffusion controlling	**(37)**
$t \propto R$	for chemical reaction controlling	**(38)**

Thus kinetic runs with different sizes of particles can distinguish between reactions in which the chemical and physical steps control.

Ash Versus Film Resistance. When a hard solid ash forms during reaction, the resistance of gas-phase reactant through this ash is usually much greater than through the gas film surrounding the particle. Hence in the presence of a nonflaking ash layer, film resistance can safely be ignored. In addition, ash resistance is unaffected by changes in gas velocity.

Predictability of Film Resistance. The magnitude of film resistance can be estimated from dimensionless correlations such as Eq. 24. Thus an observed rate approximately equal to the calculated rate suggests that film resistance controls.
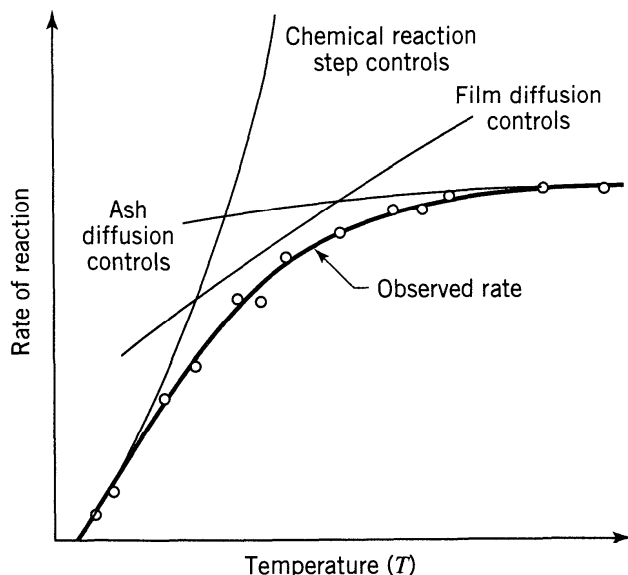
Figure 25.11 Because of the series relationship among the resistances to reaction, the net or observed rate is never higher than for any of the individual steps acting alone.

Overall Versus Individual Resistance. If a plot of individual rate coefficients is made as a function of temperature, as shown in Fig. 25.11, the overall coefficient given by Eq. 34 or 35 cannot be higher than any of the individual coefficients.

With these observations we can usually discover with a small, carefully planned experimental program which is the controlling mechanism.

Let us illustrate the interplay of resistances with the well-studied gas–solid reaction of pure carbon particles with oxygen:

$$C + O_2 \rightarrow CO_2$$

$$[B(s) + A(g) \rightarrow \text{gaseous products}]$$
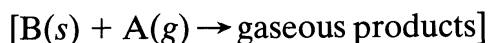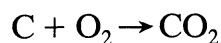
with rate equation

$$-\frac{1}{S_{ex}}\frac{dN_B}{dt} = -\frac{1}{4\pi R^2}4\pi R^2 \rho_B \frac{dR}{dt} = -\rho_B \frac{dR}{dt} = \overline{k}'' C_A \tag{27}$$

Since no ash is formed at any time during reaction, we have here a case of kinetics of shrinking particles for which two resistances at most, surface reaction and gas film, may play a role. In terms of these, the overall rate constant at any instant from Eq. 35 is

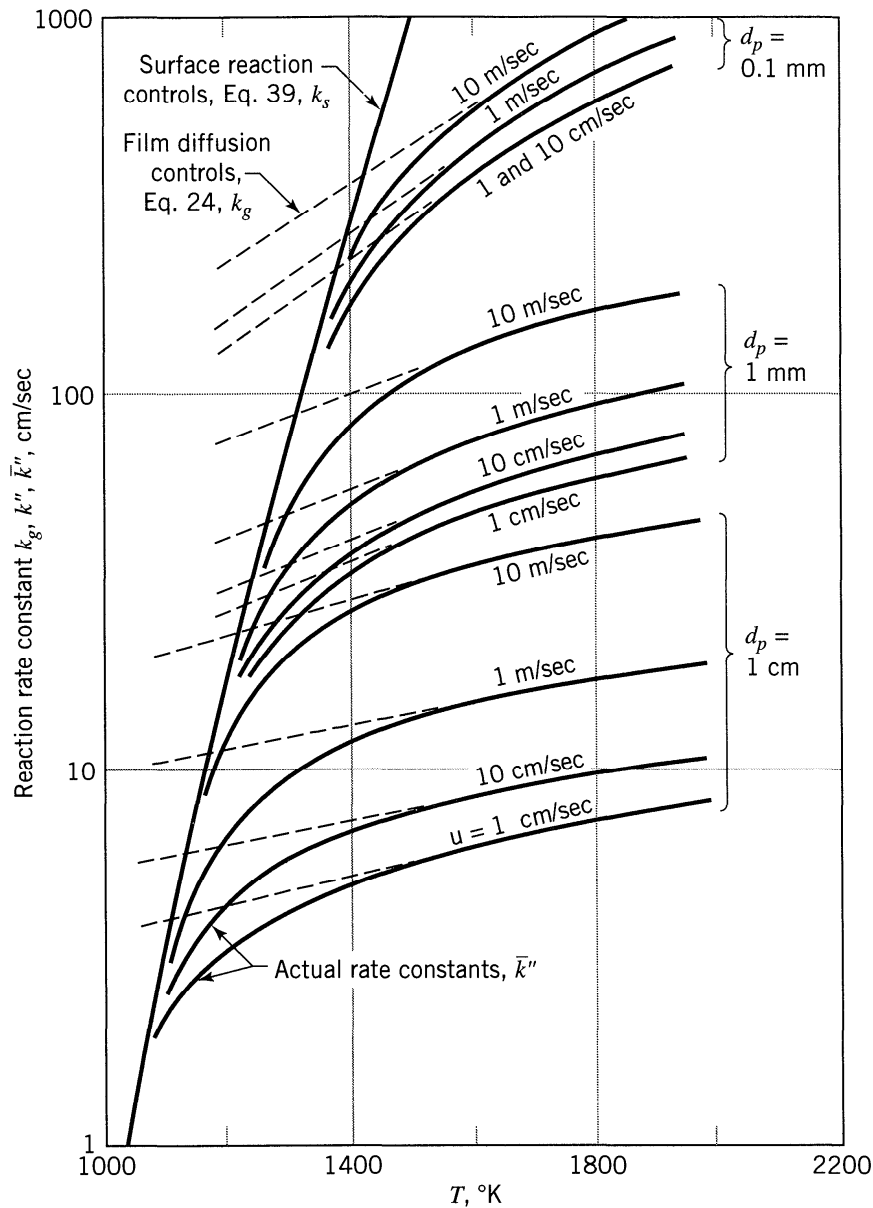$$\frac{1}{\overline{k}''} = \frac{1}{k''} + \frac{1}{k_g}$$

Figure 25.12 Rate of combustion of pure carbon particles; this figure is adapted from Yagi and Kunii (1955).

k_g is given by Eq. 24, while k'' is given by the following expression of Parker and Hottel (1936):

$$-\frac{1}{S_{ex}}\frac{dN_B}{dt} = 4.32 \times 10^{11} C_{Ag}\sqrt{T}\,e^{-(184\,000)/RT} = k_s C_{Ag} \qquad (39)$$

where **R** is in J/mol·K, T is in kelvin, and C_{Ag} is in gram moles per liter. Figure 25.12 shows all this information in convenient graphical form and allows determination of $\overline{k}''$ for different values of the system variables. Note that when film resistance controls, the reaction is rather temperature insensitive but is dependent on particle size and relative velocity between solid and gas. This is shown by the family of lines, close to parallel and practically horizontal.

In extrapolating to new untried operating conditions, we must know when to be prepared for a change in controlling step and when we may reasonably expect the rate-controlling step not to change. For example, for particles with nonflaking ash a rise in temperature and to a lesser extent an increase in particle size may cause the rate to switch from reaction to ash diffusion controlling. For reactions in which ash is not present, a rise in temperature will cause a shift from reaction to film resistance controlling.

On the other hand, if ash diffusion already controls, then a rise in temperature should not cause it to shift to reaction control or film diffusion control.

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PROBLEMS

25.1. A batch of solids of uniform size is treated by gas in a uniform environment. Solid is converted to give a nonflaking product according to the shrinking-core model. Conversion is about $\frac{7}{8}$ for a reaction time of 1 h, conversion is complete in two hours. What mechanism is rate controlling?

25.2. In a shady spot at the end of Brown Street in Lewisburg, Pennsylvania, stands a Civil War memorial—a brass general, a brass cannon which persistent undergraduate legend insists may still fire some day, and a stack of iron cannonballs. At the time this memorial was set up, 1868, the cannonballs were 30 inches in circumference. Today due to weathering, rusting, and the once-a-decade steel wire scrubbing by the DCW, the cannonballs are only 29.75 in. in circumference. Approximately, when will they disappear completely?

25.3. Calculate the time needed to burn to completion particles of graphite ($R_0 = 5$ mm, $\rho_B = 2.2$ gm/cm^3, $k'' = 20$ cm/sec) in an 8% oxygen stream.

For the high gas velocity used assume that film diffusion does not offer any resistance to transfer and reaction. Reaction temperature = 900°C.

25.4. Spherical particles of zinc blende of size $R = 1$ mm are roasted in an 8% oxygen stream at 900°C and 1 atm. The stoichiometry of the reaction is

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$
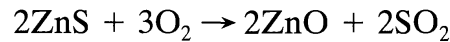
Assuming that reaction proceeds by the shrinking-core model calculate the time needed for complete conversion of a particle and the relative resistance of ash layer diffusion during this operation.

Data
Density of solid, $\rho_B = 4.13$ gm/cm^3 = 0.0425 mol/cm^3
Reaction rate constant, $k'' = 2$ cm/sec
For gases in the ZnO layer, $\mathscr{D}_e = 0.08$ cm^2/sec
Note that film resistance can safely be neglected as long as a growing ash layer is present.

On doubling the particle size from R to 2R the time for complete conversion triples. What is the contribution of ash diffusion to the overall resistance for particles of size

25.5. R?   **25.6.** $2R$?

Spherical solid particles containing B are roasted isothermally in an oven with gas of constant composition. Solids are converted to a firm nonflaking product according to the SCM as follows:

$$A(g) + B(s) \rightarrow R(g) + S(s), \quad C_A = 0.01 \text{ kmol/m}^3, \quad \rho_B = 20 \text{ kmol/m}^3$$
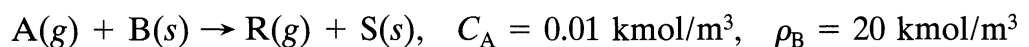
From the following conversion data (by chemical analysis) or core size data (by slicing and measuring) determine the rate controlling mechanism for the transformation of solid.

25.7. d_p, mm	X_B	t, min	**25.8.** d_p	X_B	t, sec
1	1	4	1	0.3	2
1.5	1	6	1	0.75	5

25.9. d_p, mm	X_B	t, sec	**25.10.** d_p	X_B	t, sec
1	1	200	2	0.875	1
1.5	1	450	1	1	1

25.11. Uniform-sized spherical particles UO_3 are reduced to UO_2 in a uniform environment with the following results:

t, hr	0.180	0.347	0.453	0.567	0.733
X_B	0.45	0.68	0.80	0.95	0.98

If reaction follows the SCM, find the controlling mechanism and a rate equation to represent this reduction.

25.12. A large stockpile of coal is burning. Every part of its surface is in flames. In a 24-hr period the linear size of the pile, as measured by its silhouette against the horizon, seems to decrease by about 5%.
  (a) How should the burning mass decrease in size?
  (b) When should the fire burn itself out?
  (c) State the assumptions on which your estimation is based.