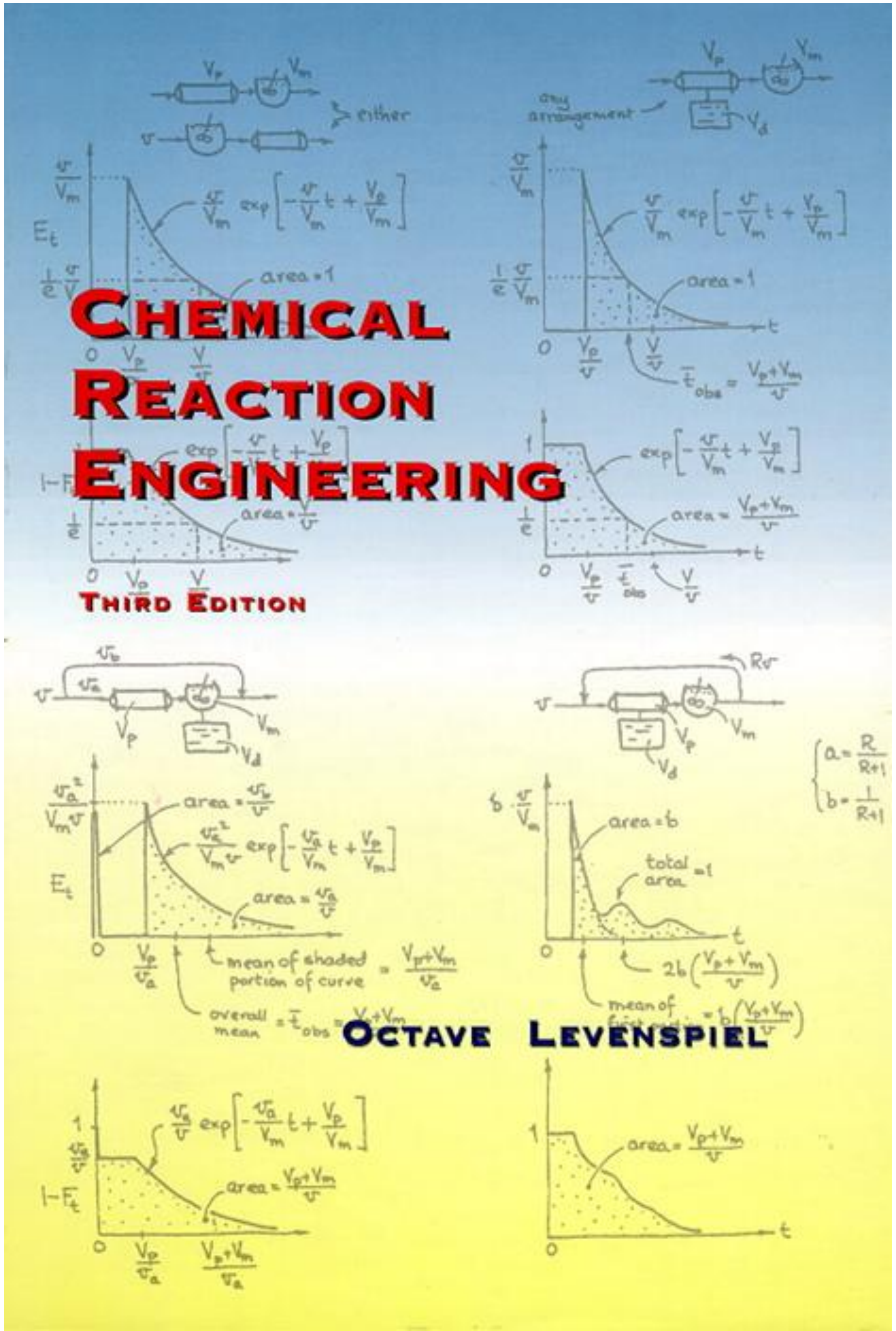


Ch25. Fluid-Particle Reactions: Kinetics

25.1 Selection of a Model
25.2 Shrinking-Core Model for Spherical Particles of Unchanging Size
25.3 Rate of Reaction for Shrinking Spherical Particles
25.4 Extensions
25.5 Determination of the Rate-Controlling Step

$$\begin{aligned} \text{A(fluid)} + b\text{B(solid)} &\rightarrow \text{fluid products} && \textbf{(1)} \\ &\rightarrow \text{solid products} && \textbf{(2)} \\ &\rightarrow \text{fluid and solid products} && \textbf{(3)} \end{aligned}$$

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

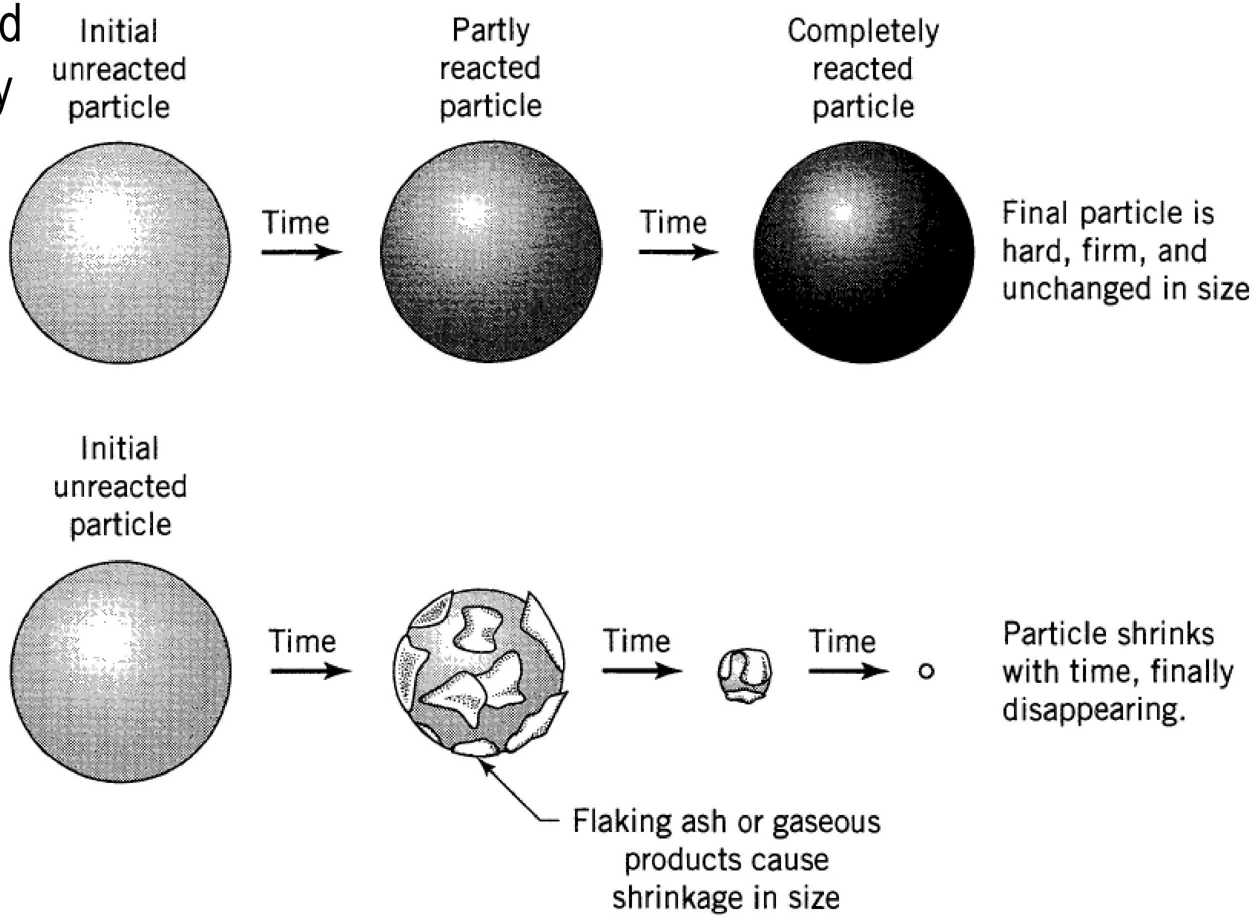


Figure 25.1 Different sorts of behavior of reacting solid particles.

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

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$

$$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

2. The preparation of metals from their oxides by reaction in reducing atmospheres.

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

3. The nitrogenation of calcium carbide to produce cyanamide

$$CaC_2(s) + N_2(g) \rightarrow CaCN_2(s) + C(\text{amorphous})$$

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.

$$C(s) + O_2(g) \rightarrow CO_2(g)$$
$$2C(s) + O_2(g) \rightarrow 2CO(g)$$
$$C(s) + CO_2(g) \rightarrow 2CO(g)$$

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$$
$$C(s) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2(g)$$

Other examples of reactions in which solids change in size are as follows.

1. The manufacture of carbon disulfide from the elements

$$C(s) + 2S(g) \xrightarrow{750\text{–}1000^\circ C} CS_2(g)$$

2. The manufacture of sodium cyanide from sodium amide

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

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

$$Na_2SO_3(\text{solution}) + S(s) \rightarrow Na_2S_2O_3(\text{solution})$$

25.1 Selection of a Model

For the noncatalytic reaction of particles with surrounding fluid, we consider two simple idealized models,

1) the progressive-conversion model and 2) the shrinking unreacted-core model.

1) Progressive-Conversion Model (PCM)

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.

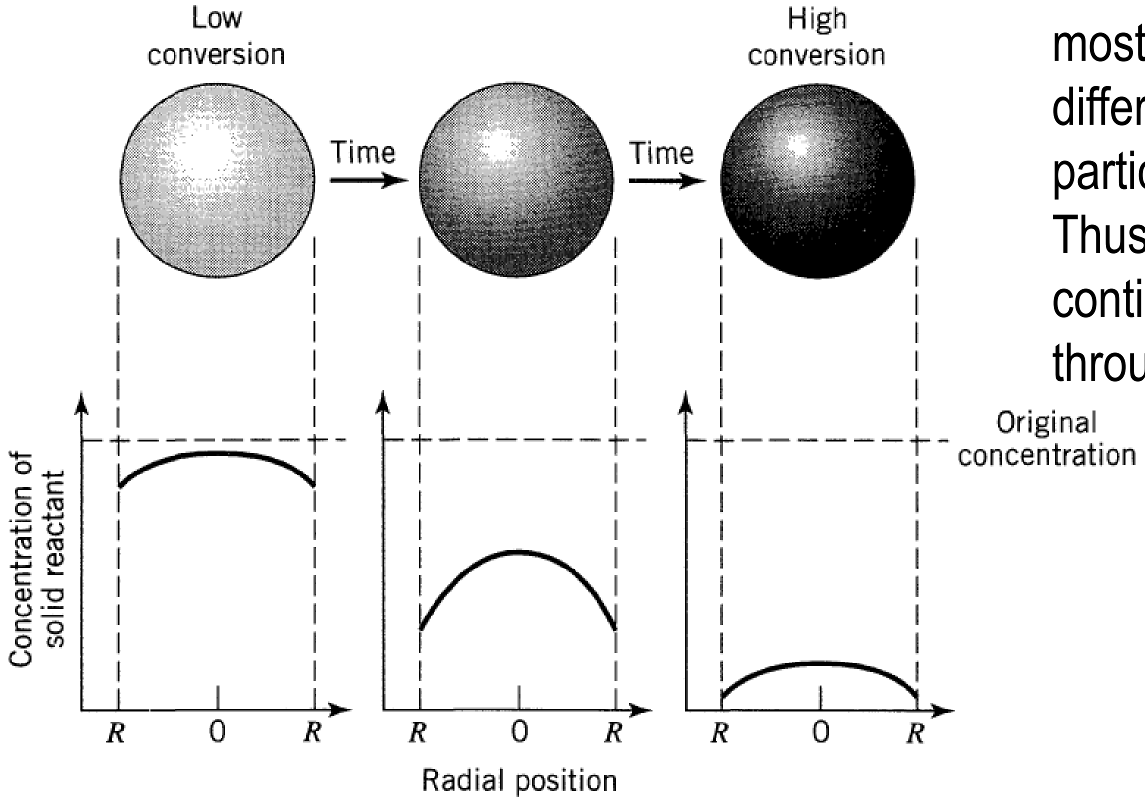


Figure 25.2 According to the progressive-conversion model, reaction proceeds continuously throughout the solid particle.

2) Shrinking-Core Model (SCM)

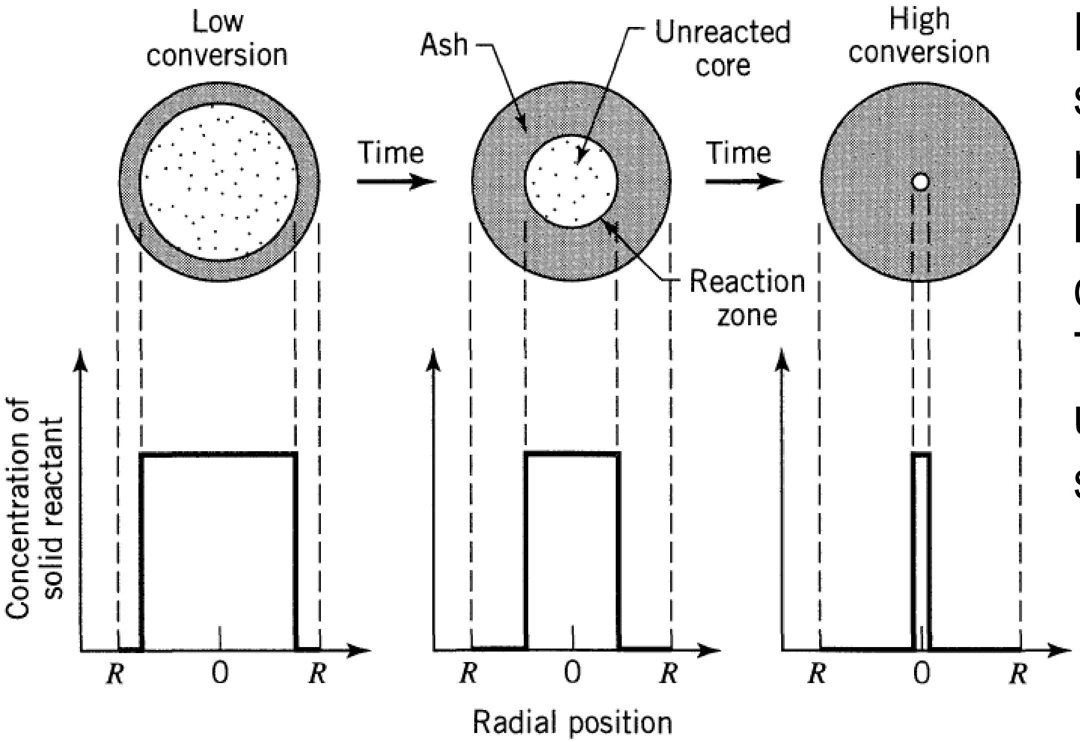


Figure 25.3 According to the shrinking-core model, reaction proceeds at a narrow front which moves into the solid particle. Reactant is completely converted as the front passes by.

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. Thus, at any time there exists an unreacted core of material which shrinks in size during reaction,

Comparison of Models with Real Situations.

In most cases, the shrinking-core model (SCM) approximates real particles more closely than does the progressive conversion model (PCM).

25.2 Shrinking-Core Model for Spherical Particles of Unchanging Size

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.

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.

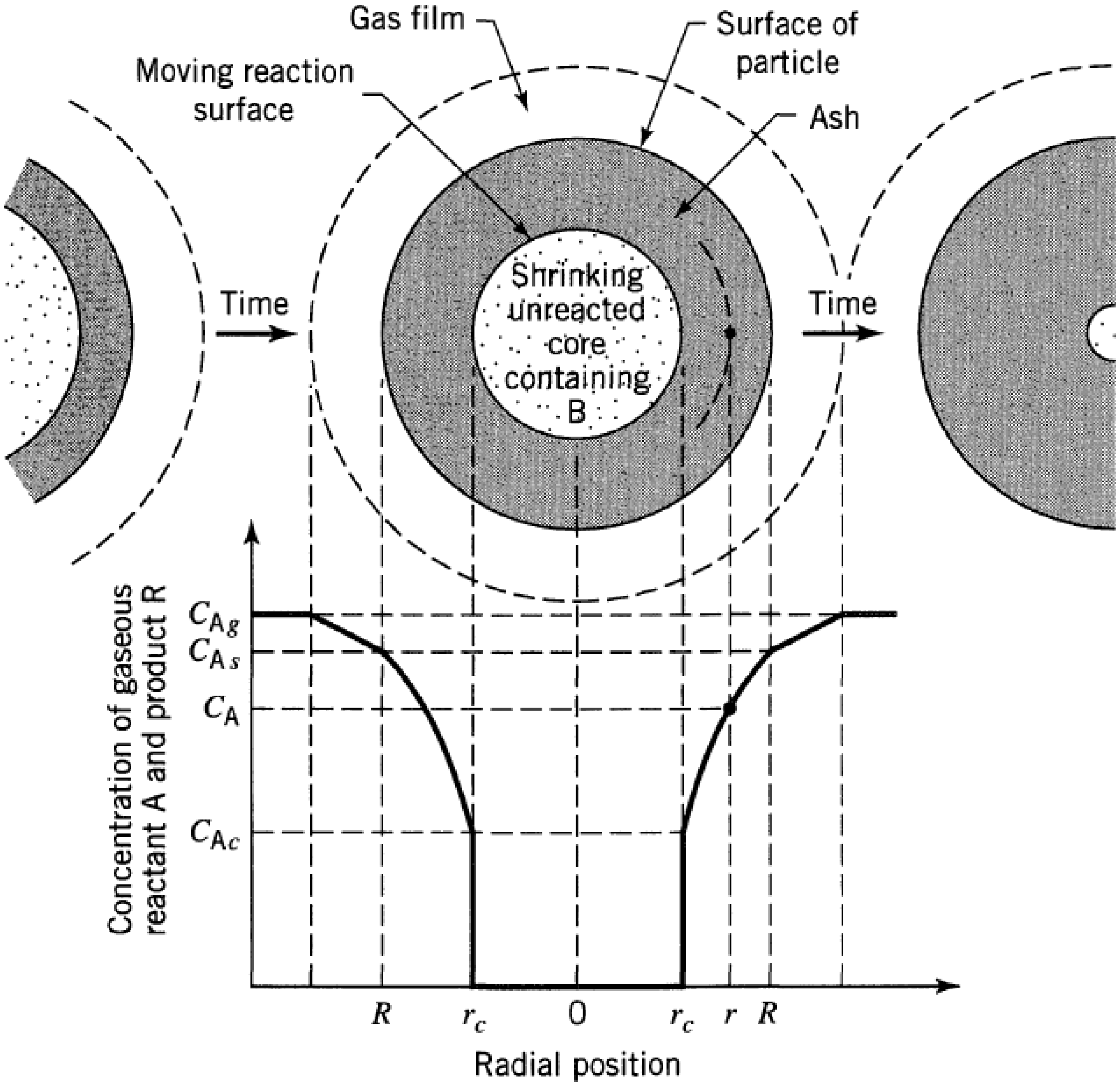


Figure 25.4 Representation of concentrations of reactants and products for the reaction $A(g) + bB(s) \rightarrow$ solid product for a particle of unchanging size.

Case 1) Diffusion Through Gas Film Controls

$$A(g) + bB(s) \rightarrow \text{solid product}$$

$$dN_B = b\,dN_A$$

$$-\frac{1}{S_{ex}}\frac{dN_B}{dt} = -\frac{1}{4\pi R^2}\frac{dN_B}{dt} = -\frac{b}{4\pi R^2}\frac{dN_A}{dt}$$

$$= bk_g(C_{Ag} - C_{As}) = bk_gC_{Ag} = \text{constant}$$

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

$$-b\,dN_A = -dN_B = -\rho_B\,dV$$

$$= -\rho_B\,d\left(\frac{4}{3}\pi r_c^3\right) = -4\pi\rho_B r_c^2\,dr_c$$

$$-\frac{1}{S_{ex}}\frac{dN_B}{dt} = -\frac{\rho_B r_c^2}{R^2}\frac{dr_c}{dt} = bk_gC_{Ag}$$

$$-\frac{\rho_B}{R^2}\int_R^{r_c} r_c^2\,dr_c = bk_gC_{Ag}\int_0^t dt$$

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.

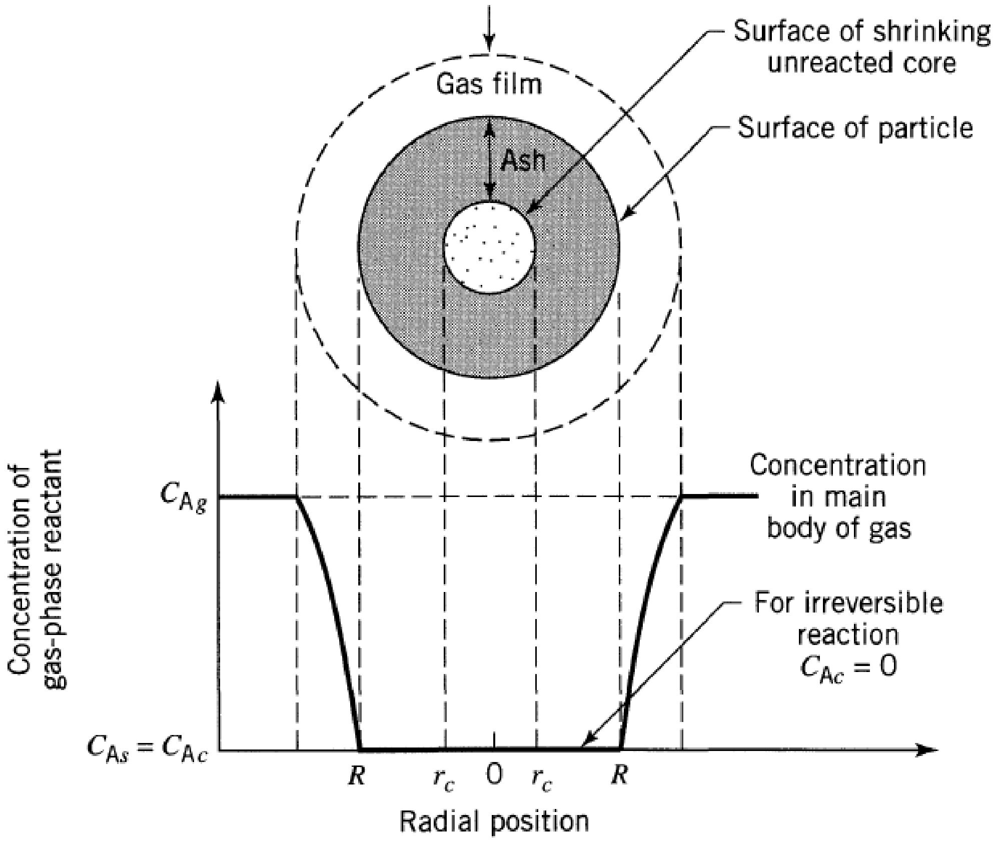


Figure 25.5 Representation of a reacting particle when diffusion through the gas film is the controlling resistance.

S_{ex}: the unchanging exterior surface of a particle

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

Let the time for complete conversion of a particle be $\boldsymbol{\tau}$

$$r_c = 0$$

$$\boxed{\boldsymbol{\tau} = \frac{\rho_B R}{3bk_g C_{Ag}}}$$

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

“The radius of unreacted core in terms of fractional time for complete conversion”

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

“The radius of unreacted core in terms of fractional conversion”

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

“the relationship of time with radius and with conversion”

Case 2) Diffusion Through Ash Layer Controls

$$A(g) + bB(s) \rightarrow \text{solid product}$$

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.

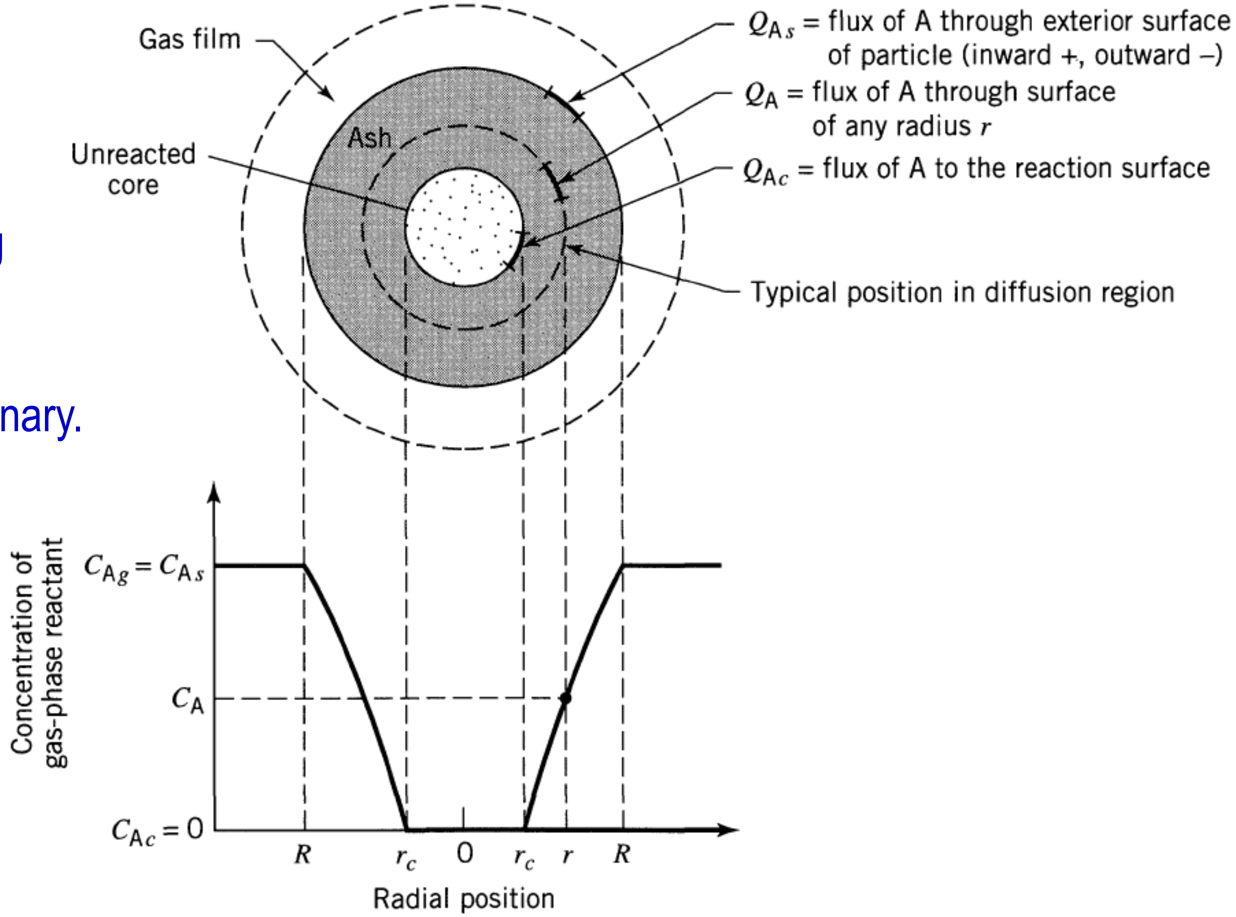


Figure 25.6 Representation of a reacting particle when diffusion through the ash layer is the controlling resistance.

For G/S systems, assume steady-state

Rate of reaction of A at any instant is given by its rate of diffusion to the reaction surface

$$-\frac{dN_{\mathrm{A}}}{dt} = 4\pi r^2 Q_{\mathrm{A}} = 4\pi R^2 Q_{\mathrm{A}s} = 4\pi r_c^2 Q_{\mathrm{A}c} = \text{constant}$$

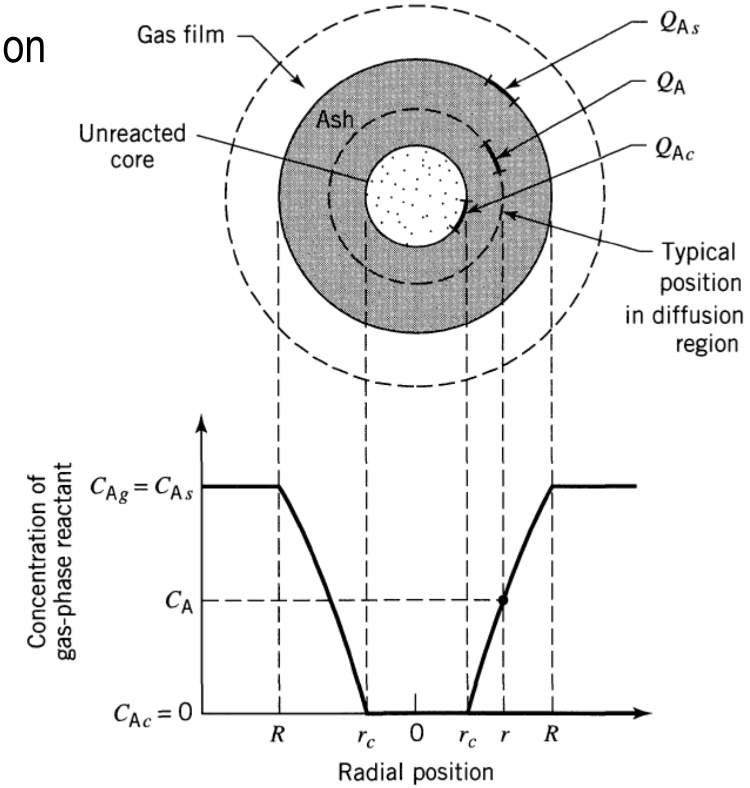
Fick's law for equimolar counter-diffusion

$$Q_{\mathrm{A}} = \mathscr{D}_e \frac{dC_{\mathrm{A}}}{dr}$$

$$-\frac{dN_{\mathrm{A}}}{dt} = 4\pi r^2 \mathscr{D}_e \frac{dC_{\mathrm{A}}}{dr} = \text{constant}$$

$$-\frac{dN_{\mathrm{A}}}{dt}\int_R^{r_c}\frac{dr}{r^2} = 4\pi\mathscr{D}_e\int_{C_{\mathrm{A}g}=C_{\mathrm{A}s}}^{C_{\mathrm{A}c}=0} dC_{\mathrm{A}}$$

$$-\frac{dN_{\mathrm{A}}}{dt}\left(\frac{1}{r_c}-\frac{1}{R}\right) = 4\pi\mathscr{D}_e C_{\mathrm{A}g}$$



$$-b\,dN_{\mathrm{A}} = -dN_{\mathrm{B}} = -\rho_{\mathrm{B}}\,dV$$
$$= -\rho_{\mathrm{B}}\,d\left(\frac{4}{3}\pi r_c^3\right) = -4\pi\rho_{\mathrm{B}} r_c^2\,dr_c$$

$$N_{\mathrm{B}} = \rho_{\mathrm{B}} V = \left(\frac{\text{moles B}}{\text{m}^3\text{ solid}}\right)(\text{m}^3\text{ solid})$$

$$\Downarrow$$

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

$$\Downarrow$$

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

Let the time for complete conversion of a particle be $\boldsymbol{\tau}$

$$r_c = 0$$

$$\boxed{\boldsymbol{\tau} = \frac{\rho_B R^2}{6b\mathscr{D}_e C_{Ag}}}$$

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

“The progression of reaction
in terms of the time required for complete conversion”

$$\Downarrow$$

$$\boxed{\frac{t}{\boldsymbol{\tau}} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)}$$

“The progression of reaction
in terms of fractional conversion”

Case 3) Chemical Reaction Controls

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

$$-\frac{1}{4\pi r_c^2}\rho_B 4\pi r_c^2 \frac{dr_c}{dt} = -\rho_B\frac{dr_c}{dt} = bk''C_{Ag}$$

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

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

$$\tau = \frac{\rho_B R}{bk''C_{Ag}}$$

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

$$A(g) + bB(s) \rightarrow \text{solid product}$$

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

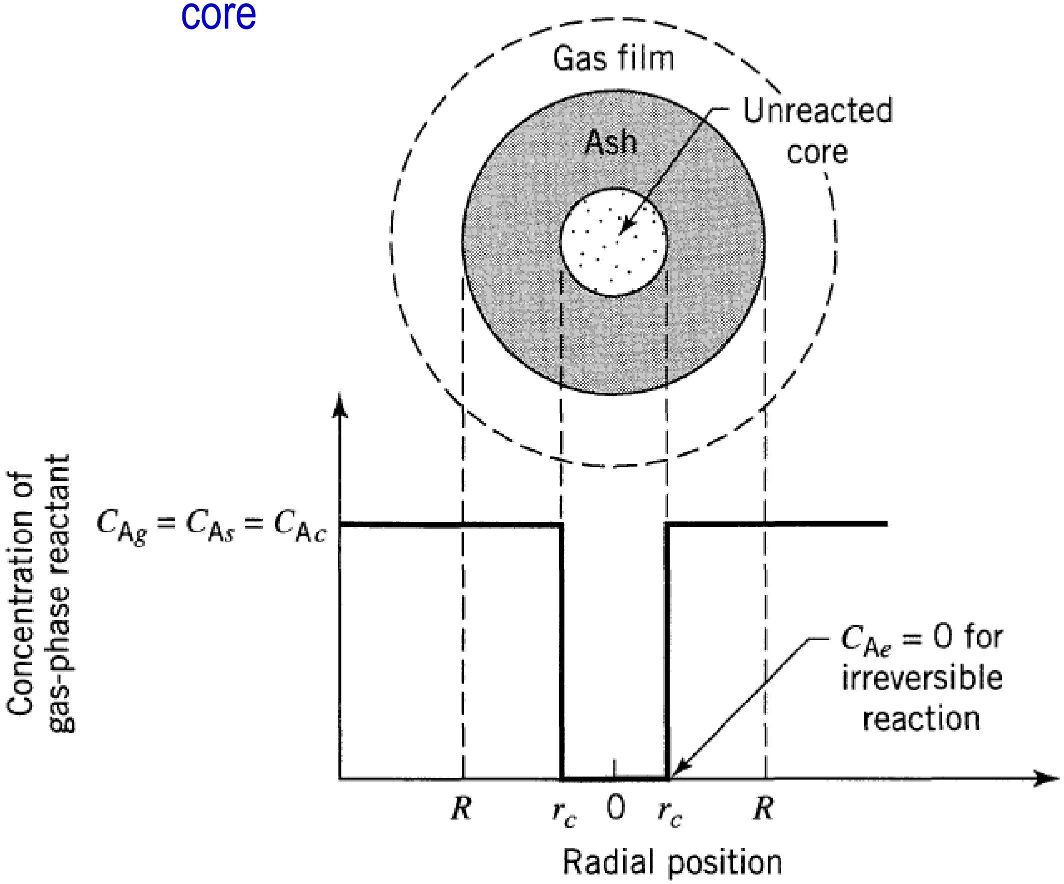


Figure 25.7 Representation of a reacting particle when chemical reaction is the controlling resistance, the reaction being $A(g) + bB(s) \rightarrow$ products.

25.3 Rate of Reaction for Shrinking Spherical Particles

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.

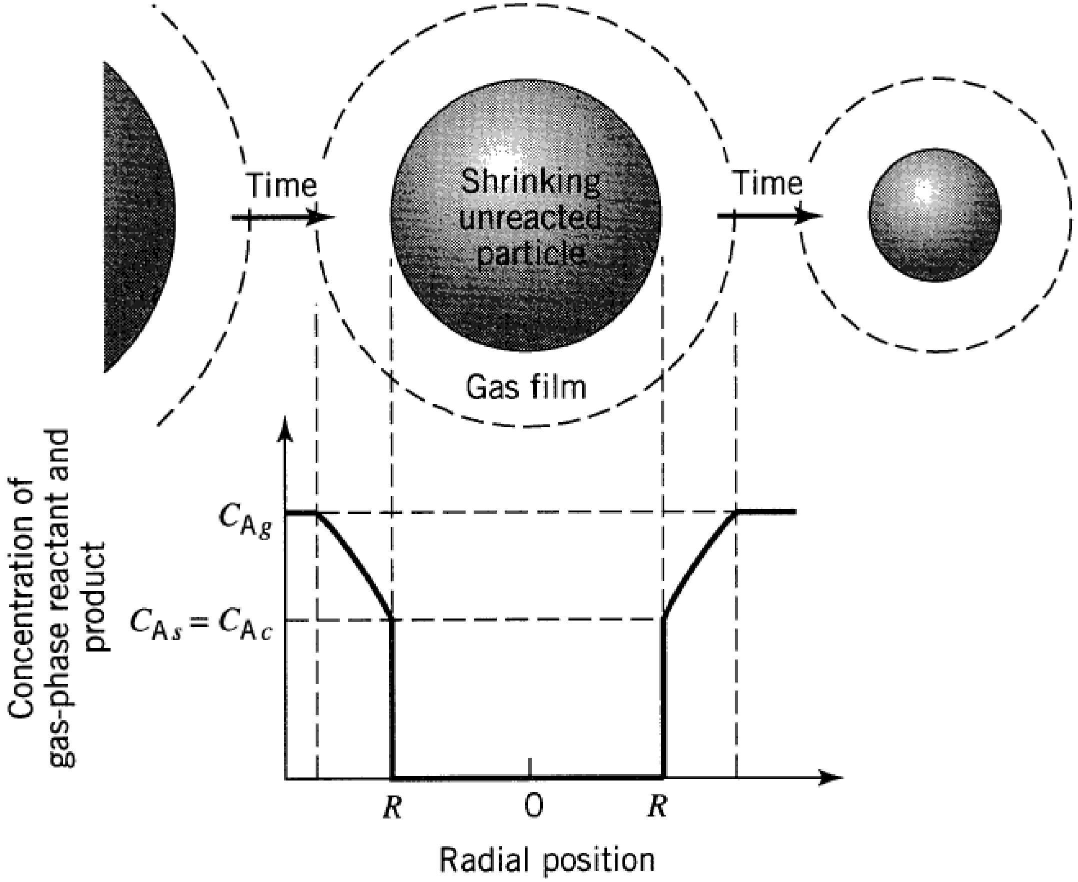


Figure 25.8 Representation of concentration of reactants and products for the reaction $A(g) + bB(s) \rightarrow rR(g)$ between a shrinking solid particle and gas.

Case 1) Chemical Reaction Controls

When chemical reaction controls, the behavior is identical to that of particles of unchanging size.

Case 2) 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 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

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

During reaction a particle changes in size; hence k_g also varies.

$$k_g \sim \frac{1}{d_p} \qquad \text{for small } d_p \text{ and } u$$

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

Case 3) Stokes Regime (Small Particles)

At the time when a particle, originally of size R_0, has shrunk to size R, we

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

$$\Downarrow$$

$$-\frac{1}{S_{ex}}\frac{dN_B}{dt} = \frac{\rho_B 4\pi R^2}{4\pi R^2}\frac{dR}{dt} = -\rho_B\frac{dR}{dt} = bk_g C_{Ag}$$

$$\Downarrow \quad \text{in the Stokes regime} \quad k_g = \frac{2\mathscr{D}}{d_p} = \frac{\mathscr{D}}{R}$$

$$\int_{R_0}^{R} R\, dR = \frac{bC_{Ag}\mathscr{D}}{\rho_B}\int_0^t dt$$

$$\Downarrow$$

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

$$\Downarrow \qquad \searrow$$

$$\boxed{\tau = \frac{\rho_B R_0^2}{2bC_{Ag}\mathscr{D}}} \quad \Rightarrow \quad \boxed{\frac{t}{\tau} = 1 - \left(\frac{R}{R_0}\right)^2 = 1 - (1 - X_B)^{2/3}}$$

25.4 Extensions

1) Particles of Different Shape

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	$\frac{t}{\tau} = X_B$ $\tau = \frac{\rho_B L}{b k_g C_{Ag}}$	$\frac{t}{\tau} = X_B^2$ $\tau = \frac{\rho_B L^2}{2b\mathscr{D}_e C_{Ag}}$	$\frac{t}{\tau} = X_B$ $\tau = \frac{\rho_B L}{bk'' C_{Ag}}$
	Cylinder $X_B = 1 - \left(\frac{r_c}{R}\right)^2$	$\frac{t}{\tau} = X_B$ $\tau = \frac{\rho_B R}{2b k_g C_{Ag}}$	$\frac{t}{\tau} = X_B + (1 - X_B)\ln(1 - X_B)$ $\tau = \frac{\rho_B R^2}{4b\mathscr{D}_e C_{Ag}}$	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/2}$ $\tau = \frac{\rho_B R}{bk'' C_{Ag}}$
	Sphere $X_B = 1 - \left(\frac{r_c}{R}\right)^3$	$\frac{t}{\tau} = X_B$ **(11)** $\tau = \frac{\rho_B R}{3b k_g C_{Ag}}$ **(10)**	$\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$ **(18)** $\tau = \frac{\rho_B R^2}{6b\mathscr{D}_e C_{Ag}}$ **(17)**	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$ **(23)** $\tau = \frac{\rho_B R}{bk'' C_{Ag}}$ **(22)**
Shrinking Sphere	**Small particle** Stokes regime	$\frac{t}{\tau} = 1 - (1 - X_B)^{2/3}$ **(30)** $\tau = \frac{\rho_B R_0^2}{2b\mathscr{D} C_{Ag}}$ **(29)**	Not applicable	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$ $\tau = \frac{\rho_B R_0}{bk'' C_{Ag}}$
	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	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$ $\tau = \frac{\rho_B R}{bk'' C_{Ag}}$

2) Combination of Resistances

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.

To account for the simultaneous action of these resistances is straightforward since they act in series and are all linear in concentration.

Thus, the time to reach any stage of conversion is the sum of the times needed if each resistance acted alone

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

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

$$-\frac{1}{S_{ex}}\frac{dN_{\text{B}}}{dt} = \frac{bC_{\text{A}}}{\dfrac{1}{k_g} + \dfrac{R(R-r_c)}{r_c\mathscr{D}_e} + \dfrac{R^2}{r_c^2 k''}}$$

$$-\frac{dr_c}{dt} = \frac{bC_{\text{A}}/\rho_{\text{B}}}{\underbrace{\dfrac{r_c^2}{R^2 k_g}}_{\text{film}} + \underbrace{\dfrac{(R-r_c)r_c}{R\mathscr{D}_e}}_{\text{ash}} + \underbrace{\dfrac{1}{k''}}_{\text{reaction}}}$$

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.

1) 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.

2) Particle Size

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

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

3) Time

Results of kinetic runs compared with these predicted curves should indicate the rate-controlling step.

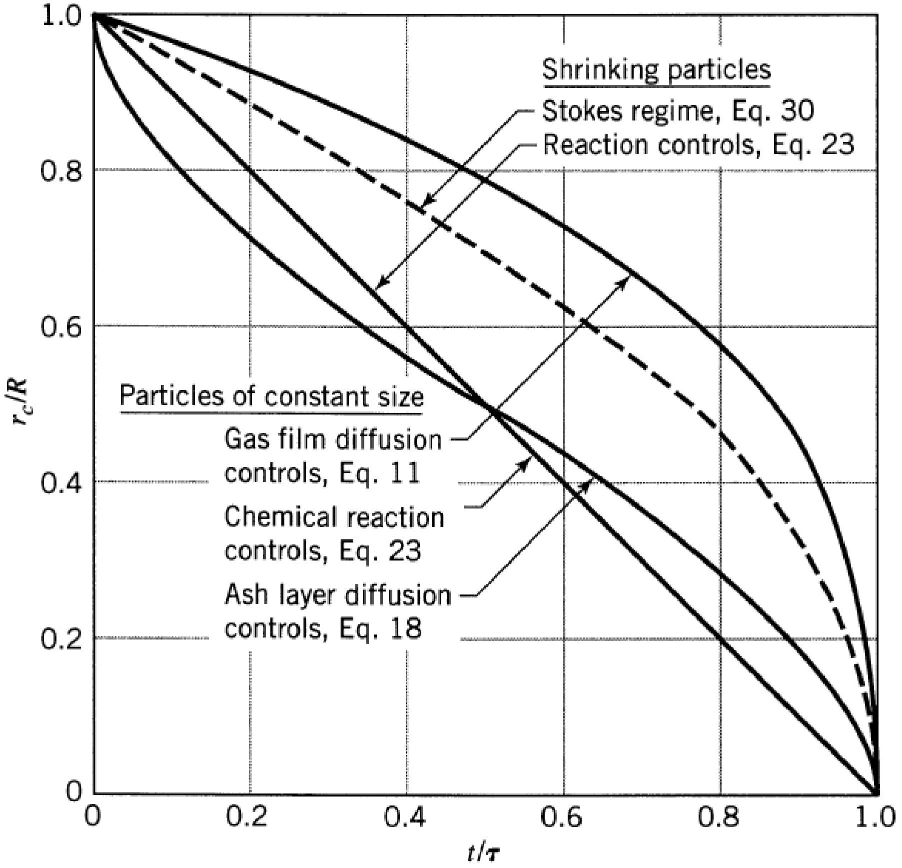


Figure 25.9 Progress of reaction of a single spherical particle with surrounding fluid measured in terms of time for complete reaction.

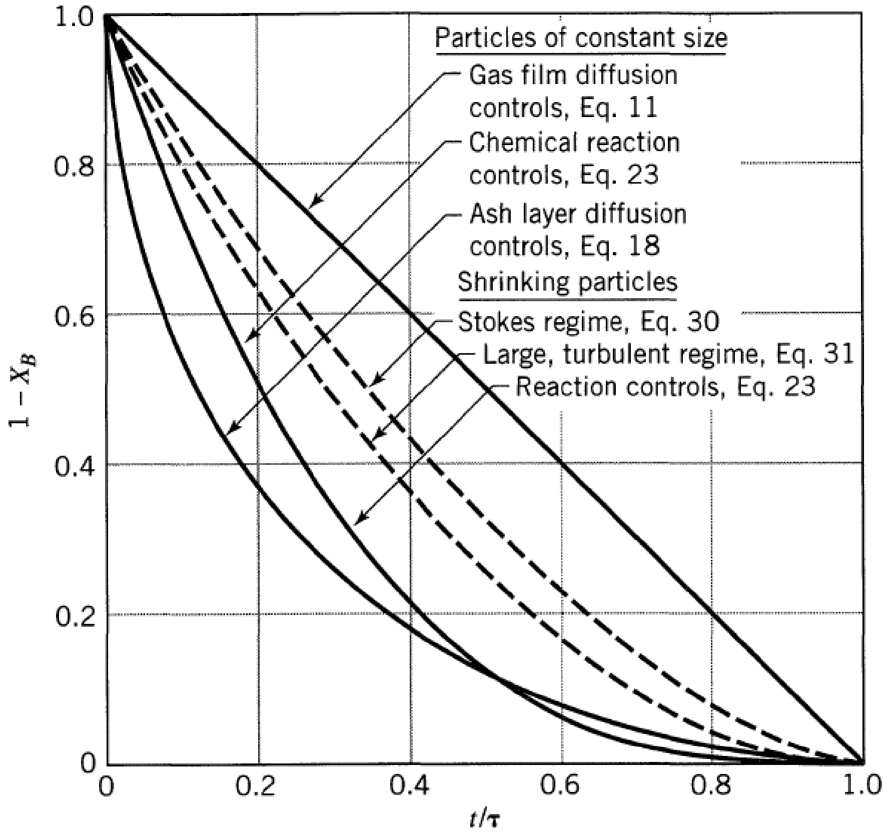


Figure 25.10 Progress of reaction of a single spherical particle with surrounding fluid measured in terms of time for complete conversion.

4) 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 non-flaking ash layer, film resistance can safely be ignored.

5) Predictability of Film Resistance

The magnitude of film resistance can be estimated from dimensionless correlations .

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

Thus an observed rate approximately equal to the calculated rate suggests that film resistance controls.

6) Overall Versus Individual Resistance

If a plot of individual rate coefficients is made as a function of temperature, the overall coefficient 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.

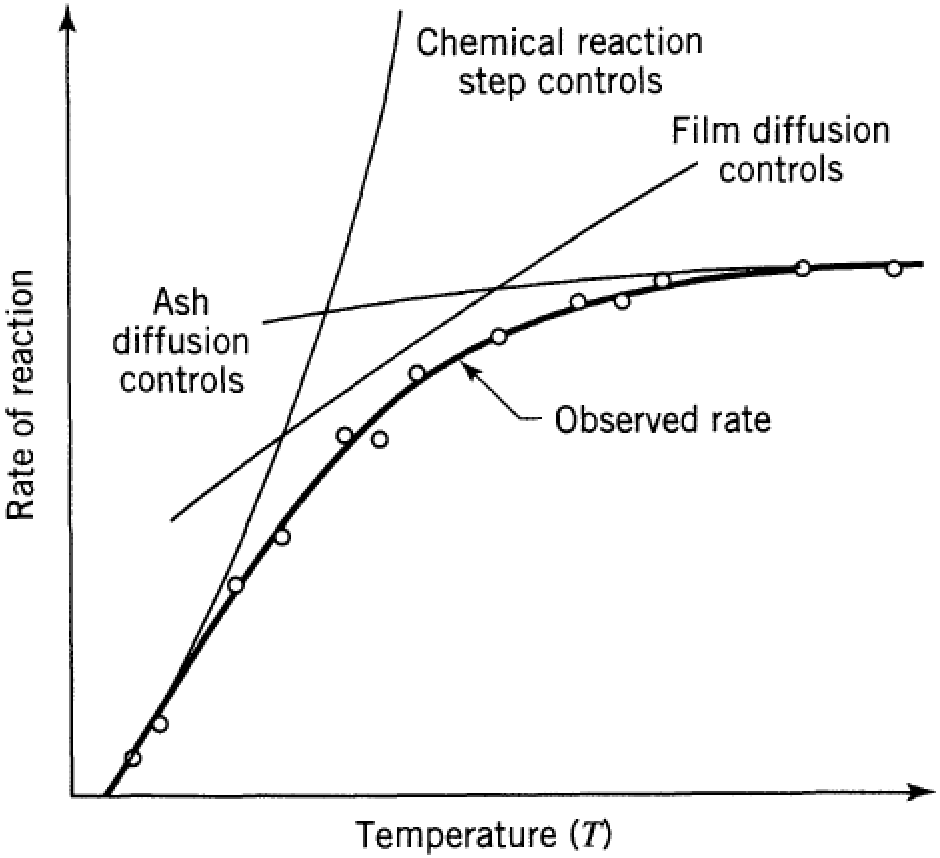


Figure 25.11 Because of the series relationship among the resistances to reaction, the net or observed rate is never higher than for any of the individual steps acting alone.