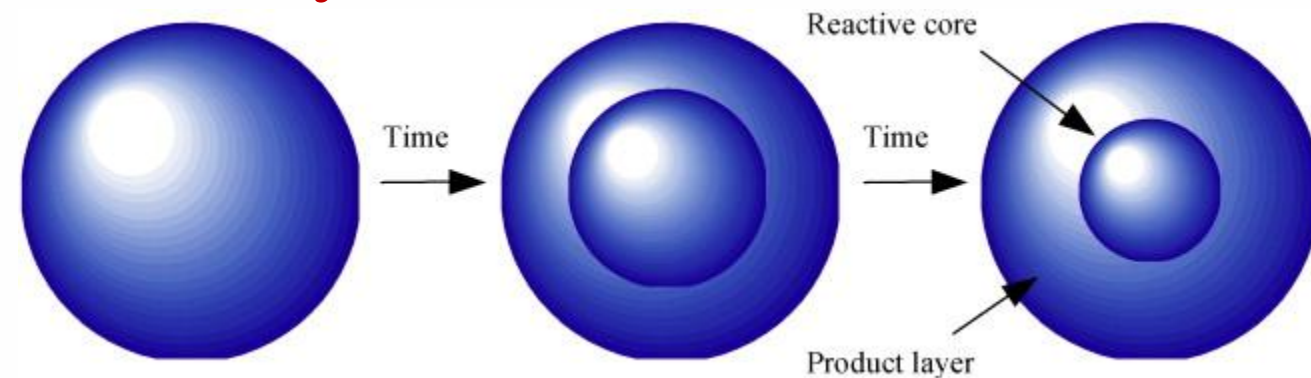


# Chemical Reaction Engineering -II (2170501)

## Chapter-04: Fluid-Particle systems



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# Fluid-Particle systems : Introduction



Combustion

Gas solid system

Chemical Engg?

Time for Complete combustion?

Time for Complete dissolution?

Rate of reaction?

Rate controlling steps?

Process modelling?



Dissolution

Liquid solid system

# Chapter-04: GTU syllabus

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## **Fluid-Particle systems:**

Fluid particle reaction kinetics, selection of a model, Shrinking Core Model for unchanging and changing size spherical particles, Diffusion through gas film and through ash layer controlling, Chemical reaction controlling, Shrinking core model, its limitations, Determination of rate controlling step.

# Fluid-Particle Reactions: Kinetics

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



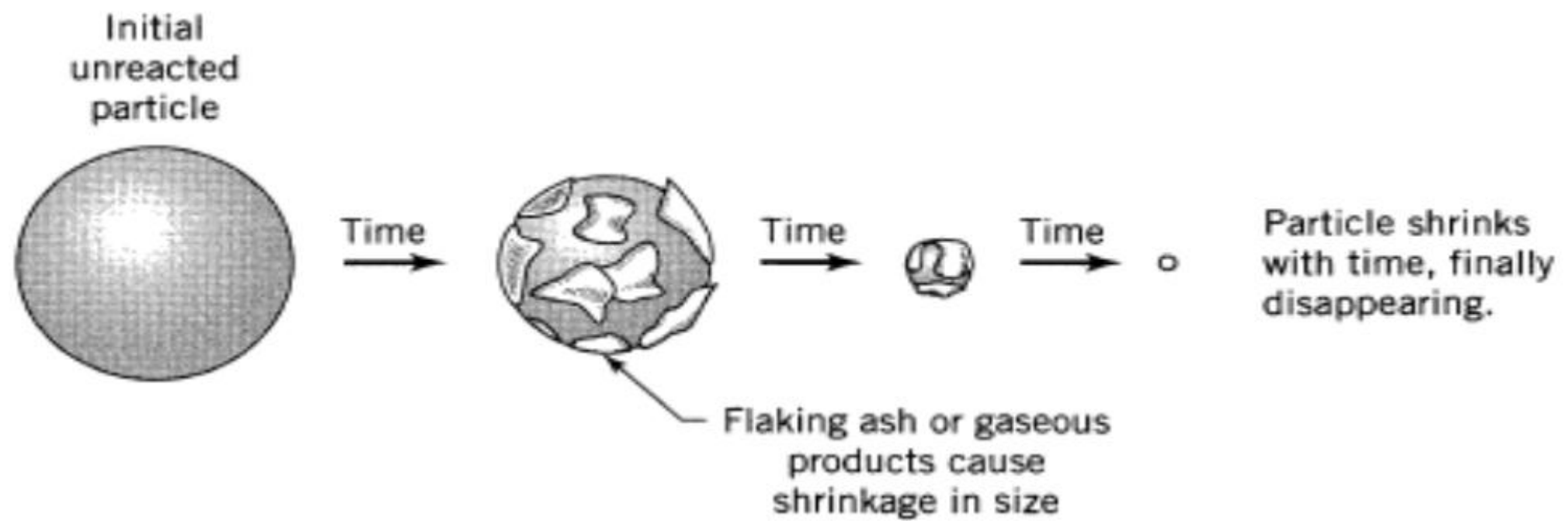
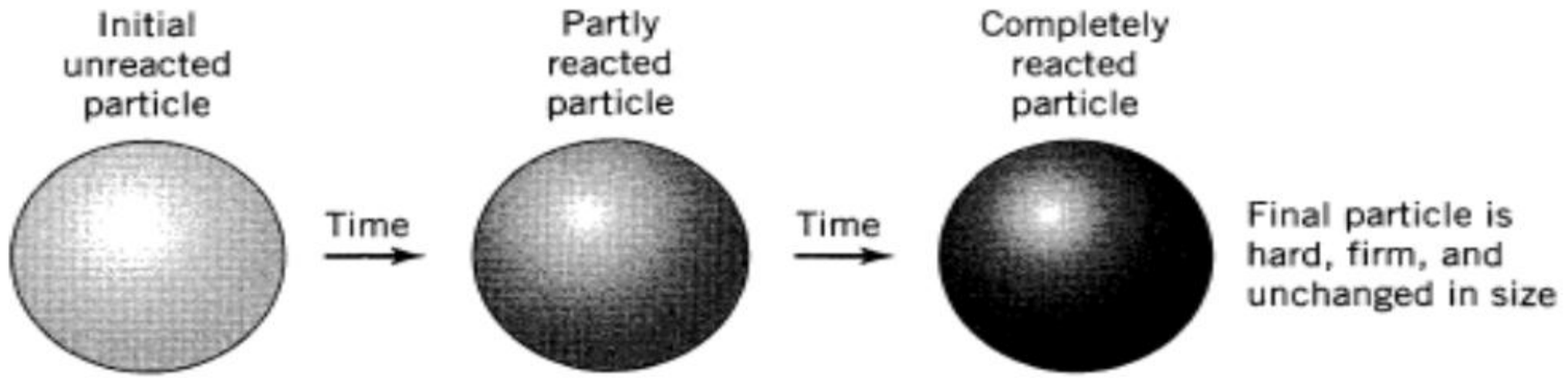


Figure: Different sorts of behavior of reacting solid particles (octave page-567)

- 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:

The roasting (or oxidation) of sulfide ores to yield the metal oxides



Similarly, iron pyrites react as follows:



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.



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

The manufacture of sodium thiosulfate from sulfur and sodium sulfite



Still other examples are the dissolution reactions, the attack of metal chips by acids, and the rusting of iron.

# Observations

Particle size remain unchanged in process

Particle shrink during process  
(*unreacted-core*)



# SELECTION OF A MODEL

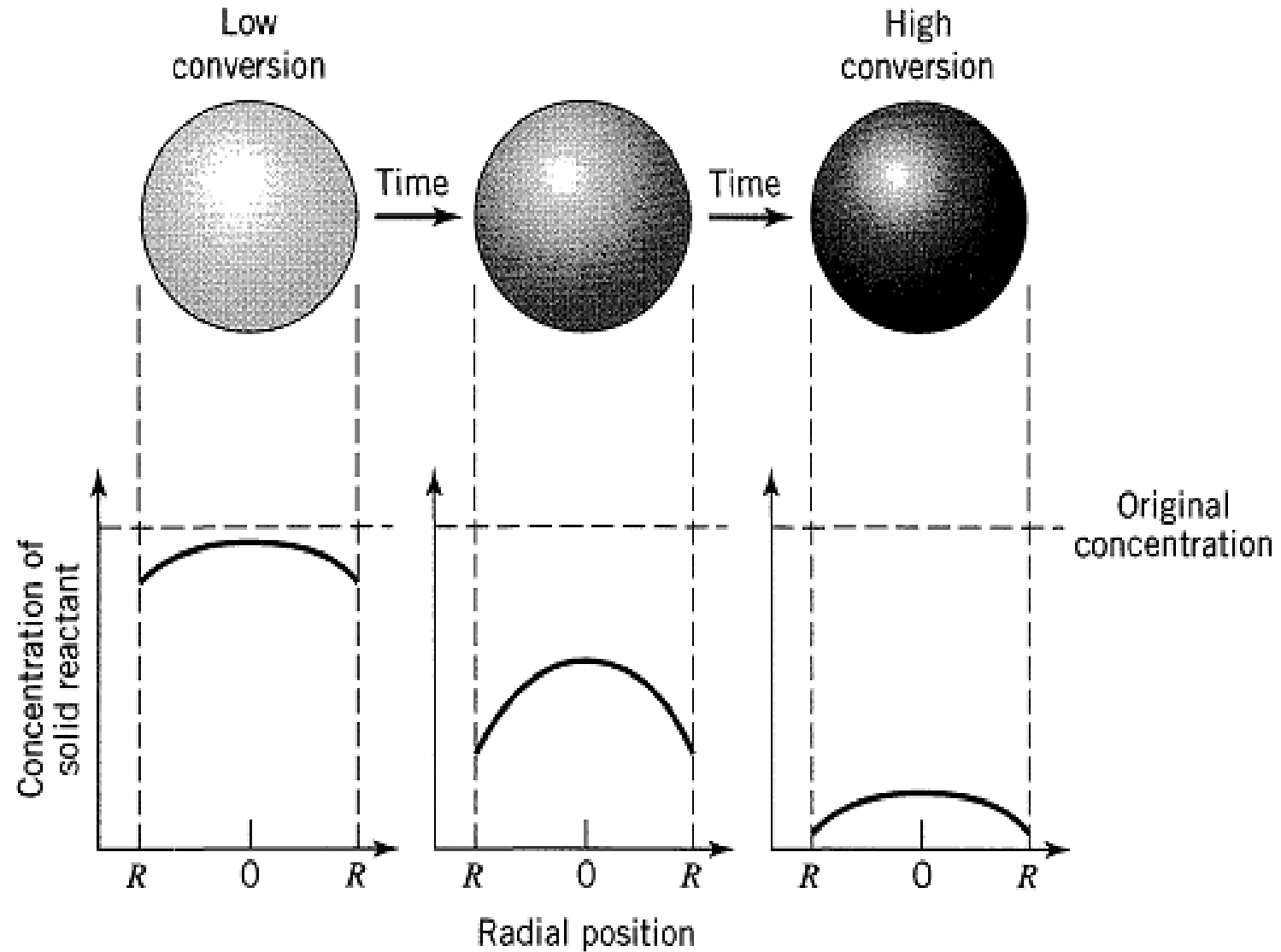
- We should clearly understand that every conceptual picture or model for the progress of reaction comes with its mathematical representation, its rate equation.
- Consequently, if we choose a model we must accept its rate equation, and vice versa.
- If a model corresponds closely to what really takes 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

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. (octave)



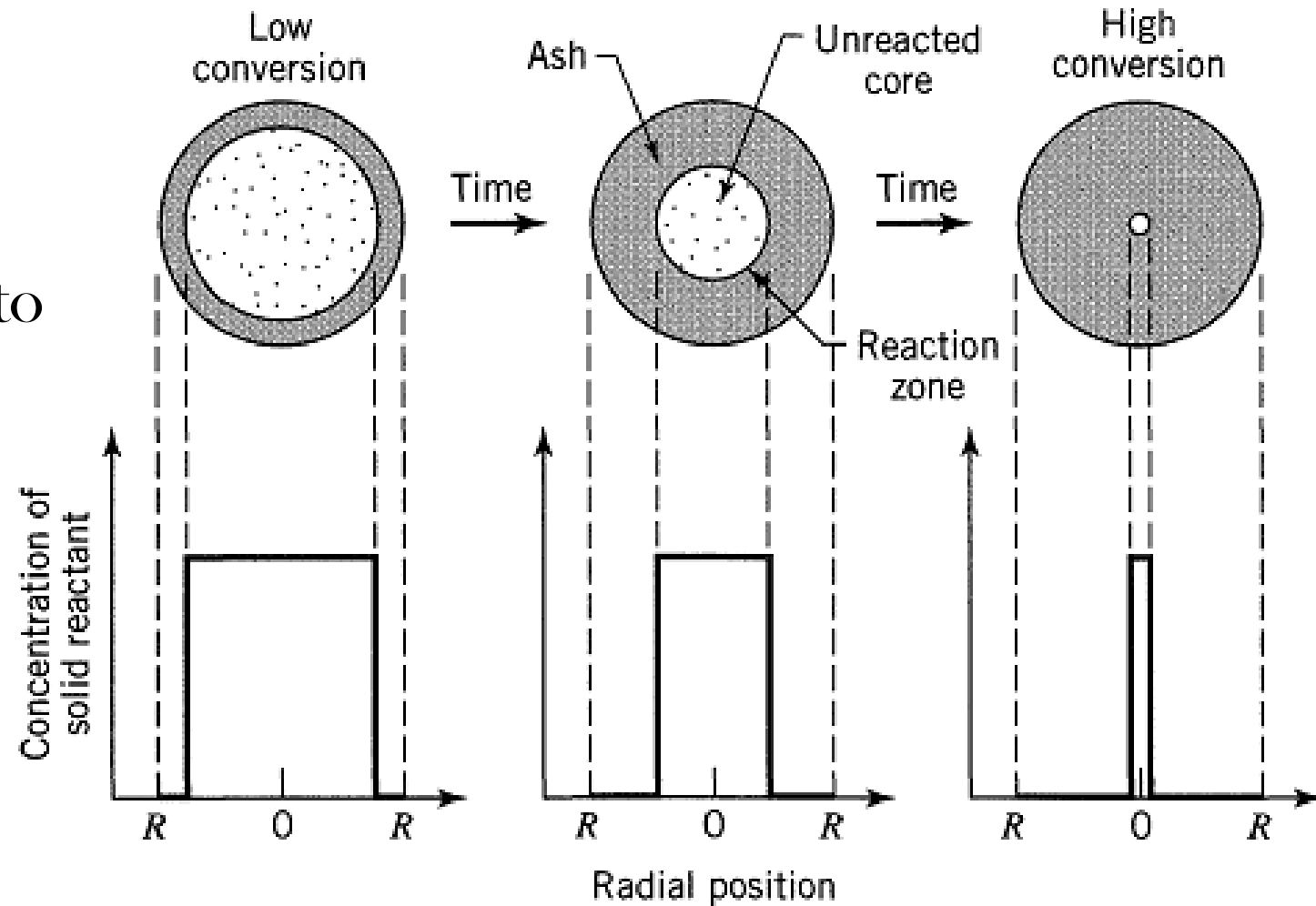
**Figure 25.2** According to the progressive-conversion model, reaction proceeds continuously throughout the solid particle.

# 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.**



**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.

# Comparison of Models with Real Situations.

- In 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 always be as sharply defined as the model pictures it; however, **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 favour the shrinking-core model.**
- 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.**

# ***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).

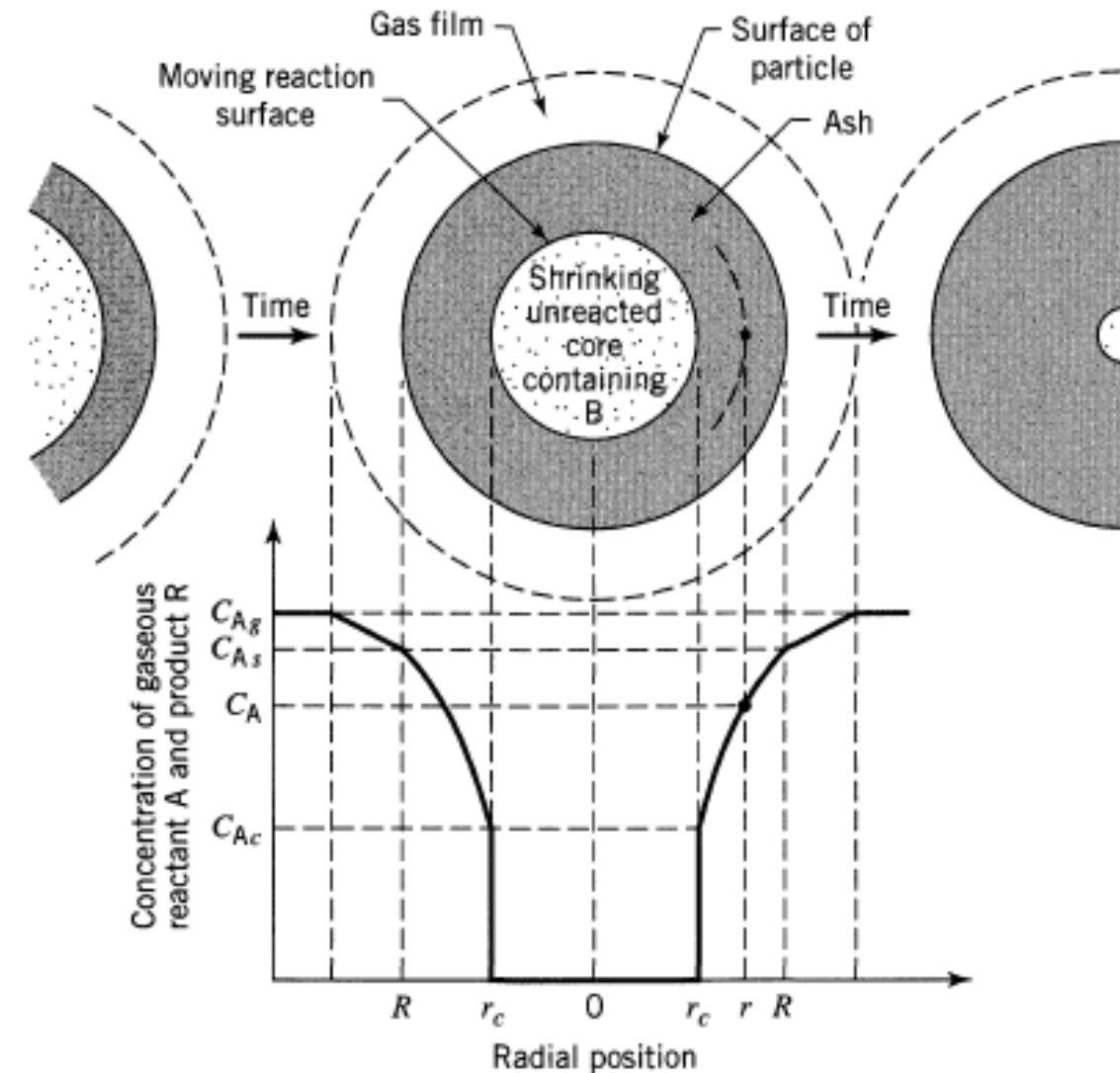
**Step 1. Diffusion of gaseous reactant A through the film** surrounding the particle to the surface of the solid.

**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

**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.

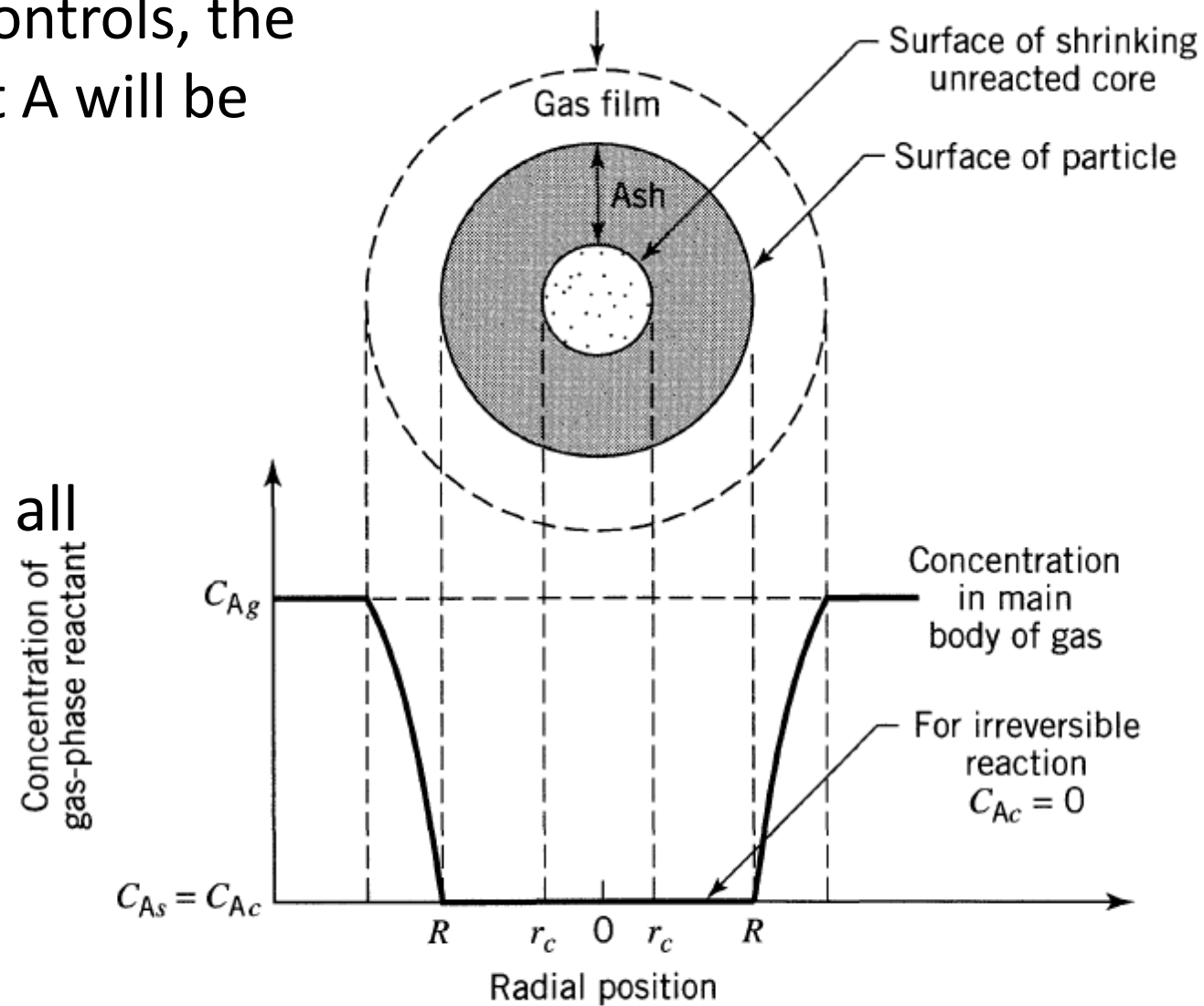
# Diffusion Through Gas Film Controls

Whenever the resistance of the gas film controls, the concentration profile for gaseous reactant A will be shown as in Fig. 25.5.

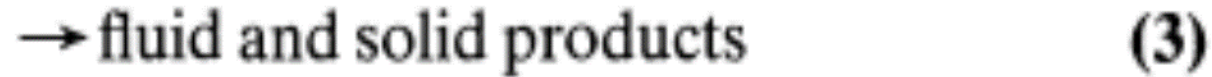
From this figure we see that no gaseous reactant is present at the particle surface; hence, the concentration driving force,  $C_{Ag} - C_{As}$  becomes  $C_{Ag}$  and is constant at all times during reaction of the particle.

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  $S_{ext}$



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



Noting from the stoichiometry of Eqs. 1, 2, and 3 that  $dN_B = bdN_A$ ,

$$-\frac{1}{S_{ext}} \frac{dN_B}{dt} = -\frac{1}{4\pi R^2} \frac{dN_B}{dt} = -\frac{b}{4\pi R^2} \frac{dN_A}{dt} = bk_g(C_{Ag} - C_{As}) = bk_g C_{Ag} = \text{constant} \quad (4)$$

If we let  $\rho_B$  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

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

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

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

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

$$-\frac{1}{S_{ext}} \frac{dN_B}{dt} = -\frac{\rho_B r_c^2}{R^2} \frac{dr_c}{dt} = bk_g C_{Ag} \quad (7)$$

where  $k_g$  is the mass transfer coefficient between fluid and particle. Rearranging and integrating, we find how the unreacted core shrinks with time. Thus,



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

$$t = \frac{\rho_B R}{3bk_g C_{Ag}} \left[ 1 - \left( \frac{r_c}{R} \right)^3 \right] \quad \text{eq 8}$$

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

$$\boxed{\tau = \frac{\rho_B R}{3bk_g C_{Ag}}} \quad \text{(9)}$$

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

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

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

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

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

Therefore

$$\boxed{\frac{t}{\tau} = 1 - \left(\frac{r_c}{R}\right)^3 = X_B} \quad \mathbf{(11)}$$

Thus we obtain the relationship of time with radius and with conversion

# Diffusion through Ash Layer Controls

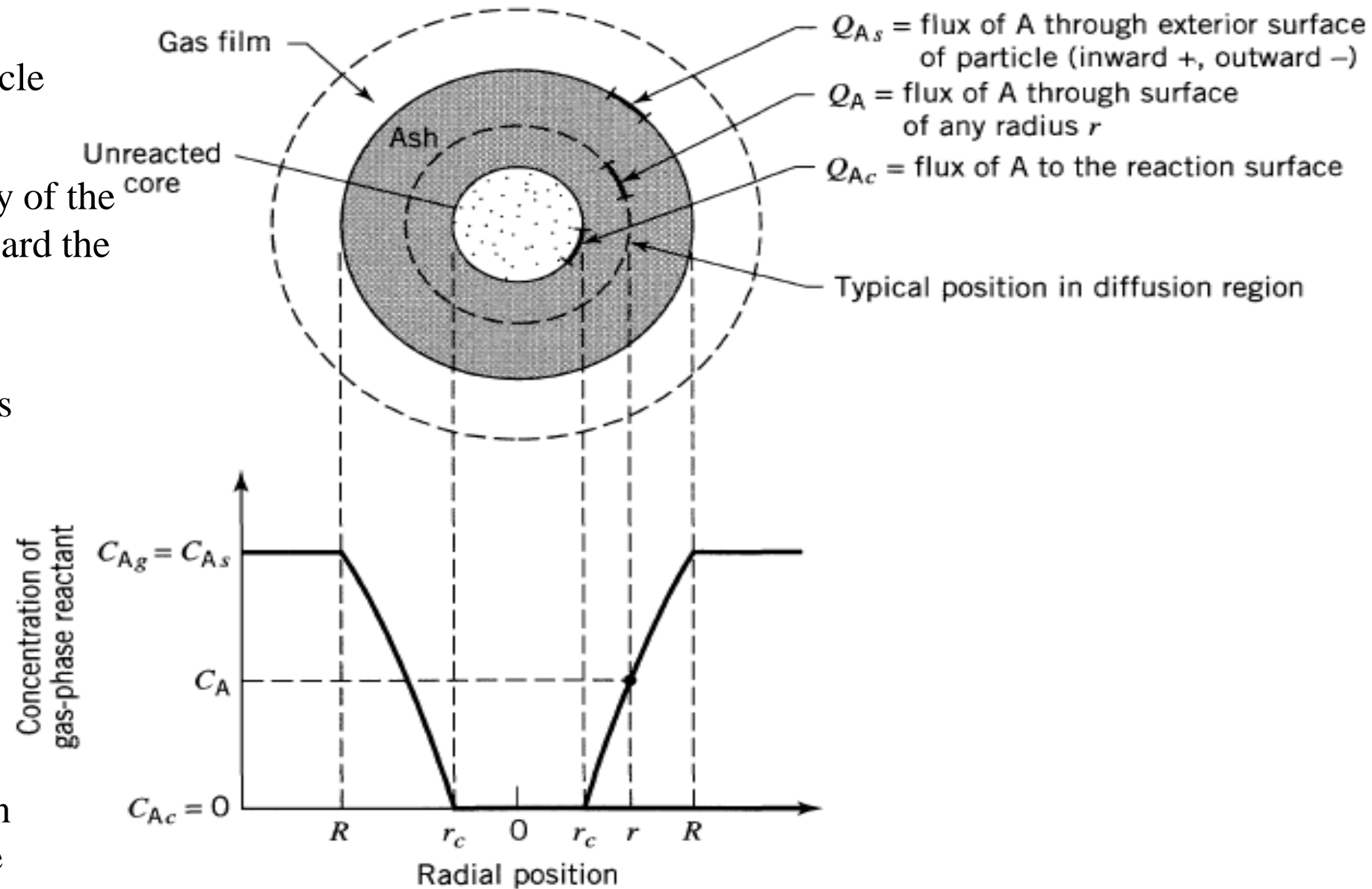
Consider a partially reacted particle as shown in Fig. 25.6

Both reactant A and the boundary of the unreacted core move inward toward the center of the particle

But for **GIS** 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 the use of the steady-state assumption, Thus the rate of reaction of A at any instant is given by its rate of diffusion to the reaction surface, or

$$-\frac{dN_A}{dt} = 4\pi r^2 Q_A = 4\pi R^2 Q_{As} = 4\pi r_c^2 Q_{Ac} = \text{constant} \quad \text{----- (1)}$$

For convenience, let the flux of A within the ash layer be expressed by Fick's law for equimolar counter diffusion, we have

$$Q_A = \mathcal{D}_e \frac{dC_A}{dr} \quad \text{----- (2)}$$

where  $\mathcal{D}_e$  is the effective diffusion coefficient of gaseous reactant in the ash layer.

Combining Eqs (1) & (2)

$$-\frac{dN_A}{dt} = 4\pi r^2 \mathcal{D}_e \frac{dC_A}{dr} = \text{constant} \quad \text{----- (3)}$$

Integrating eqn (3) across the ash layer form R to  $r_c$ , we obtained

$$-\frac{dN_A}{dt} \frac{dr}{r^2} = 4\pi \mathcal{D}_e dC_A$$

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

$$-\frac{dN_A}{dt} \left[ -\frac{1}{r} \right]_R^{r_c} = 4\pi \mathcal{D}_e [CA]_{CAg}^0$$

$$-\frac{dN_A}{dt} \left( \frac{1}{r_c} - \frac{1}{R} \right) = 4\pi \mathcal{D}_e C_{Ag} \quad \text{----- (4)}$$

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 (4)

$$-\frac{dN_A}{dt} \left( \frac{1}{r_c} - \frac{1}{R} \right) = 4\pi \mathcal{D}_e C_{Ag} \quad \text{----- (4)}$$

Here reaction under considerations  
 $A + bB \rightarrow \text{Products}$ , then

$$-\frac{1}{b} \frac{dN_B}{dt} \left( \frac{1}{r_c} - \frac{1}{R} \right) = 4\pi \mathcal{D}_e C_{Ag} \quad \text{----- (5)}$$

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

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

$$-\frac{1}{b} 4\pi \rho_B r_c^2 \frac{dr_c}{dt} \left( \frac{1}{r_c} - \frac{1}{R} \right) = 4\pi \mathcal{D}_e C_{Ag}$$

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

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

$$-\rho_B \left[ \frac{r_c^2}{2} - \frac{r_c^3}{3R} \right]_R^{r_c} = b \mathcal{D}_e C_{Ag} [t]_0^t$$

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

Multiplied by 6

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

$$-\rho_B \left[ \frac{6r_c^2}{2} - \frac{6r_c^3}{3R} - \frac{6R^2}{2} + \frac{6R^3}{3R} \right] = 6b \mathcal{D}_e \mathcal{C}_{Ag} t$$

$$-\rho_B \left[ \frac{3r_c^2}{1} - \frac{2r_c^3}{R} - 3R^2 + 2R^2 \right] = 6b \mathcal{D}_e \mathcal{C}_{Ag} t$$

$$-\rho_B \left[ \frac{3r_c^2}{1} - \frac{2r_c^3}{R} - R^2 \right] = 6b \mathcal{D}_e \mathcal{C}_{Ag} t$$

$$\rho_B \left[ R^2 - \frac{3r_c^2}{1} + \frac{2r_c^3}{R} \right] = 6b \mathcal{D}_e \mathcal{C}_{Ag} t$$

$$\rho_B R^2 \left[ 1 - 3 \frac{r_c^2}{R^2} + 2 \frac{r_c^3}{R^3} \right] = 6b \mathcal{D}_e \mathcal{C}_{Ag} t$$

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

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

$$\tau = \frac{\rho_B R^2}{6b \mathcal{D}_e \mathcal{C}_{Ag}} \text{ ---- (7)}$$

$$\frac{t}{\tau} = 1 - 3 \left( \frac{r_c}{R} \right)^2 + 2 \left( \frac{r_c}{R} \right)^3 \text{ ---- (8)}$$

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

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

$$\frac{t}{\tau} = 1 - 3 (1 - X_B)^{2/3} + 2(1 - X_B) \text{ ---- (9)}$$

Equation (9) is the final expression when diffusion through ash layer controls

# Chemical Reaction Controls

# Chemical Reaction Controls

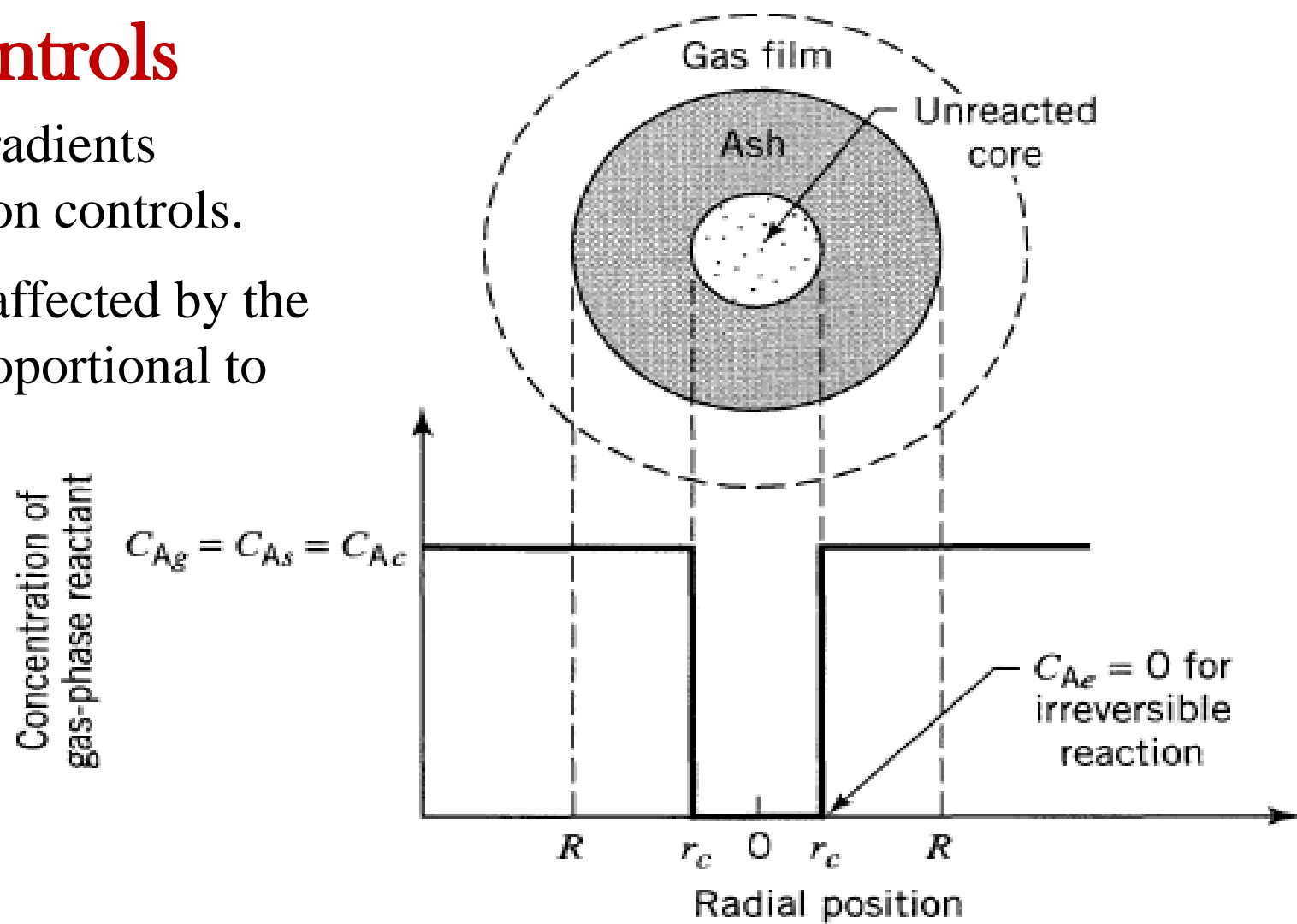
Figure 25.7 illustrates concentration gradients within a particle when chemical reaction controls.

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, is



$$\begin{aligned} -\frac{1}{S_{ext}} \frac{dN_B}{dt} &= -\frac{1}{4\pi r_c^2} \frac{dN_B}{dt} \\ &= -\frac{b}{4\pi r_c^2} \frac{dN_A}{dt} = bK''C_{Ag} \end{aligned}$$



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





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

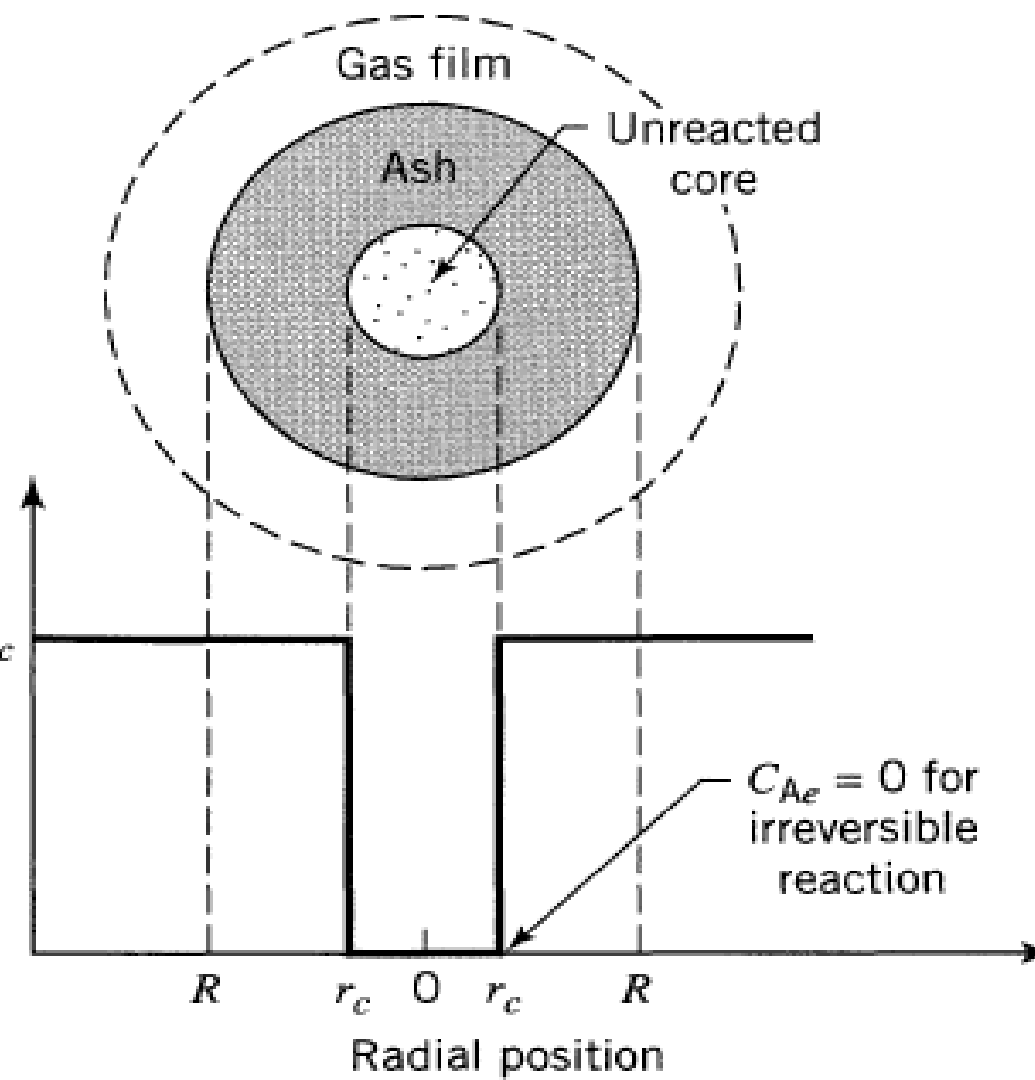
where  $k''$  is the first-order rate constant for the surface reaction.

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

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

$$-\rho_B \frac{dr_c}{dt} = bK''C_{Ag} \text{ ----- (2)}$$

$$C_{Ag} = C_{As} = C_{Ac}$$



$$-\rho_B \frac{dr_c}{dt} = bK''C_{Ag}$$

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

$$-\rho_B [r_c]_R^{r_c} = bK''C_{Ag} [t]_0^t$$

$$-\rho_B (r_c - R) = bK''C_{Ag} [t - 0]$$

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

$$t = \frac{\rho_B R}{bK''C_{Ag}} \left(1 - \frac{r_c}{R}\right) \text{ ----- (3)}$$

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

$$\tau = \frac{\rho_B R}{bK''C_{Ag}} \text{ ---- (4)}$$

The decrease in radius or increase in fractional conversion of the particle in terms of  $r$  is found by combining Eqs. 3 and 4 Thus,

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

# 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.

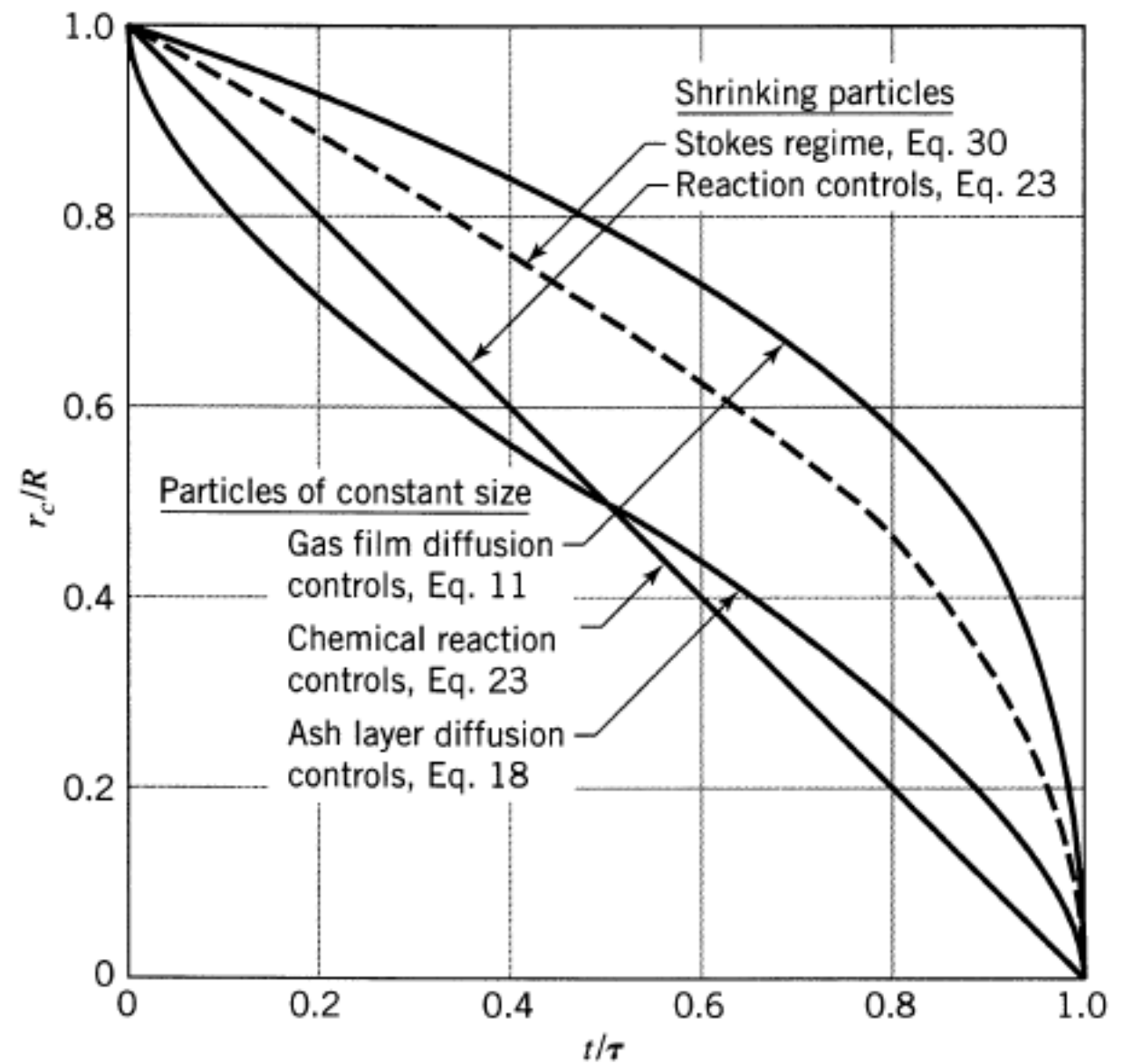
The second exception occurs when solid is converted by the **action of heat, and without needing contact with gas. Baking bread**, boiling missionaries, and roasting puppies are mouthwatering examples of such reactions. Here again the continuous reaction model is a better representation of reality. **Wen (1968) and Kunii and Levenspiel (1991) treat these kinetics.**

## 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.

*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 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.

**Particle Size.** Equations of time required for specific conversion level is depended on the particle size , show that the time needed to achieve the same fractional conversion for particles of different but unchanging sizes is given by

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

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

$$\frac{k_g d_p y}{\mathcal{D}} = 2 + 0.6(\text{Sc})^{1/3}(\text{Re})^{1/2} = 2 + 0.6 \left( \frac{\mu}{\rho \mathcal{D}} \right)^{1/3} \left( \frac{d_p u \rho}{\mu} \right)^{1/2} \quad \text{Eq. (A).}$$

Gas film Controls

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

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

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

Ash layer controls

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

$$\tau = \frac{\rho_B R^2}{6b D_e C_{Ag}}$$

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

Chemical Reaction Controls

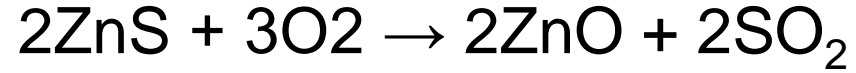
$$t = \frac{\rho_B R}{bK'' C_{Ag}} \left( 1 - \frac{r_c}{R} \right)$$

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

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

**Example 1:** A batch of solids of uniform size is treated by gas in a uniform environment. Solid is converted to give a flaking product, according to shrinking core model. Conversion is  $7/8$  for the reaction time of 1 hr, conversion is 100% in 2 hrs. Which mechanism is rate control?

**Example -2** : Spherical particles of zinc blend of size  $R = 0.05$  mm are roasted in a **10%** oxygen stream **at 900 °C and 1 atm**. The reaction stoichiometry of reaction is



Assuming reaction proceeds by shrinking core model and gas film resistance is negligible, calculate the time needed for complete conversion of particle and relative resistance of ash layer diffusion during this operation

**Data:** Density of solid =  $4.13 \text{ gm/cm}^3$ , Reaction rate constant  $k_s = 2 \text{ cm/sec}$ ,  $D_e = 0.08 \text{ cm}^2/\text{sec}$

**Example -3** : Calculate the time required for complete combustion of spherical particles of graphite (radius 12 mm, bulk density  $2.4 \text{ g/cm}^3$ , ) in 12% oxygen stream at  $900 \text{ }^\circ\text{C}$  and 1 atm . Assume gas film resistance to be negligible

**Data:** Reaction rate constant  $k_s = 25 \text{ cm/sec}$ ,

Note: graphite consists more 99 % Carbon..

**Ans : 7699.8 seconds**

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Thank You