# Fluid-Particle Reaction: Kinetics and Reactor Design

Shrinking core model for shrinking spherical particles

In case of burning solids such as pure carbon, there is no ash formation and the reacting particle shrinks during reaction, finally disappearing

This process involves **three steps**:

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

Step 2: Reaction between gaseous A and the solid on the reaction surface

Step 3: Diffusion of reaction products from the surface of the solid through the gas film back into the main body of the gas

There is no contribution of the ash layer as it is absent

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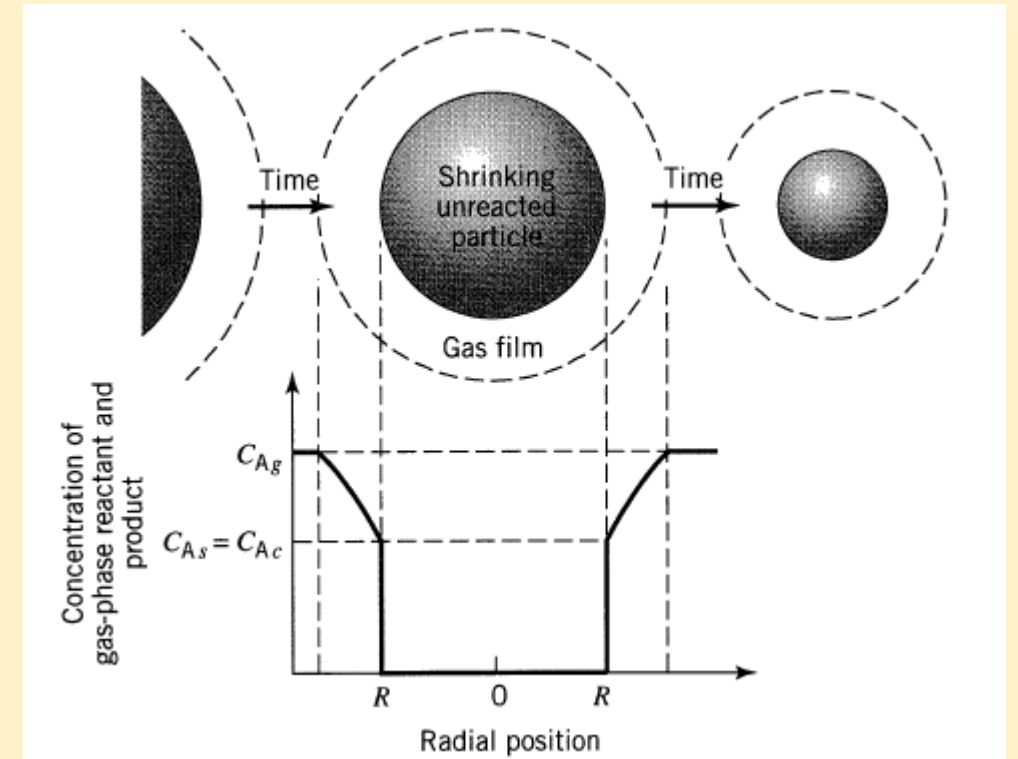
Diffusion through gas film controls

- Film resistance on the surface of a particle is dependent on factors such as

  (a) the relative velocity between particle and fluid

  (b) size of particle   (c) fluid properties

- Various *correlations are available* depending on ways of contacting fluids and solid

  For example, mass transfer of a component of mole fraction y in a fluid to free falling solids is given by,

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

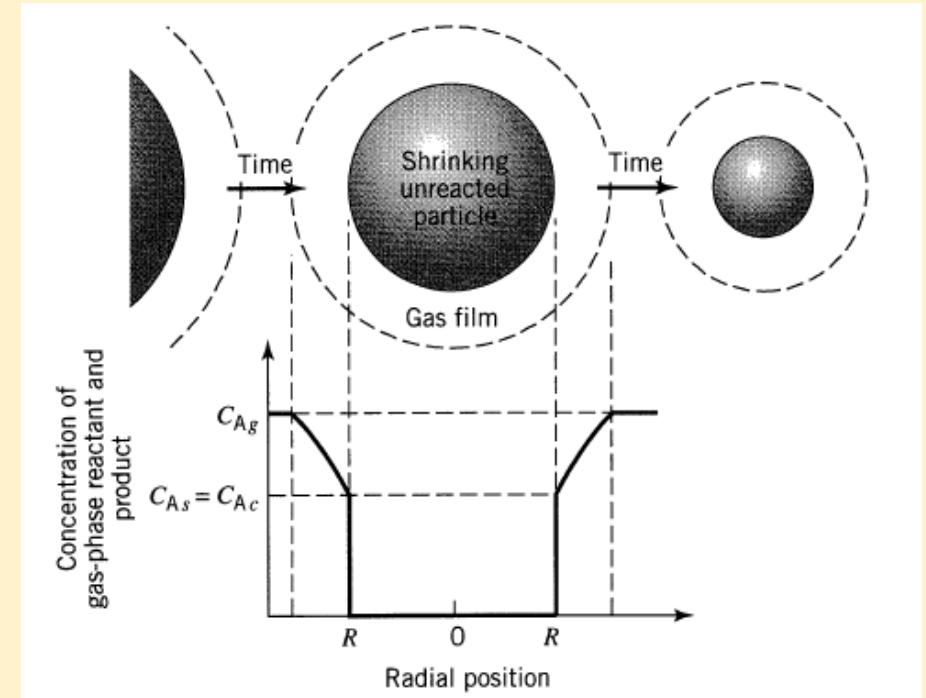- During the reaction *a particle changes in size, hence, k_g also varies*

- In general k_g rises for an increase in gas velocity and for small particles

$$k_g \sim \frac{1}{d_p}$$ for small d_p and u (Stokes law regime)

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

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- Conversion-time expressions for the Stokes law regime are given as,

- Initial radius of the particle = R_o

- Radius of shrinking particle = R

$$-dN_B = -\rho_B dV = -\rho_B d\left(\frac{4}{3}\pi R^3\right) = -4\pi\rho_B R^2 dR$$

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

Since, $k_g = \frac{2D}{d_p} = \frac{D}{R}$ in Stokes law regime

$$-\rho_B\frac{dR}{dt} = b\frac{D}{R}C_{Ag}$$

$$-\int_{R_o}^{R} RdR = \frac{bC_{Ag}D}{\rho_B}\int_0^t dt$$

$$\left(\frac{R_o^2}{2} - \frac{R^2}{2}\right) = \frac{bC_{Ag}D}{\rho_B}t$$

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

- Time for complete disappearance is

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

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

Chemical reaction controls

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

$$\frac{t}{\tau} = \left[1 - \left(\frac{R}{R_o}\right)\right] = \left[1 - (1 - X_B)^{1/3}\right]$$

Particles of different shape

The above conversion-time equations were derived for spherical particles

Similar expressions can be obtained for other particles shapes such as flat plate, cylinder etc (Refer to Levenspiel, Table 25.1, Page 580)

Combination of resistances

- The <u>conversion-time expressions</u> assume that <u>a single resistance controls</u> throughout reaction of the particle

- This, however, may not be true - the <u>relative importance of the gas film, ash layer, and reaction steps will vary as particle conversion progresses</u>

- (a) At the <u>beginning of the reaction</u>, the <u>ash layer is non existent</u> and there is <u>no resistance of this layer</u> – this <u>resistance becomes progressively more and more important</u> as the ash layer builds up (b) the <u>gas film resistance remains constant for a constant size particle</u> (c) the <u>resistance to reaction increases as surface of unreacted core decreases</u>

- In general, then, it may not be reasonable to consider that just one step controls throughout reaction

- When <u>more than one resistance is important</u>, it is seen that the <u>resistances are in series and are all linear in concentration</u>

- Thus the reactions for the different controlling regimes are combined with their individual driving forces and after eliminating intermediate concentrations, it is seen that the <u>time to reach any stage of conversion is the sum of the times needed if each resistance acted alone</u>,

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

- Similarly for complete conversion,

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

$$-\frac{1}{S_{ex}}\frac{dN_B}{dt} = \frac{bC_{Ag}}{\dfrac{1}{k_g} + \dfrac{R(R-r_c)}{r_c D_e} + \dfrac{R^2}{r_c^2 k}}$$

For gas film controls, $-\dfrac{1}{S_{ex}}\dfrac{dN_B}{dt} = -\dfrac{4\pi\,\rho_B\,r_c^2}{4\pi R^2}\dfrac{dr_c}{dt} = bk_g C_{Ag}$

$$\therefore -\dfrac{dr_c}{dt} = \dfrac{bk_g C_{Ag} R^2}{\rho_B\, r_c^2}$$

For ash layer controls, $-\dfrac{1}{S_{ex}}\dfrac{dN_B}{dt} = -\dfrac{b}{S_{ex}}\dfrac{dN_A}{dt} = \dfrac{b}{4\pi R^2}\dfrac{4\pi D_e\, C_{Ag}}{\left[\frac{1}{r_c}-\frac{1}{R}\right]} = \dfrac{b\, D_e\, C_{Ag}}{R^2\left[\frac{1}{r_c}-\frac{1}{R}\right]}$

$$-\dfrac{1}{S_{ex}}\dfrac{dN_B}{dt} = -\dfrac{1}{4\pi R^2}\dfrac{-4\pi\rho_B r_c^2 dr_c}{dt} = \dfrac{b\, D_e\, C_{Ag}}{R^2\left[\frac{1}{r_c}-\frac{1}{R}\right]}$$

$$\therefore -\dfrac{dr_c}{dt} = \dfrac{b\, D_e\, C_{Ag} R^2}{\rho_B\, r_c^2 R^2\left[\frac{1}{r_c}-\frac{1}{R}\right]} = \dfrac{b\, D_e\, C_{Ag}}{\rho_B\,(R-r_c)\frac{r_c}{R}}$$

For reaction controls, $-\dfrac{1}{S_{ex}}\dfrac{dN_B}{dt} = \dfrac{1}{4\pi R^2}\times 4\pi r_c^2 bk C_{Ag} = \dfrac{bk C_{Ag} r_c^2}{R^2}$ $\quad \left[\because -\dfrac{1}{4\pi r_c^2}\dfrac{dN_B}{dt} = -\dfrac{b}{4\pi r_c^2}\dfrac{dN_A}{dt} = bk C_{Ag}\right]$

$$-\dfrac{dN_B}{dt} = \dfrac{-4\pi\rho_B r_c^2 dr_c}{dt} = bk C_{Ag}\, 4\pi r_c^2$$

$$\therefore -\dfrac{dr_c}{dt} = \dfrac{bk\, C_{Ag}}{\rho_B}$$

$$-\dfrac{dr_c}{dt} = \dfrac{\dfrac{b\, C_{Ag}}{\rho_B}}{\dfrac{r_c^2}{R^2 k_g} + \dfrac{r_c(R-r_c)}{R D_e} + \dfrac{1}{k}}$$

For ash free particles which shrink with reaction, only two resistances, gas film and reaction is present

Limitations of shrinking core model

- In case the reaction occurs along a diffuse front rather than along a sharp interface between ash and fresh solid, the *behaviour is in between a shrinking core model and the progressive conversion model*

- For *fast reactions*, rate of heat release may be high enough to cause significant *temperature gradient within the particle or between particle and fluid*

- Shrinking core models *do not work in conditions where there is slow reaction of a gas with porous solid* or when the *solid is converted by the action of heat* and without needing contact with gas

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**

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

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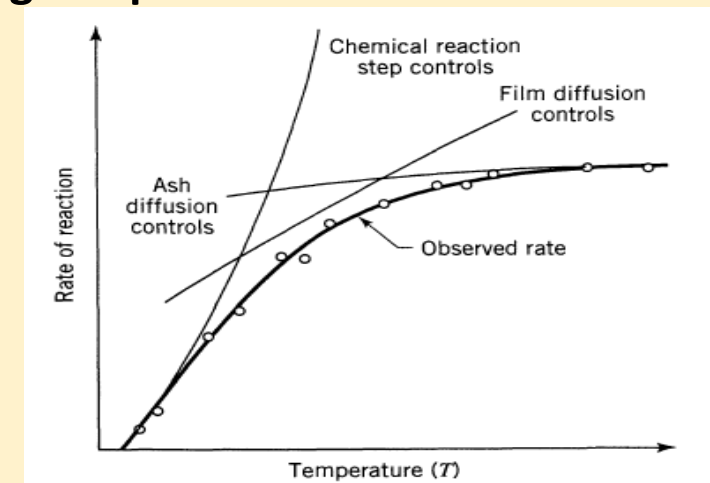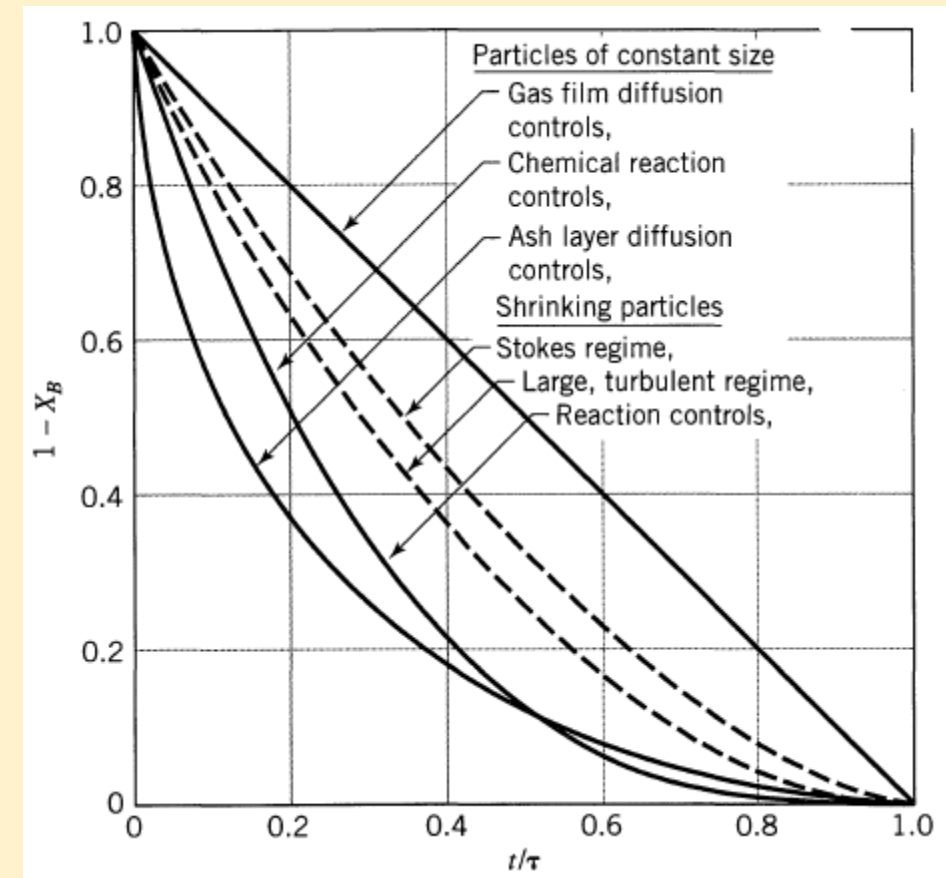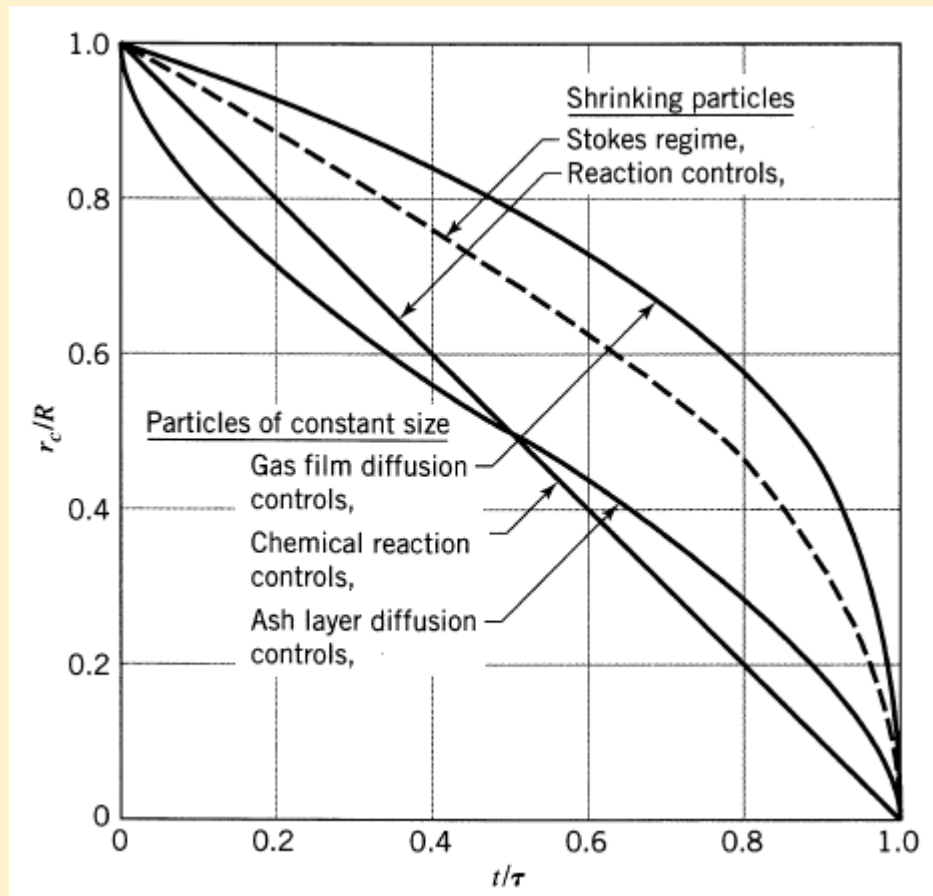
- **Time:** The figures show progressive conversion of spherical solids when chemical reaction, film diffusion and ash diffusion in turn controls
- *Comparing results of kinetic runs with the predicted curves should indicate the rate controlling step.* Unfortunately, the difference between ash diffusion controlling and reaction controlling is not too much and it may be difficult to distinguish between them if the experimental data is scattered

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- **Particle size**: The equations for t for the different control regimes and the equation for mass transfer coefficients (k_g) show that the <u>time needed to achieve the same fractional conversion for particles of different but unchanging size</u> is given by,

  $t \propto R^{1.5 \; to \; 2.0}$ for film diffusion controlling (the exponent decreases as Reynolds number rises)

  $t \propto R^2$ for ash diffusion controlling

  $t \propto R$ for chemical reaction controlling

  Kinetic runs with different sizes of particles can distinguish between the different controlling steps

- **Ash versus film resistance:** When hard solid ash forms during the reaction, the <u>resistance of the gas phase reactant through the ash is usually greater than through the gas film surrounding the particles</u>

  Hence, in the <u>presence of a non-flaking ash layer</u> (constant size particle), <u>film resistance can be safely ignored</u>

 Also, <u>ash resistance is unaffected by changes in gas velocity</u>

- **Predictability of film resistance:** The magnitude of film resistance can be estimated from empirical relations

  such as $\dfrac{k_g d_p y}{D} = 2 + 0.6 \left(\dfrac{\mu}{\rho D}\right)^{1/3} \left(\dfrac{d_p u \rho}{\mu}\right)^{1/2}$

  Thus, an <u>observed rate approximately equal to calculated rate suggests film resistance controls</u>

Example

Spherical solid particles containing B are roasted isothermally in an oven with gas of constant composition. Solids are converted to a firm non-flaking product according to shrinking core model (SCM) as follows:

$$A(g) + B(s) \rightarrow R(g) + S(s)$$
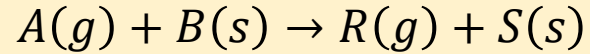
Here, $C_A = 0.01$ kmol/m³ and $\rho_B = 20$ kmol/m³

From the conversion or core size data, determine the rate controlling mechanism for the transformation of solid

(a)

d_p (mm)	X_B	t, sec
1	1	200
1.5	1	400

(b)

d_p (mm)	X_B	t, sec
2	0.875	1
1	1	1

For gas film controls, $\quad t = \dfrac{\rho_B R}{3bk_g C_{Ag}}\left[1 - \left(\dfrac{r_c}{R}\right)^3\right] = \dfrac{\rho_B R}{3bk_g C_{Ag}} X_B$

For diffusion through ash controls, $\quad t = \dfrac{\rho_B R^2}{6bD_e C_{Ag}}\left[1 - 3\left(\dfrac{r_c}{R}\right)^2 + 2\left(\dfrac{r_c}{R}\right)^3\right] = \dfrac{\rho_B R^2}{6bD_e C_{Ag}}\left[1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)\right]$

For chemical reaction controls, $\quad t = \dfrac{\rho_B R}{bk C_{Ag}}\left[1 - \dfrac{r_c}{R}\right] = \dfrac{\rho_B R}{bk C_{Ag}}\left[1 - (1 - X_B)^{1/3}\right]$

Hence for gas film controls, $\dfrac{RX_B}{t} = \dfrac{3bk_gC_{Ag}}{\rho_B}$

For diffusion through ash controls, $\dfrac{R^2\left[1-3(1-X_B)^{2/3}+2(1-X_B)\right]}{t} = \dfrac{6bD_eC_{Ag}}{\rho_B}$

For chemical reaction controls, $\dfrac{R\left[1-(1-X_B)^{1/3}\right]}{t} = \dfrac{bkC_{Ag}}{\rho_B}$

Rate controlling

(a)

d_p (mm)	X_B	t, sec	$\dfrac{RX_B}{t}$	$\dfrac{R^2\left[1-3(1-X_B)^{2/3}+2(1-X_B)\right]}{t}$	$\dfrac{R\left[1-(1-X_B)\right.}{t}$
1	1	200	2.5 x 10⁻³	1.25 x 10⁻³	2.25 x 10⁻³
1.5	1	400	1.67 x 10⁻³	1.25 x 10⁻³	1.67 x 10⁻³

Diffusion through ash layer is rate controlling

Rate controlling

(b)

d_p (mm)	X_B	t, sec	$\dfrac{RX_B}{t}$	$\dfrac{R^2\left[1-3(1-X_B)^{2/3}+2(1-X_B)\right]}{t}$	$\dfrac{R\left[1-(1-X_B)\right.}{t}$
2	0.875	1	0.875	1	0.5
1	1	1	0.5	0.25	0.5

Chemical reaction is rate controlling