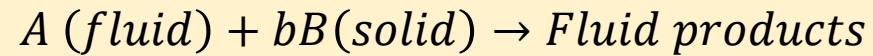


Fluid-Particle Reaction: Kinetics and Reactor Design

Book: *Chemical Reaction Engineering*, O. Levenspiel, (Chapter 25 and 26), 3rd Edition, Wiley and Sons

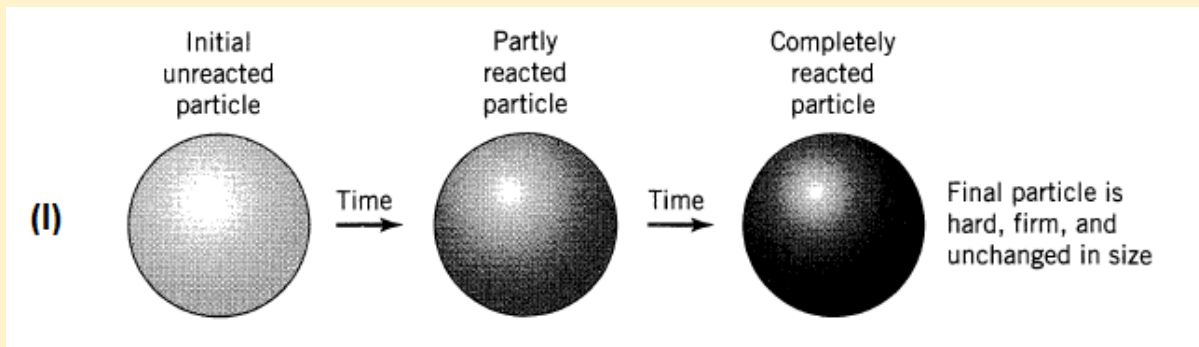
- This section deals with the class of heterogenous reactions in which a **gas or liquid contacts a solid, reacts** with it and transforms it into a **product which could be a solid or a fluid**
- These are essentially **non-catalytic systems**



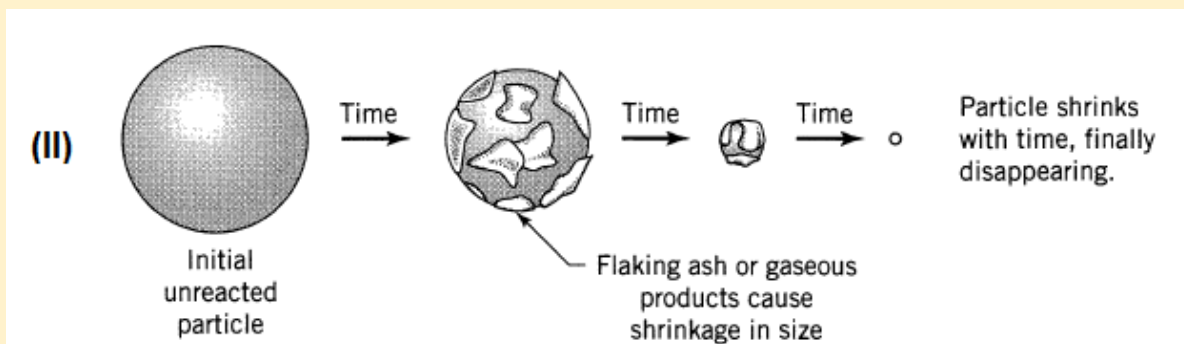
→ *Solid products*

→ *Fluid/Solid products*

Behaviour of reacting solid particles



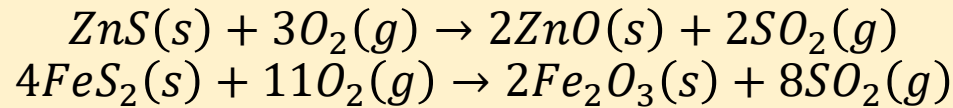
Here the solid particle **remains unchanged in size during reaction** when they contain large amounts of impurities which remain as non-flaking ash or if they form a firm solid product



Here the solid particle **shrink in size during reaction** when a flaking ash or product material is formed or when pure *B* is used in the reaction

Examples of **fluid-solid reactions where the solid does not appreciably change in size**:

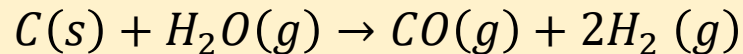
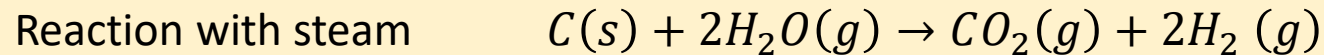
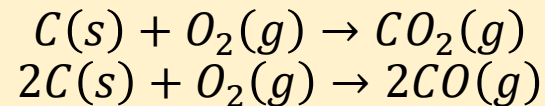
- Roasting (or oxidation) of sulphide ores to yield the metal oxides



- Preparation of metals from the oxides by reduction $\text{Fe}_3\text{O}_4(s) + 4\text{H}_2(g) \rightarrow 3\text{Fe}(s) + 4\text{H}_2\text{O}(g)$
- Nitrogenation of calcium carbide to produce cyanamide $\text{CaC}_2(s) + \text{N}_2(g) \rightarrow \text{CaCN}_2(s) + \text{C}(\text{amorphous})$
- Plating of metals

Examples of **fluid-solid reactions in which the size of solid changes** are:

- Carbonaceous materials having low ash content react with air



- Manufacture of carbon disulphide $\text{C}(s) + 2\text{S}(g) \xrightarrow{750-1000^\circ\text{C}} \text{CS}_2(g)$
- Manufacture of sodium cyanide from sodium amide $\text{NaNH}_2(l) + \text{C}(s) \xrightarrow{800^\circ\text{C}} \text{NaCN}(l) + \text{H}_2(g)$
- Manufacture of sodium thiosulphate from sulphur and sodium sulphite $\text{Na}_2\text{SO}_3(\text{soln}) + \text{S}(s) \rightarrow \text{Na}_2\text{S}_2\text{O}_3(\text{soln})$

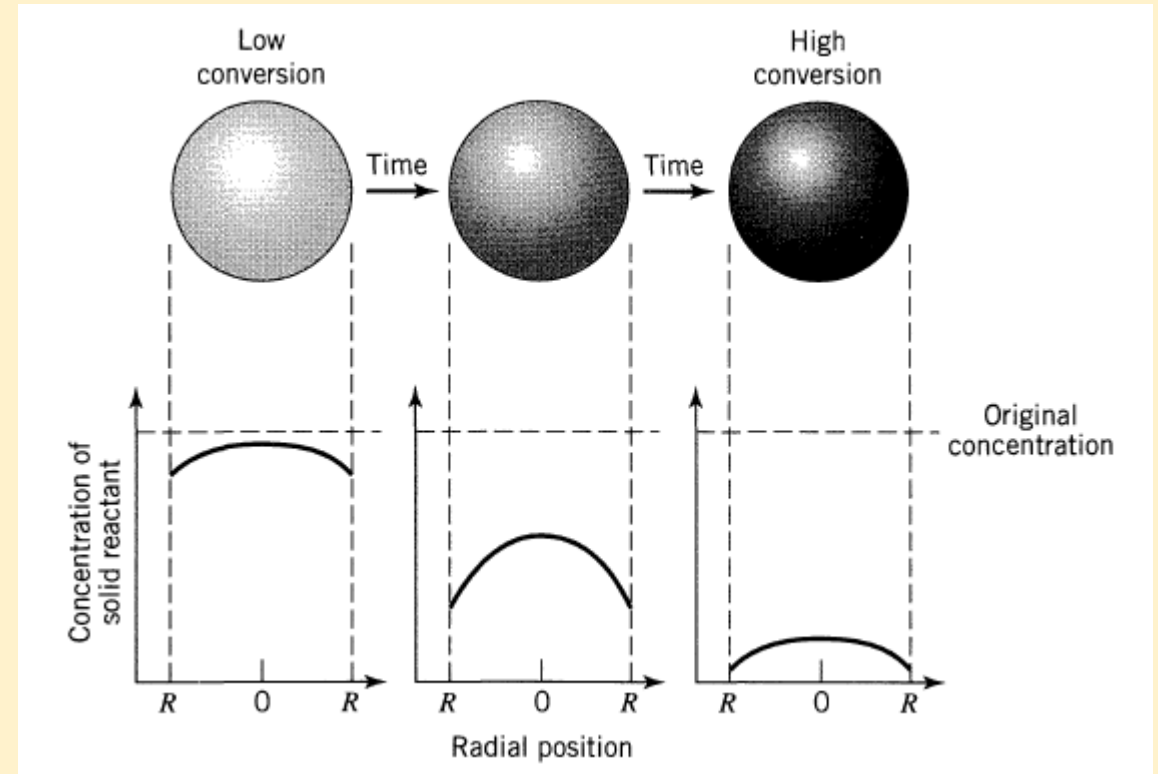
Models for non-catalytic fluid-solid reactions

For non-catalytic reaction of particles with surrounding fluid, we consider two simple idealized models:

- progressive conversion model and
- shrinking core model

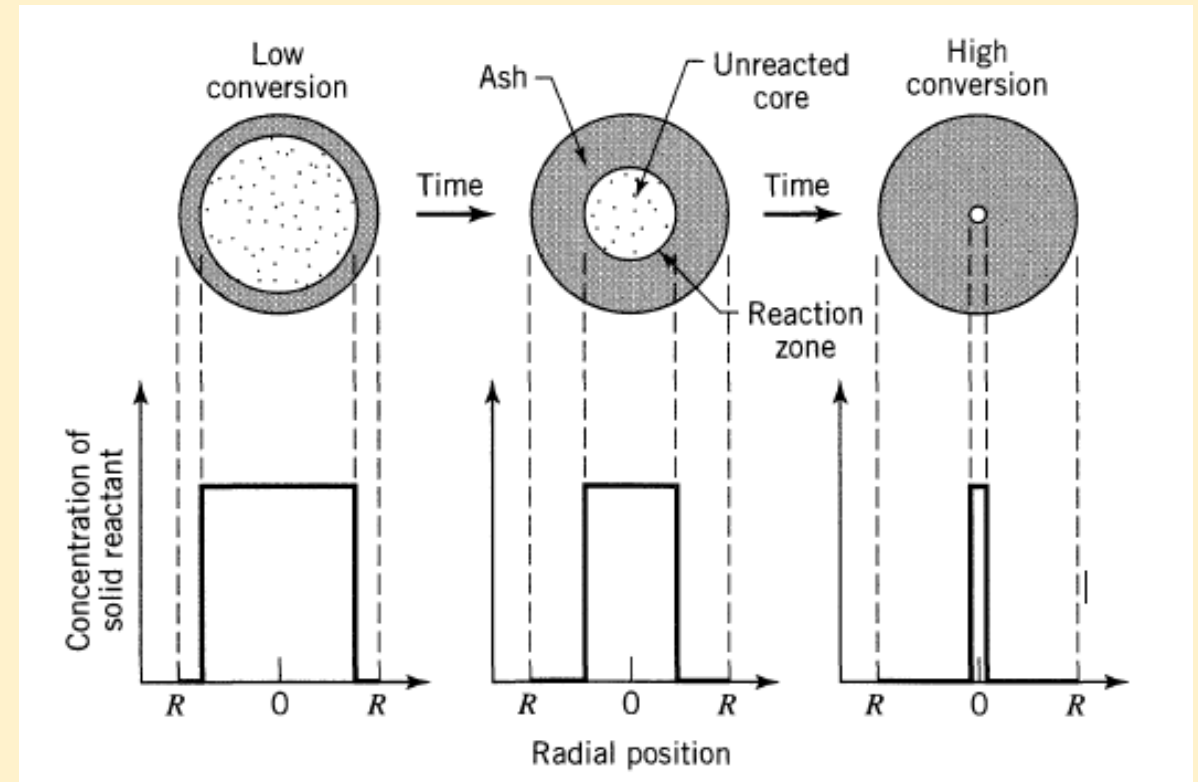
Progressive Conversion Model (PCM)

- In this model, it is assumed that the reactant gas enters and reacts throughout the particle at all times most likely at different rates at different locations within the particle
- Solid reactant is converted continuously and progressively throughout the particle



Shrinking Core Model (SCM)

- Here the reaction first occurs at the outer skin of the particles
- The zone of reaction then moves into the solid, leaving behind completely converted material and inert solid – this is referred to as ‘ash’
- Thus at any time there exists an unreacted core of material which shrinks in size during reaction



- When a partly reacted solid material is sliced through the middle, the unreacted solid material surrounded by a layer of ash is usually found
- In most cases, the shrinking core model approximates real particles more accurately than does the progressive conversion model

Shrinking core model for spherical particles of unchanging size

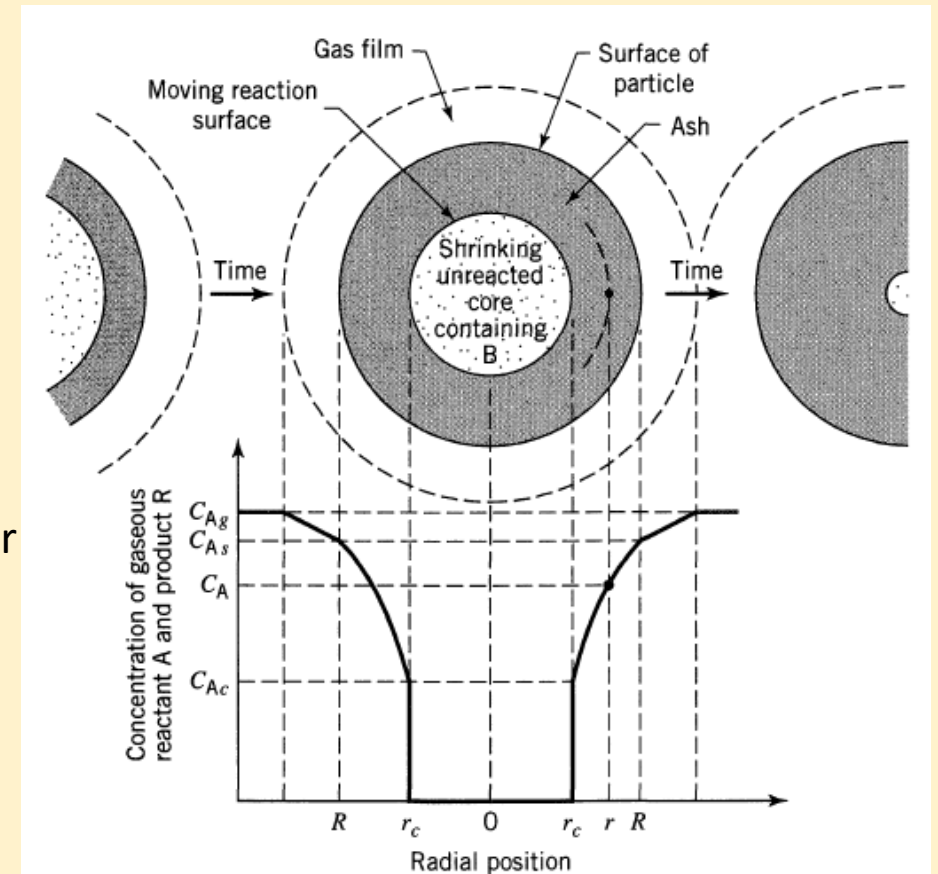
According to the model, **five steps** were visualized to occur in succession during the reaction

- 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 gaseous reactant 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 the fluid

In some cases (such as when no gaseous products are formed) some steps may be missing (step 4 and 5 not present)

Resistances of the different steps usually vary greatly from one another and the **step with the highest resistance is considered to be rate controlling**

The conversion equations for spherical particles are developed in which steps 1, 2 and 3, in turn, are considered rate controlling



Diffusion through gas film controls

- The concentration profile for gaseous reactant A is shown in the figure when resistance in the gas film controls
- The concentration of the gaseous reactant at the surface of the catalyst is zero and hence the driving force is $= C_{Ag} - C_{As} = C_{Ag}$ and is constant at all times during reaction
- From the stoichiometry ($A + bB \rightarrow products$), $dN_B = bdN_A$

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

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

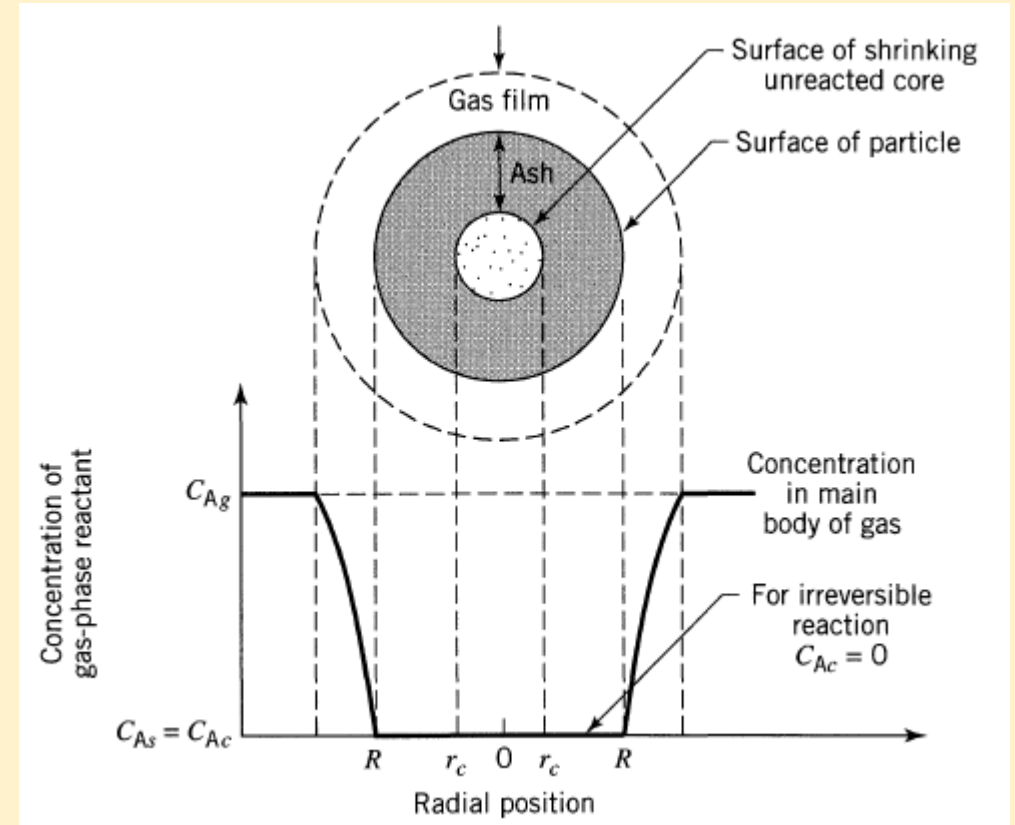
where S_{ex} = external surface area

If ρ_B = molar density of B in the solid and V = volume of particle

Moles of B present in the particle $N_B = \rho_B V$

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

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



- Rate of reaction in terms of the radius of the shrinking core is,

$$-\frac{1}{4\pi R^2} \frac{dN_B}{dt} = -\frac{4\pi \rho_B r_c^2}{4\pi R^2} \frac{dr_c}{dt} = bk_g C_{Ag}$$

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

$$\frac{-\rho_B}{3R^2} [r_c^3 - R^3] = bk_g C_{Ag} t$$

$$\frac{\rho_B}{3R^2} [R^3 - r_c^3] = bk_g C_{Ag} t$$

$$\frac{\rho_B R^3}{3R^2} \left[1 - \frac{r_c^3}{R^3} \right] = bk_g C_{Ag} t$$

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

The time for complete conversion of a particle = τ and after complete conversion, $r_c = 0$

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

- The unreacted core shrinks with time according to ,

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

- The time for complete conversion of a particle is given by,

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

- The radius of the unreacted core in terms of fractional time for complete conversion is,

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

- If X_B is the conversion,

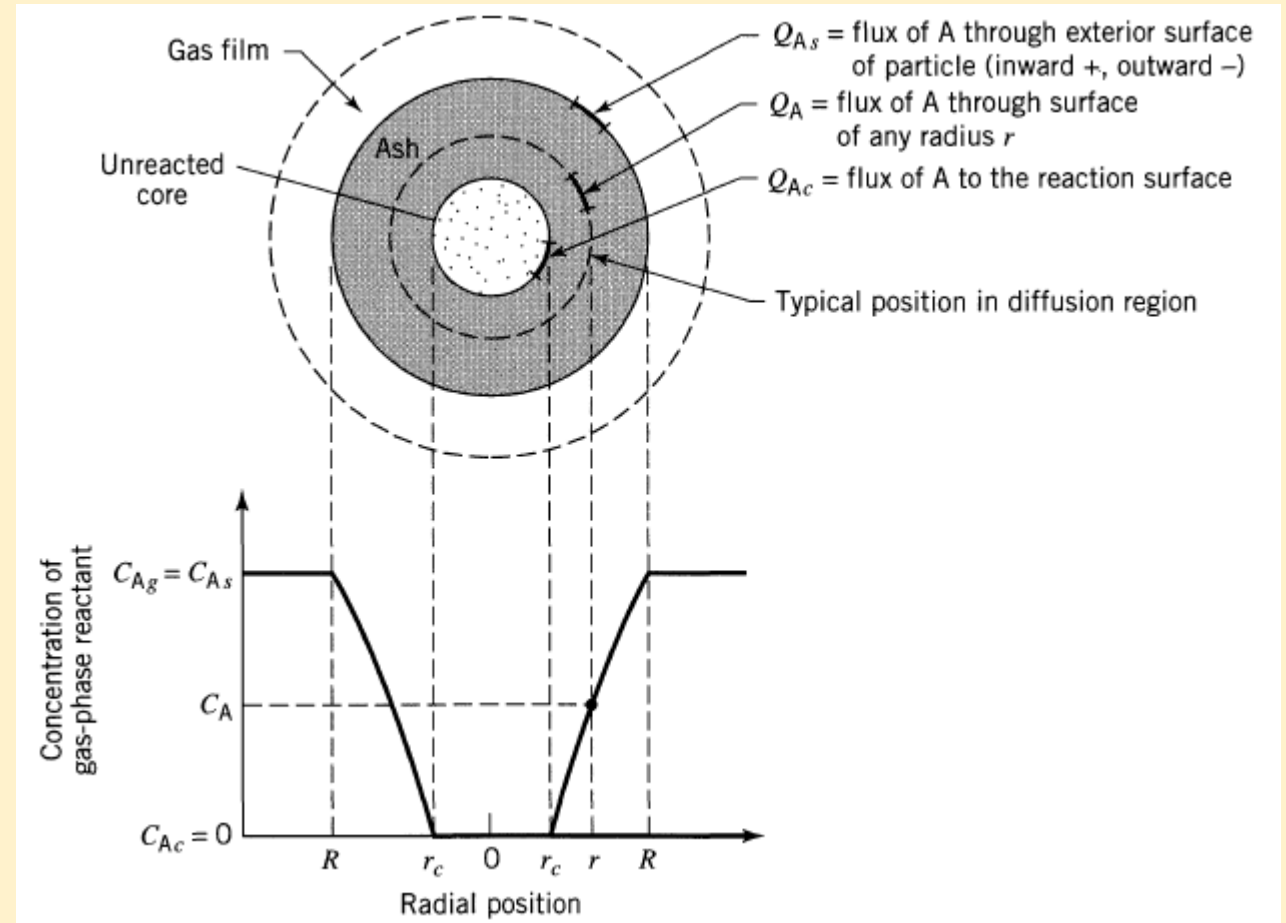
$$1 - X_B = \frac{\text{volume of unreacted core}}{\text{total volume of particle}} = \frac{\frac{4}{3}\pi r_c^3}{\frac{4}{3}\pi R^3} = \left(\frac{r_c}{R} \right)^3$$

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

This gives the **relationship between time, radius and conversion**

Diffusion through ash layer controls

- The concentration profile for gaseous reactant A is shown in the figure when diffusion through the ash layer controls
- If we consider a partially reacted particle, both reactant A and the boundary of the unreacted core moves inwards towards the centre
- For gas –solid systems the shrinkage of the unreacted core is slower than the flow rate of A towards the unreacted core by a factor of 1000 which is roughly the ratio of the density of solid to gas
- Hence it is reasonable to assume that in considering the concentration gradient of A in the ash layer at any time, that the unreacted core is stationary (steady state conditions may be used)



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

$$-\frac{dN_A}{dt} = 4\pi r^2 Q_A = 4\pi R^2 Q_{A_s} = 4\pi r_c^2 Q_{A_c} = \text{constant}$$

The flux Q_A is written as per Fick's law for equimolar counter diffusion as

$$Q_A = D_e \frac{dC_A}{dr}$$

$$-\frac{dN_A}{dt} = 4\pi r^2 D_e \frac{dC_A}{dr} = \text{constant}$$

$$-\frac{dN_A}{dt} \int_R^{r_c} \frac{dr}{r^2} = 4\pi D_e \int_{C_{As}}^0 dC_A$$

$$-\frac{dN_A}{dt} \left[\frac{1}{r_c} - \frac{1}{R} \right] = 4\pi D_e C_{As} = 4\pi D_e C_{Ag}$$

The above is the condition of the reacting particle at any time (pseudo quasi steady state)

Now, if the size of the unreacted core changes with time, then we see that the ash layer becomes thicker lowering the rate of diffusion, though $\frac{dN_A}{dt}$ is constant for a given size of the unreacted core

As we have seen before,

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

Replacing the value of in the flux equation we get,

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

$$\begin{aligned}
 -\rho_B \int_R^{r_c} \left(r_c - \frac{r_c^2}{R} \right) dr_c &= bD_e C_{Ag} \int_0^t dt \\
 -\rho_B \left[\left(\frac{r_c^2}{2} - \frac{R^2}{2} \right) - \left(\frac{r_c^3}{3R} - \frac{R^3}{3R} \right) \right] &= bD_e C_{Ag} t \\
 \rho_B R^2 \left[\frac{1}{2} - \frac{1}{2} \left(\frac{r_c}{R} \right)^2 - \frac{1}{3} + \frac{1}{3} \left(\frac{r_c}{R} \right)^3 \right] &= bD_e C_{Ag} t \\
 \boxed{t = \frac{\rho_B R^2}{6bD_e C_{Ag}} \left[1 - 3 \left(\frac{r_c}{R} \right)^2 + 2 \left(\frac{r_c}{R} \right)^3 \right]}
 \end{aligned}$$

For complete conversion of a particle, $t = \tau$ and $r_c = 0$

$$\boxed{\tau = \frac{\rho_B R^2}{6bD_e C_{Ag}}}$$

Progression of reaction in terms of time for complete conversion is given by,

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

It was seen that, $\left(\frac{r_c}{R} \right)^3 = 1 - X_B$ and hence,

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

Chemical reaction controls

- The figure shows the concentration gradient within a particle when chemical reaction controls
- As the reaction is unaffected by the presence of any ash layer, the rate is proportional to the available surface of unreacted core
- Rate of reaction based on unit surface of unreacted core, r_c is,

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

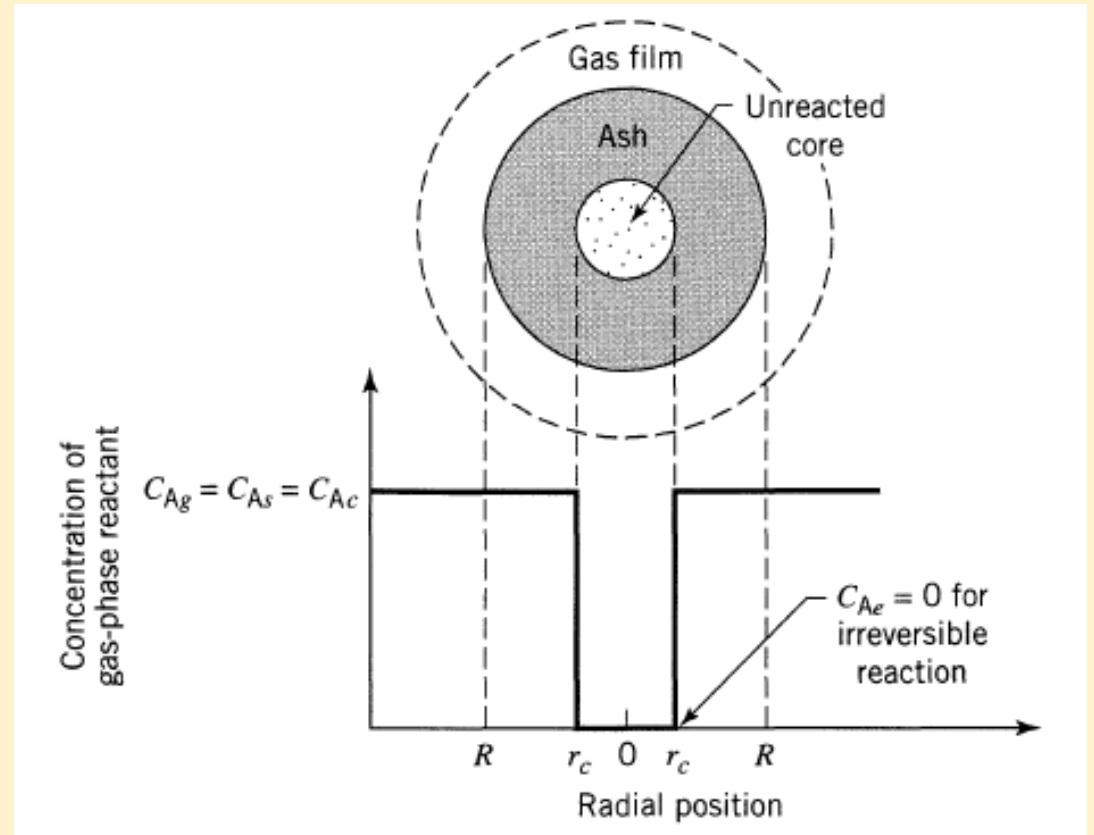
where k is the first order reaction rate constant

Now, as, $-dN_B = -\rho_B dV = -4\pi\rho_B r_c^2 dr_c$

$$-\frac{4\pi\rho_B r_c^2}{4\pi r_c^2} \frac{dr_c}{dt} = -\rho_B \frac{dr_c}{dt} = bkC_{Ag}$$

$$-\rho_B \int_R^{r_c} dr_c = bkC_{Ag} \int_0^t dt$$

$$t = \frac{\rho_B(R - r_c)}{bkC_{Ag}}$$



- The unreacted core shrinks with time according to ,

$$t = \frac{\rho_B(R - r_c)}{bkC_{Ag}} = \frac{\rho_B R \left(1 - \frac{r_c}{R}\right)}{bkC_{Ag}}$$

- The time for complete conversion of a particle, τ is given by,

$$\tau = \frac{\rho_B R}{bkC_{Ag}}$$

- The decrease in radius or increase in conversion of the particle in terms of τ is given by,

$$\frac{t}{\tau} = 1 - \frac{r_c}{R}$$

- If X_B is the conversion,

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

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