Consider a spherical solid particle dissolving in a fluid. The reaction is given by

\[ A_{\text{fluid}} + B_{\text{solid}} \rightarrow C_{\text{fluid}} \]

There is no solid product layer, corresponding to the shell in shrinking core model. Since the size of the particle changes with time, the boundary layer around the particle also evolves with time. This means that the mass transfer coefficient changes with time.

Let \( R \) be the radius of the particle, and \( R_i \) is the ‘initial’ radius of the particle at time \( t=0 \). We will consider two cases (i) when mass transfer in the fluid is rate limiting and (ii) when reaction on the solid surface is rate limiting.

(i) **Mass transfer in the fluid boundary layer is rate limiting.**

\[
\frac{k_g d_p y}{D} = Sh = 2 + 0.552 \frac{Re}{Sc} \frac{1}{\sqrt[3]{Sh}}
\]

Here, \( d_p \) is the particle diameter = 2 \( R \), ‘\( y \)’ is the mole fraction of inerts (not the reacting component in the liquid) and \( D \) is the diffusivity. \( k_g \) is the mass transfer coefficient.

\( Re \) is the Reynolds number defined as

\[
Re = \frac{dp V_{av} \rho_f}{\mu},
\]

where \( \rho_f \) is the fluid density, \( V_{av} = \) average fluid velocity relative to the particle and \( \mu \) is the fluid viscosity. \( Sc \) is Schmidt number given by

\[
Sc = \frac{\mu}{\rho_f D}.
\]

(a) **If the fluid is stagnant (\( V_{av} = 0 \)) or particle size is small (\( d_p \ll \)),**

then \( Re \) will be negligible and we can write

\[
\frac{k_g d_p y}{D} \approx 2
\]

Writing in terms of radius (\( R \)), we can write

\[
\frac{k_g 2R y}{D} = 2 \text{ and hence } k_g = \frac{D}{Ry}
\]

The rate of consumption of fluid \( A = \frac{-dN_A}{dt} = 4\pi R^2 \times k_g \left(C_{Ag} - C_{As}\right)\)

When mass transfer is rate limiting, we can take \( C_{As} \approx 0 \)

Since one mole of A reacts with one mole of B, we can write
\[-\frac{dN_A}{dt} = 4\pi R^2 \times k_g (C_{Ag} - C_{As}) \approx 4\pi R^2 \times k_g C_{Ag}\]
\[-\frac{dN_B}{dt} = d\left(\rho_B \frac{4\pi R^3}{3}\right) = -4\pi R^2 \rho_B \frac{dR}{dt}\]
This leads to \(\frac{dR}{dt} = \frac{-k_g C_{Ag}}{\rho_B}\)

Substituting for \(k_g\) in terms of \(R\), we see that \(\frac{dR}{dt} = \frac{-C_{Ag} D}{\rho_B y} \frac{1}{R}\)

Integrating, we get \(\frac{R^2}{2} = \frac{-C_{Ag} D}{\rho_B y} t + C_1\)

Based on initial condition, \(t=0, R=R_i\), we can see that \(C_1 = \frac{R_i^2}{2}\)

\[(R_i^2 - R^2) = \frac{2DC_{Ag}}{\rho_B y} t\]

Time for complete conversion (\(\tau\)) is given by \(R = 0\),
\(\tau = \frac{R_i^2 \rho_B y}{2DC_{Ag}}\) and thus we can write \(t = \frac{1}{\tau} = 1 - \left(\frac{R}{R_i}\right)^2\). Thus time for complete conversion is proportional to the square of initial radius.

(b) if the fluid is vigorously stirred and/or particle diameter is large such that \(Re^{1/2} Sc^{1/3} \gg 2\), we can write

\[\frac{k_g d_p y}{D} = Sh \approx 0.552 Re^{1/2} Sc^{1/3} = 0.552 \left(d_p \frac{V_{av} \rho_f}{\mu}\right)^{1/2} \left(\frac{\mu}{\rho_f D}\right)^{1/3}\]

Remember that \(d_p = 2 R\).

Now \(k_g = C_2 R^{1/2} = \frac{C_2}{R^{1/2}}\) where
\[C_2 = \frac{0.552}{\sqrt{2}} \left(\frac{V_{av} \rho_f}{\mu}\right)^{1/2} \left(\frac{\mu}{\rho_f D}\right)^{1/3} \frac{D}{y} = \frac{0.552}{\sqrt{2}} \left(\frac{V_{av}}{\mu}\right)^{1/2} \left(\frac{\rho_f}{\mu}\right)^{1/6} \frac{D^{2/3}}{y}\]

Following the same procedure as done in section (a), we can write that
\[\frac{dR}{dt} = \frac{-k_g C_{Ag}}{\rho_B}\]
Substituting for $k_g$ in terms of $R$, we see that

$$\frac{dR}{dt} = -\frac{C_{Ag}}{\rho_B} \frac{C_2}{R^{3/2}}$$

Integrating we get

$$R^{3/2} \frac{2}{3} = \frac{-C_{Ag}C_2}{\rho_B} t + C_3$$

Substituting for initial conditions, $t = 0$, $R = R_i$ we get $C_3 = R_i^{3/2} \frac{2}{3}$ and

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

where $\tau = \frac{2}{3} \frac{\rho_B (R_i)^{3/2}}{C_2 C_{Ag}}$. This suggests that the time for complete conversion is proportional to $(R_i)^{1.5}$. But we should note that as the particle size becomes smaller, Reynolds number will become smaller and Sh number will be ~ 2. When particle size becomes very small, kinetics will be rate limiting, as shown below.

(ii) **When surface reaction kinetics are rate limiting.**

If mass transfer is rapid, then we can write $C_{A_s} \approx C_{Ag}$ and the rate of consumption of A is given by

$$4\pi R^2 \times k_s \left(C_{A_s}\right) \approx 4\pi R^2 k_s C_{Ag}$$

and this equated with the rate of consumption of B

i.e. \[ \frac{-dN_B}{dt} = 4\pi R^2 \rho_B \frac{dR}{dt} = 4\pi R^2 k_s C_{Ag} \]

Therefore

$$\frac{dR}{dt} = -\frac{k_s C_{Ag}}{\rho_B}$$

Integrating, we get

$$R = -\frac{k_s C_{Ag}}{\rho_B} t + C_4$$

With the initial condition $t = 0$, $R = R_i$, we get $C_4 = C_s = R_i$ and

$$\frac{t}{\tau} = \left(1 - \frac{R}{R_i}\right)$$

Here $\tau = \frac{\rho_B R_i}{k_s C_{Ag}}$. Thus time for complete conversion is proportional to $R$. 
Accounting for mass transfer and surface reaction kinetics effects

When both kinetics and mass transfer play a role, (and assuming that $\text{Sh} \sim 2$), we can write

$$\frac{-dR}{dt} = \text{Resistance} = \frac{C_{Ag}}{\rho_B y R} \left( \frac{\rho_B y R}{D} \right) + \frac{C_{Ag}}{k_s}$$

Therefore, $\left( \frac{\rho_B y R}{D} \right) \frac{R^2}{2} + \left( \frac{\rho_B}{k_s} \right) R = -C_{Ag} t + C_5$

With the initial condition $t = 0, R = R_i$, we get $C_5 = \left( \frac{\rho_B y R}{D} \right) \frac{R_i^2}{2} + \left( \frac{\rho_B}{k_s} \right) R_i$ and

$$t = \frac{1}{C_{Ag}} \left[ \left( \frac{\rho_B y}{D} \right) \frac{R^2}{2} \left( 1 - \left( \frac{R}{R_i} \right)^2 \right) + \left( \frac{\rho_B}{k_s} \right) R \left( 1 - \frac{R}{R_i} \right) \right]$$

This is another form of writing

$$t = \frac{1}{C_{Ag}} \left[ \left( \frac{\rho_B y}{D} \right) \frac{R^2}{2} - \left( \frac{\rho_B y}{D} \right) \frac{R^2}{2} + \left( \frac{\rho_B}{k_s} \right) R_i - \left( \frac{\rho_B}{k_s} \right) R \right] = a' + b' R + c' R^2,$$

i.e. a quadratic equation in ‘$R’.

Here, $c' = -\frac{1}{2C_{Ag}} \left( \frac{\rho_B y}{D} \right) = -\frac{\tau_{MT}}{R_i^2}$. (subscript MT = Mass Transfer)

$$b' = -\frac{1}{C_{Ag}} \left( \frac{\rho_B}{k_s} \right) = -\frac{\tau_{kinetics}}{R_i}$$

and $a' = \frac{1}{C_{Ag}} \left[ \left( \frac{\rho_B y}{D} \right) \frac{R_i^2}{2} + \left( \frac{\rho_B}{k_s} \right) R_i \right] = \tau_{MT} + \frac{\tau_{kinetics}}{\tau_{Total}}$.

We can write the time for complete conversion as $\tau_{Total} = \frac{1}{C_{Ag}} \left[ \left( \frac{\rho_B y}{D} \right) \frac{R_i^2}{2} + \left( \frac{\rho_B}{k_s} \right) R_i \right]$

$$\frac{t}{\tau_{Total}} = 1 - \frac{\tau_{kinetics}}{\tau_{Total}} \left( \frac{R}{R_i} \right) - \frac{\tau_{MT}}{\tau_{Total}} \left( \frac{R}{R_i} \right)^2$$

Note that there are only two independent parameters here since $\tau_{Total} = \tau_{MT} + \tau_{kinetics}$
Particular value of radius when mass transfer and kinetic resistances are equal.

Consider the equation

$$\frac{-dR}{dt} = \frac{C_{Ag}}{\text{Resistance}} = \frac{C_{Ag}}{\left(\frac{\rho_B yR}{D} + \frac{\rho_B}{k_s}\right)}$$

where mass transfer and kinetics resistances are considered (mass transfer with the assumption that $Re \sim 0$)

When both resistances are equal, i.e. $\left(\frac{\rho_B yR}{D}\right) = \left(\frac{\rho_B}{k_s}\right)$, we can write $R^* = \left(\frac{D}{y k_s}\right)$. If the particle radius ($R$) is much larger than this value ($R^*$), then mass transfer is rate limiting. If the particle radius is significantly smaller than $R^*$, then kinetics is rate limiting.

In some books, this is written in terms of diameter of the particle, i.e. $D^* = 2D/(y k_s)$. We avoid using $D$ for particle diameter since we use $D$ to denote diffusivity and this can lead to confusion.