1. Shrinking Core Model (SHM)

The shrinking core model is based on the assumption of a reactive solid core (species B; reactions take place only at the core surface), that is surrounded by a porous ash layer (no reactions can occur in the ash layer). Mass transfer from the surrounding fluid (i.e., from the "bulk gas") to the particle surface is taken into account via a mass transfer coefficient. In summary, the fluid species (A) and the solid (B) react irreversibly to form a gaseous product (C) and the ash layer (D).:

$$\nu_A A + \nu_B B \xrightarrow{r_R} \nu_C C + \nu_D D$$

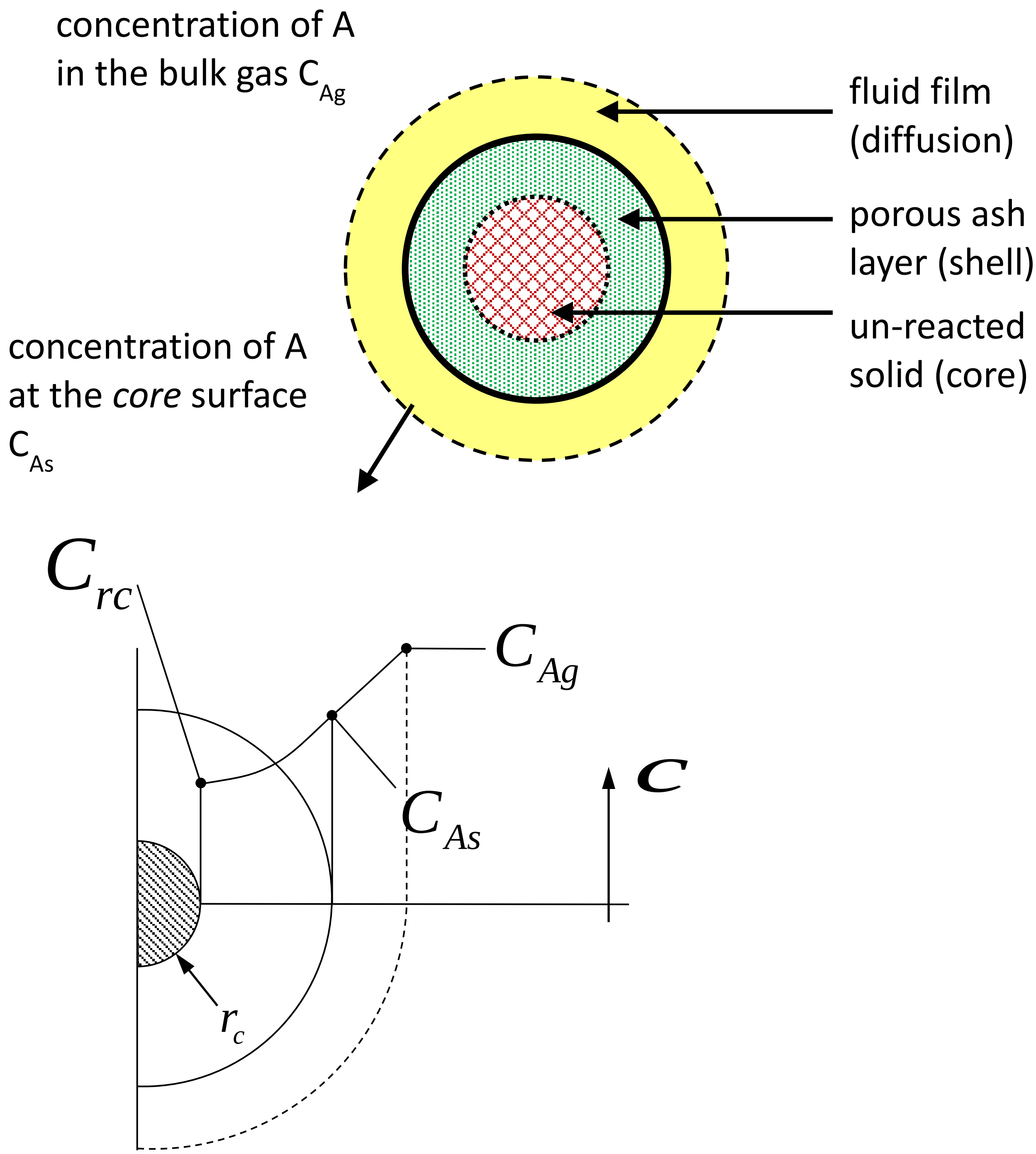
The reaction kinetics are modelled to be first order with respect to the concentration of species A, i.e., the area-specific reaction rate is

$$r_R = k_s C_{rc} \tag{1.1}$$

The core unknown variable in the SHM is the core radius, which can be computed from the molar rate of consumption of B.

More information about the SHM can be found in:

- Jerkiewicz, Feliu, Popov: "*Hydrongen at Surface and Interfaces*", 2000
- Gavhane, Prakashan: "*Chemical Reaction Engineering II*", 2009


concentration of A
in the bulk gas C_{Ag}
fluid film
(diffusion)
porous ash
layer (shell)
un-reacted
solid (core)
concentration of A
at the *core* surface
C_{As}
C_{rc}
C_{Ag}
C_{As}
C
r_c

2. Classical SHM for a Spherical Particle

The classical SHM (for a spherical particle) is based on a steady-state balance of the molar transport rates through the fluid film, the porous ash layer, and the reaction at the core surface:

$$R_A = \nu_A R_R = k_g\left(C_{Ag} - C_{As}\right)4\pi R^2 = \frac{D_e}{\left(\frac{1}{r_c} - \frac{1}{R}\right)}\left(C_{As} - C_{rc}\right)4\pi = \nu_A k_s C_{rc} 4\pi r_c^{\ 2} \tag{1.2}$$

2.1. Reaction and Consumption Rates

By eliminating the unknown concentrations C_{As} and C_{rc}, one can derive an expression for the reaction rate:

$$R_R = \frac{C_{Ag}}{\frac{\nu_A}{k_g 4\pi R^2} + \frac{\nu_A}{\frac{4\pi D_e}{\left(\frac{1}{r_c} - \frac{1}{R}\right)}} + \frac{1}{k_s 4\pi r_c^2}} \tag{1.3}$$

The molar consumption rates of gas-phase species A and the solid (B) are:

$$R_A = \frac{C_{Ag}}{\frac{1}{k_g 4\pi R^2} + \frac{1}{\frac{4\pi D_e}{\left(\frac{1}{r_c} - \frac{1}{R}\right)}} + \frac{1}{\nu_A k_s 4\pi r_c^2}} \tag{1.4}$$

$$R_B = \frac{\nu_B}{\nu_A}\frac{C_{Ag}}{\frac{1}{k_g 4\pi R^2} + \frac{1}{\frac{4\pi D_e}{\left(\frac{1}{r_c} - \frac{1}{R}\right)}} + \frac{1}{\nu_A k_s 4\pi r_c^2}} \tag{1.5}$$

2.2. Evolution Equation for the Core Radius

Thus, the evolution equation of the core radius can be computed from

$$-\rho_B 4\pi r_c^2 \frac{dr_c}{dt} = \frac{\nu_B}{\nu_A}\frac{C_{Ag}}{\frac{1}{k_g 4\pi R^2} + \frac{1}{\frac{4\pi D_e}{\left(\frac{1}{r_c} - \frac{1}{R}\right)}} + \frac{1}{\nu_A k_s 4\pi r_c^2}} \tag{1.6}$$

$$-\frac{dr_c}{dt} = \frac{\nu_B}{\nu_A}\frac{C_{Ag}/\rho_B}{\frac{r_c^{\ 2}}{k_g R^2} + \frac{\left(R - r_c\right)r_c}{RD_e} + \frac{1}{\nu_A k_s}} \tag{1.7}$$

Finally, we get in terms of the normalized core radius $u = r_c/R$:

$$\frac{du}{dt}=\frac{\nu_B}{\nu_A}\frac{C_{Ag}/\rho_B}{\frac{r_c^{\,2}}{k_g R}+\frac{(R-r_c)r_c}{D_e}+\frac{R}{\nu_A k_s}} \tag{1.8}$$

2.3. Total Solids Conversion

The total conversion of the particle can be calculated from the radius of the core:

$$1-X_B=\frac{\text{volume of unreacted core}}{\text{original volume of the unreacted particle}}=\frac{\frac{4}{3}\pi r_c^{\,3}}{\frac{4}{3}\pi R^3}=\left(\frac{r_c}{R}\right)^3 \tag{1.9}$$

2.4. Concentrations and Concentration Profile

The unknown concentrations are:

$$C_{As}=C_{Ag}\left(\frac{\frac{k_g R\left(\frac{R}{r_c}-1\right)}{4D_e}+\frac{k_g}{\nu_A k_s}\left(\frac{R}{r_c}\right)^2}{1+\frac{k_g R\left(\frac{R}{r_c}-1\right)}{4D_e}+\frac{k_g}{\nu_A k_s}\left(\frac{R}{r_c}\right)^2}\right) \tag{1.10}$$

$$C_{rc}=\frac{C_{Ag}}{\frac{\nu_A k_s r_c^{\,2}}{k_g R^2}+\frac{\nu_A k_s r_c\left(1-\frac{r_c}{R}\right)}{D_e}+1} \tag{1.11}$$

The concentration in the porous ash layer is:

$$C_{(r)}=C_{As}+\left(C_{rc}-C_{As}\right)\frac{(R-r)r_c}{r(R-r_c)} \tag{1.12}$$

3. Nomenclature

Latin Symbols

C	Concentration	[kmol/m³]
C_{Ag}	Concentration of A in the bulk gas phase	[kmol/m³]
C_{As}	Concentration of A at the shell surface	[kmol/m³]
C_{rc}	Concentration of A at the core surface	[kmol/m³]
D	Diffusivity of A through the gas film	[m²/s]
D_e	Effective diffusivity of A through the ash layer	[m²/s]
k_g	Mass transfer coefficient gas phase	[m/s]
k_s	Reaction rate constant	[m/s]
N_B	Number of nuclei (as a replacement for C)	
R_i	consumption rate of species i	[kmol/s]
R_R	Reaction rate	[kmol/s]
R_A	Reaction rate of species A	[kmol/s]
R_B	Reaction rate of species B	[kmol/s]
r_R	Area-specific reaction rate	[kmol/m²/s]
R	Particle radius	[m]
r_c	Core radius	[m]
t	Time	[s]
X_B	Total conversion of the solid	

Greek Symbols

δ	Boundary layer thickness	[m]
ν_i	Stoichiometric factor of species i in the reaction	
ρ_B	Molar density of the solid B	[kg/m³]
τ	Total time taken for complete reaction	[s]

4. Appendix A – Diffusive Fluxes through the Porous Ash Layer

4.1. Spherical SHM

The diffusive flux is constant across the porous ash layer, hence:

$$\frac{-dN_A}{dt} = D_e 4r^2\pi \frac{\partial C_A}{\partial r} = \text{const}$$

$$4\pi D_e \left(C_{As} - C_{rc}\right) = \frac{-dN_A}{dt}\left(\frac{1}{R} - \frac{1}{r_c}\right)$$

$$\frac{-dN_A}{dt} = \frac{4\pi D_e \left(C_{As} - C_{rc}\right)}{\left(\frac{1}{R} - \frac{1}{r_c}\right)}$$

4.2. Cylindrical SHM

The diffusive flux is constant across the porous ash layer, hence:

$$\frac{-dN_A}{dt} = D_e 2r\pi h \frac{\partial C_A}{\partial r} = \text{const}$$

$$2\pi D_e h\left(C_{As} - C_{rc}\right) = \frac{-dN_A}{dt}\left(\ln\frac{R}{r_c}\right)$$

$$\frac{-dN_A}{dt} = \frac{2\pi D_e h\left(C_{As} - C_{rc}\right)}{\ln\left(\frac{R}{r_c}\right)}$$

5. Appendix B – Limiting Cases

5.1. Diffusion of A through the Gas Film is Limiting

In case r_c is very close to R, we obtain

$$\frac{D_e}{\left(\frac{1}{r_c}-\frac{1}{R}\right)}\left(C_{As}-C_{rc}\right)4\pi \approx \frac{D_e}{\left(R-r_c\right)}\left(C_{As}-C_{rc}\right)4\pi R^2 \tag{1.13}$$

Assuming that D_e and k_s are very large, and k_g is small, we get

Net reaction rate = constant:

$$k_g\left(C_{Ag}-C_{As}\right)4\pi R^2 \approx k_g C_{Ag}4\pi R^2 \tag{1.14}$$

Rate of formation of B:

$$-\rho_B 4\pi r_c^{\,2}\frac{dr_c}{dt}=k_g C_{Ag}4\pi R^2 \tag{1.15}$$

$$t=\frac{-\rho_B r_c^{\,3}}{3k_g C_{Ag}R^2}+\text{constant} \tag{1.16}$$

$t=0\ ,\ r_c=R$

$$\text{constant}=\frac{\rho_B R}{3k_g C_{Ag}} \tag{1.17}$$

$$t=\frac{\rho_B R}{3k_g C_{Ag}}\left(1-\left(\frac{r_c}{R}\right)^3\right) \tag{1.18}$$

5.1.1. Time for complete conversion

$$\tau=\frac{\rho_B R}{3k_g C_{Ag}} \tag{1.19}$$

$$\frac{t}{\tau}=\left(1-\left(\frac{r_c}{R}\right)^3\right) \tag{1.20}$$

$$\frac{t}{\tau}=X_B \tag{1.21}$$

5.2. Diffusion of A through the Porous Ash Layer is Limiting

D and k_s are very large, D_e is small

$r_c \le r \le R$

$$\frac{-dN_A}{dt} = D_e \frac{\partial C_A}{\partial r} 4\pi r^2 = \text{constant} \tag{2.1}$$

$$4\pi D_e \partial C_A = \left(\frac{-dN_A}{dt}\right)\frac{\partial r}{r^2} \tag{2.2}$$

$$4\pi D_e (C_{As} - C_{rc}) = \left(\frac{-dN_A}{dt}\right)\left(\frac{1}{r_c} - \frac{1}{R}\right) \tag{2.3}$$

$$\left(\frac{-dN_A}{dt}\right) = \frac{4\pi D_e \left(C_{As} - C_{rc}\right)}{\left(\frac{1}{r_c} - \frac{1}{R}\right)} \tag{2.4}$$

$C_{Ag} = C_{As}$

C_{As} is approximately zero

$$\frac{4\pi D_e \left(C_{As} - C_{rc}\right)}{\left(\frac{1}{r_c} - \frac{1}{R}\right)} \approx \frac{4\pi D_e C_{Ag}}{\left(\frac{1}{r_c} - \frac{1}{R}\right)} \tag{2.5}$$

Rate of consumption of A = Rate of consumption of B

$$\frac{4\pi D_e C_{Ag}}{\left(\frac{1}{r_c} - \frac{1}{R}\right)} = \frac{-dN_B}{dt} = -\rho_B 4\pi r_c^{\,2} \frac{dr_c}{dt} \tag{2.6}$$

$$\left(r_c - \frac{r_c^{\,2}}{R}\right) dr_c = \frac{-D_e C_{Ag}}{\rho_B} dt \tag{2.7}$$

$$\int_{r_c=R}^{r_c=r_c} \left(r_c - \frac{r_c^{\,2}}{R}\right) dr_c = \frac{-D_e C_{Ag}}{\rho_B} \int_{t=0}^{t=t} dt \tag{2.8}$$

Integrate and apply the limits to get

$$\left(\frac{r_c^{\,2}}{2} - \frac{r_c^{\,3}}{3R} - \frac{R^2}{2} + \frac{R^3}{3R}\right) = \frac{-D_e C_{Ag}}{\rho_B} t \tag{2.9}$$

On the LHS, multiply and divide by $R^2/6$ to get

$$\left(3\frac{r_c^{\ 2}}{R^2}-2\frac{r_c^{\ 3}}{R^3}-1\right)\frac{R^2}{6}=\frac{-D_eC_{Ag}}{\rho_B}t \tag{2.10}$$

$$t=\frac{\rho_BR^2}{6D_eC_{Ag}}\left(1-3\left(\frac{r_c}{R}\right)^2+2\left(\frac{r_c}{R}\right)^3\right) \tag{2.11}$$

5.2.1. Time for complete conversion

$$\tau=\frac{\rho_BR^2}{6D_eC_{Ag}} \tag{2.12}$$

$$\frac{t}{\tau}=\left(1-3\left(\frac{r_c}{R}\right)^2+2\left(\frac{r_c}{R}\right)^3\right) \tag{2.13}$$

$$1-X_B=\left(\frac{r_c}{R}\right)^3 \tag{2.14}$$

5.3.Surface reaction is Limiting

$(C_{Ag} = C_{rc})$

Rate of consumption of A:

$$\frac{-dN_A}{dt} = 4\pi r_c^2 k_s C_{Ag} = \frac{-dN_B}{dt} = 4\pi r_c^2 \rho_B \frac{dr_c}{dt} \tag{3.1}$$

$t = 0$, $r_c = R$

$$\frac{dr_c}{dt} = \frac{k_s C_{Ag}}{\rho_B} \tag{3.2}$$

$$t = \frac{\rho_B}{k_s C_{Ag}}(R - r_c) = \frac{\rho_B R}{k_s C_{Ag}}\left(1 - \frac{r_c}{R}\right) \tag{3.3}$$

5.3.1. Time for complete conversion

$$\tau = \frac{\rho_B R}{k_s C_{Ag}} \tag{3.4}$$

$$1 - X_B = \left(\frac{r_c}{R}\right)^3 \tag{3.5}$$

$$t = \tau\left(1 - \frac{r_c}{R}\right) = \tau\left(1 - (1 - X_B)^{\frac{1}{3}}\right) \tag{3.6}$$

Change of radius $\frac{dr_c}{dt}$ is a constant

6. Appendix C – Derivation of the Concentration Profile in the Ash Layer

$$\frac{Dc}{Dt} = \frac{1}{r^2} D_r \left(D_e r^2 D_r c \right) = 0$$

$$J = -D_e \frac{Dc}{Dr} = c_{(r)}$$

$$D_e D_r \left(r^2 D_r c \right) = 0$$

$$r^2 D_r c = \text{const}$$

$$dc = \frac{\text{const}}{r^2} dr$$

$$c = \frac{c_1}{2} \frac{1}{r} + c_2$$

$$c_2 = C_{As} - \frac{C_{rc} - C_{As}}{R\left(\frac{1}{r_c} - \frac{1}{R} \right)}$$

$$c_1 = \frac{2\left(C_{rc} - C_{As} \right)}{\frac{1}{r_c} - \frac{1}{R}}$$

$$C_{(r)} = \frac{C_{rc} - C_{As}}{r\left(\frac{1}{r_c} - \frac{1}{R} \right)} + C_{As} - \frac{C_{rc} - C_{As}}{R\left(\frac{1}{r_c} - \frac{1}{R} \right)}$$

$$C_{(r)} = C_{As} + (C_{rc} - C_{As}) \frac{\left(R - r \right) r_c}{r\left(R - r_c \right)}$$