

BT209

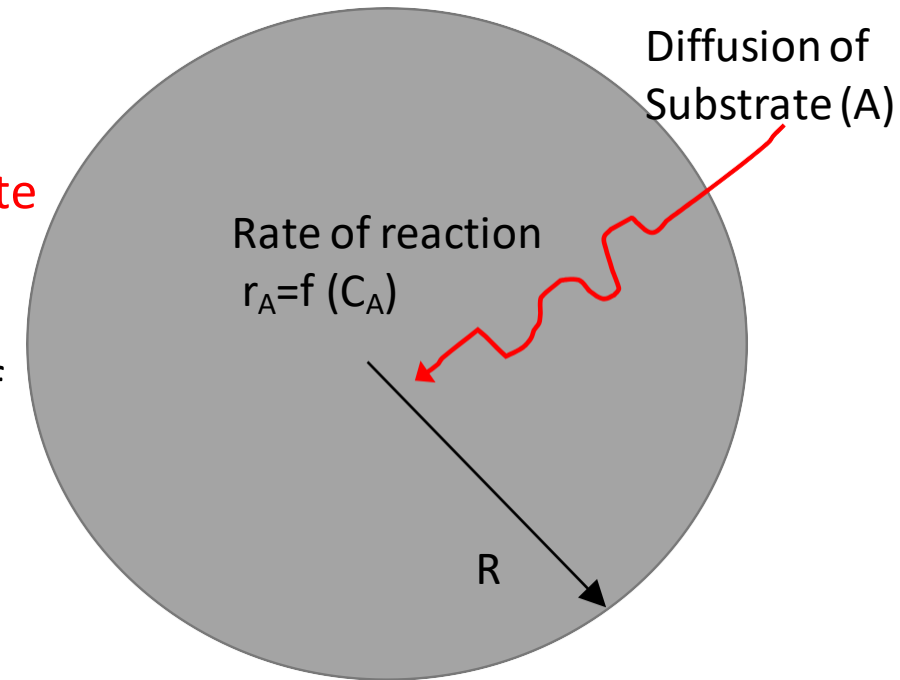
Bioreaction Engineering

13/04/2023

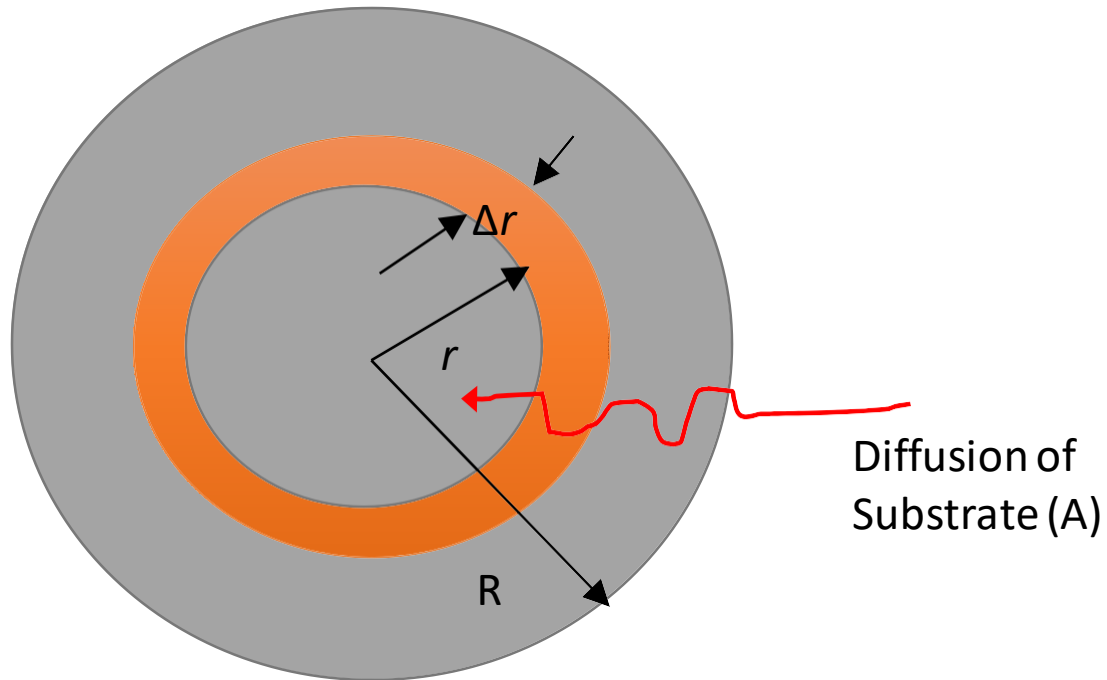
Heterogeneous reaction

Internal mass transfer and reaction in heterogeneous systems

- ❑ Rates of reaction and substrate mass transfer are **not independent**
- ❑ The **rate of mass transfer depends on the concentration gradient** established in the system; this in **turn depends on** the rate of **substrate depletion by reaction**.
- ❑ On the other hand, the **rate of reaction depends** on the availability of **substrate**, which depends on the rate of mass transfer.
- ❑ Possible to **determine the relative influences** of mass transfer and reaction **on observed reaction** rates.
- ❑ If a **reaction proceeds slowly even in the presence of adequate substrate**, it is likely that mass transfer will be rapid enough to meet the demands of the reaction. In this case, the **observed rate would reflect more directly the reaction process** rather than mass transfer.
- ❑ Conversely, **if the reaction tends to be very rapid**, it is likely that **mass transfer will be too slow to supply substrate** at the rate required. The **observed rate would then reflect strongly the rate of mass transfer**.
- ❑ **Improving mass transfer and eliminating mass transfer restrictions** are desired objectives



Internal mass transfer and reaction



Assumption

- ✓ The particle is isothermal
- ✓ The particle is homogeneous
- ✓ Mass transfer occurs by diffusion only
- ✓ Diffusion can be described using Fick's law with constant effective diffusivity
- ✓ The substrate partition coefficient is unity
- ✓ The particle is at steady state

For a shell mass balance on substrate A

Rate of mass accumulation

= Rate of mass in - rate of mass out + rate mass of generation - rate of mass consumption

$$\left(\mathcal{D}_{Ae} \frac{dC_A}{dr} 4\pi r^2 \right) \Big|_{r+\Delta r} - \left(\mathcal{D}_{Ae} \frac{dC_A}{dr} 4\pi r^2 \right) \Big|_r + 0 - r_A 4\pi r^2 \Delta r = 0$$

\mathcal{D}_{Ae} is the effective diffusivity of substrate A in the particle

Internal mass transfer and reaction

$$\Rightarrow \left(\mathcal{D}_{Ae} \frac{dC_A}{dr} 4\pi r^2 \right) \Big|_{r+\Delta r} - \left(\mathcal{D}_{Ae} \frac{dC_A}{dr} 4\pi r^2 \right) \Big|_r + 0 - r_A 4\pi r^2 \Delta r$$

$$\Rightarrow \lim_{\Delta r \rightarrow 0} \frac{\left(\mathcal{D}_{Ae} \frac{dC_A}{dr} 4\pi r^2 \right) \Big|_{r+\Delta r} - \left(\mathcal{D}_{Ae} \frac{dC_A}{dr} 4\pi r^2 \right) \Big|_r}{\Delta r} - r_A r^2 = 0$$

$$\Rightarrow \frac{d}{dr} \left(r^2 \frac{dC_A}{dr} \right) - r_A r^2 = 0$$

$$\Rightarrow \mathcal{D}_{Ae} \left(\frac{d^2 C_A}{dr^2} r^2 + 2r \frac{dC_A}{dr} \right) - r_A r^2 = 0$$

Concentration profile: First order Kinetics

$$\mathcal{D}_{Ae} \left(\frac{d^2 C_A}{dr^2} r^2 + 2r \frac{dC_A}{dr} \right) - r_A r^2 = 0$$

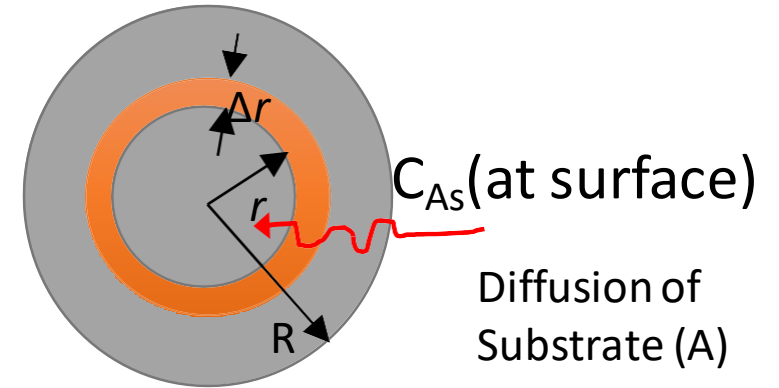
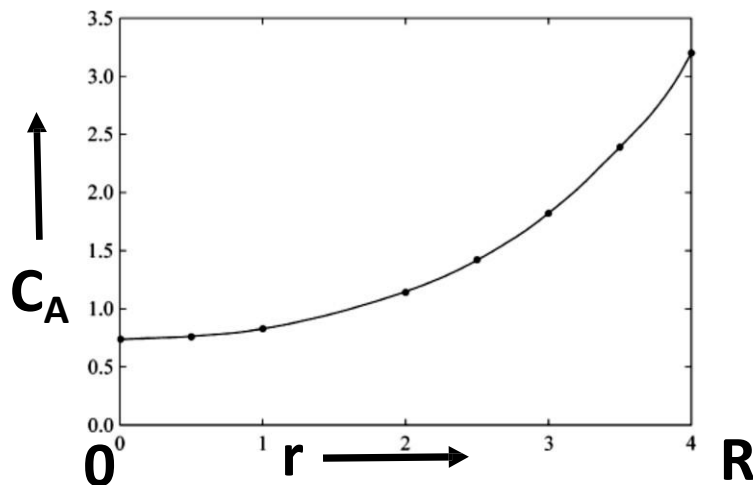
$$\mathcal{D}_{Ae} \left(\frac{d^2 C_A}{dr^2} r^2 + 2r \frac{dC_A}{dr} \right) - k_1 C_A r^2 = 0$$



$$C_A = C_{As} \frac{R}{r} \frac{\sinh(r \sqrt{k_1 / \mathcal{D}_{Ae}})}{\sinh(R \sqrt{k_1 / \mathcal{D}_{Ae}})}$$

use

$$\sinh x = \frac{e^x - e^{-x}}{2}$$



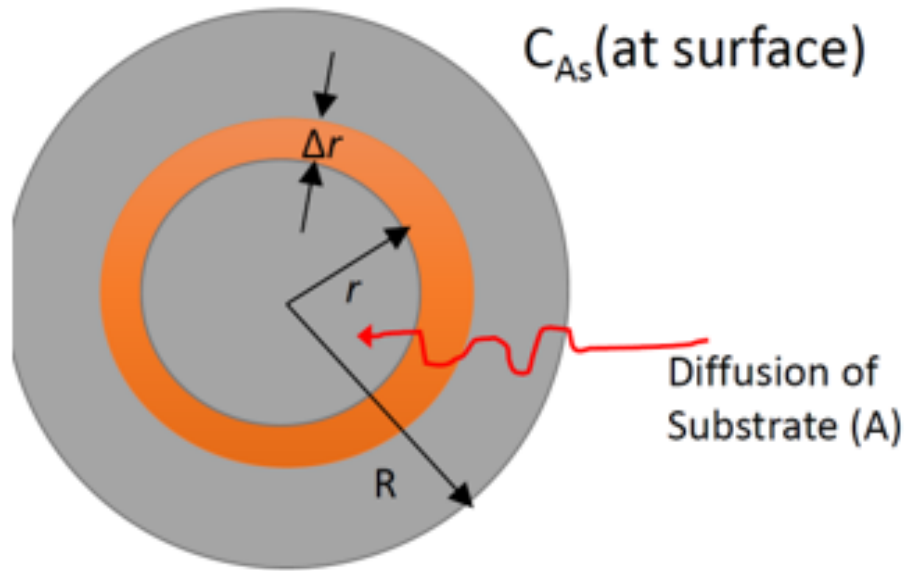
Two boundary condition

$$C_A = C_{As} \quad \text{at } r = R$$

$$\frac{dC_A}{dr} = 0 \quad \text{at } r = 0$$

(Symmetric, minimum at center)

Prediction of observed reaction rate: 1st Order Kinetics



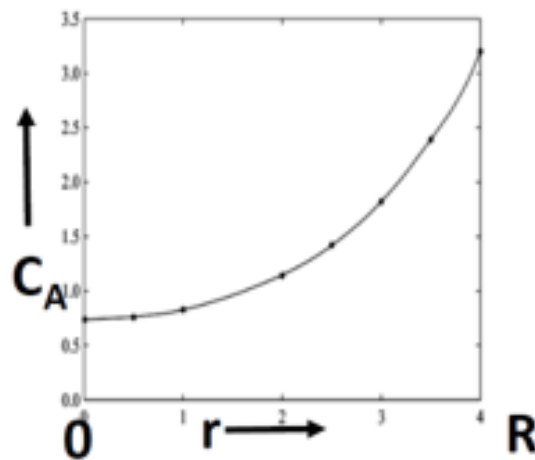
- Concentration is changes across radius (r)
- Rate, $r_A = kC_A$ is different in different radial position

$$C_A = C_{As} \frac{R}{r} \frac{\sinh(r\sqrt{k_1/\mathcal{D}_{Ae}})}{\sinh(R\sqrt{k_1/\mathcal{D}_{Ae}})}$$

$$r_{A,obs} = \frac{4}{3}\pi R^3 \frac{\int_0^R r_A dV}{V - 0} \quad \text{V: volume}$$

$$r_{A,obs} = \frac{4}{3}\pi R^3 \frac{k \int_0^R C_A 4\pi r^2 dr}{\frac{4}{3}\pi R^3}$$

$$r_{A,obs} = 4\pi R \mathcal{D}_{Ae} C_{As} \left[R\sqrt{k_1/\mathcal{D}_{Ae}} \coth\left(R\sqrt{k_1/\mathcal{D}_{Ae}}\right) - 1 \right]$$



Concentration profile: zero order Kinetics

$$\mathcal{D}_{Ae} \left(\frac{d^2 C_A}{dr^2} r^2 + 2r \frac{dC_A}{dr} \right) - r_A r^2 = 0$$

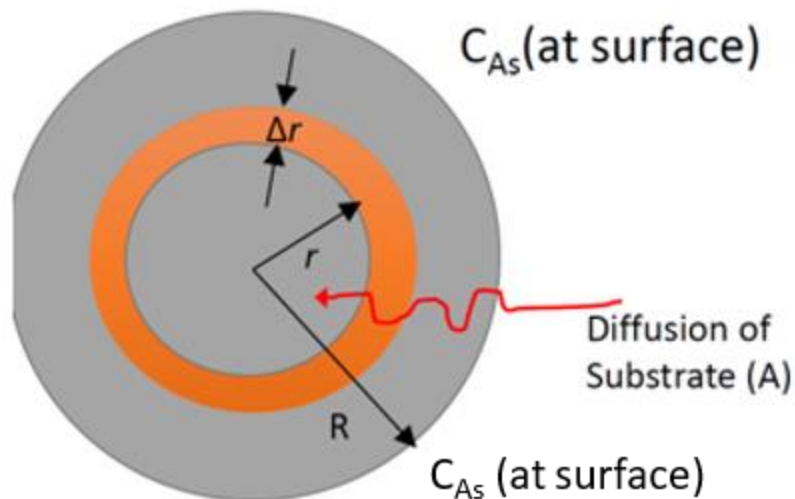
$$\mathcal{D}_{Ae} \left(\frac{d^2 C_A}{dr^2} r^2 + 2r \frac{dC_A}{dr} \right) - k_0 r^2 = 0$$

(k_0 : zero order rate constant)

Two boundary condition

$$C_A = C_{As} \quad \text{at } r = R$$

$$\frac{dC_A}{dr} = 0 \quad \text{at } r = 0$$



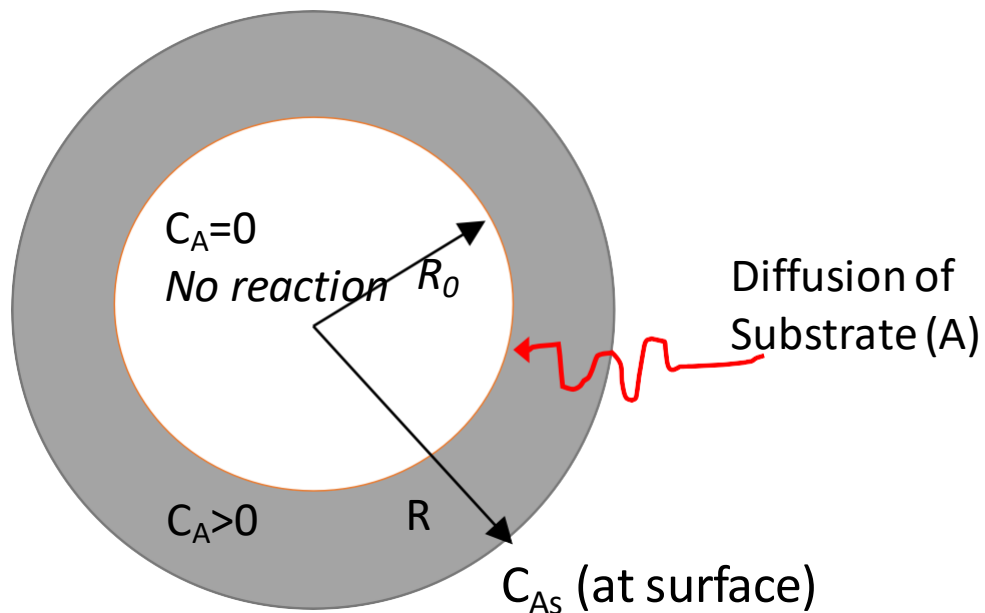
$$C_A = C_{As} + \frac{k_0}{6\mathcal{D}_{Ae}} (r^2 - R^2)$$

Zero order Kinetics with no reaction zone

$$\mathcal{D}_{Ae} \left(\frac{d^2 C_A}{dr^2} r^2 + 2r \frac{dC_A}{dr} \right) - r_A r^2 = 0$$

$$\mathcal{D}_{Ae} \left(\frac{d^2 C_A}{dr^2} r^2 + 2r \frac{dC_A}{dr} \right) - k_0 r^2 = 0$$

(K_0 : zero order rate constant)



Two boundary condition

$$C_A = C_{As} \quad \text{at } r = R$$

$$\frac{dC_A}{dr} = 0 \quad \text{at } r = R_0$$

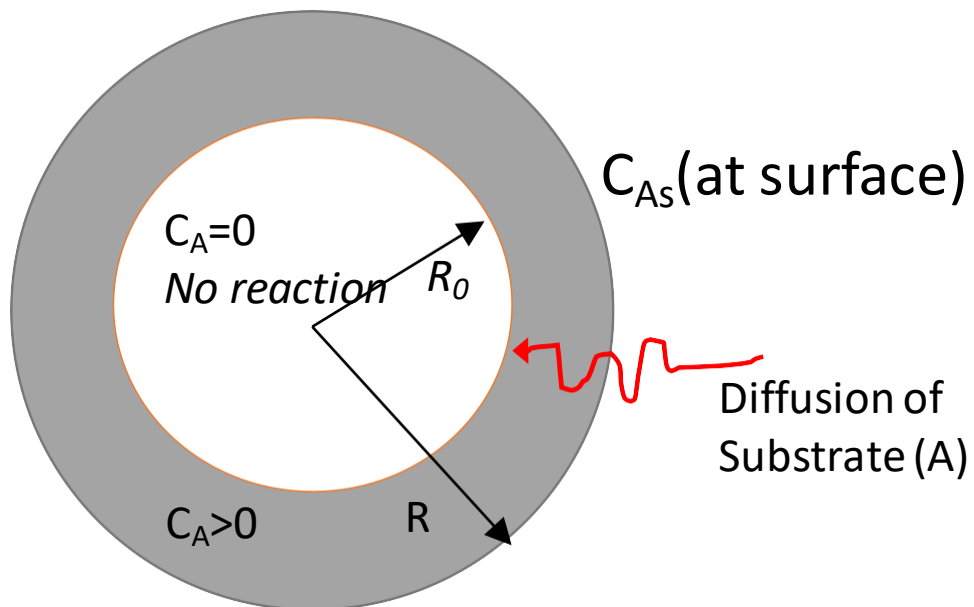
$$C_A = C_{As} + \frac{k_0 R^2}{6 \mathcal{D}_{Ae}} \left(\frac{r^2}{R^2} - 1 + \frac{2R_0^3}{rR^2} - \frac{2R_0^3}{R^3} \right)$$

However, the equation can be simplified if C_A remains > 0 everywhere so that R_0 no longer exists. Substituting $R_0 = 0$ into above Eq. gives:

$$C_A = C_{As} + \frac{k_0}{6 \mathcal{D}_{Ae}} (r^2 - R^2)$$

Maximum particle radius for zero order Kinetics

- ❑ It is important that the core of particle **does not become starved** of substrate
 - This could be **happened upon increasing the size of the bead**
 - ✓ **Need to calculate the maximum particle size** such that $C_A > 0$ and substrate is depleted just at the centre point



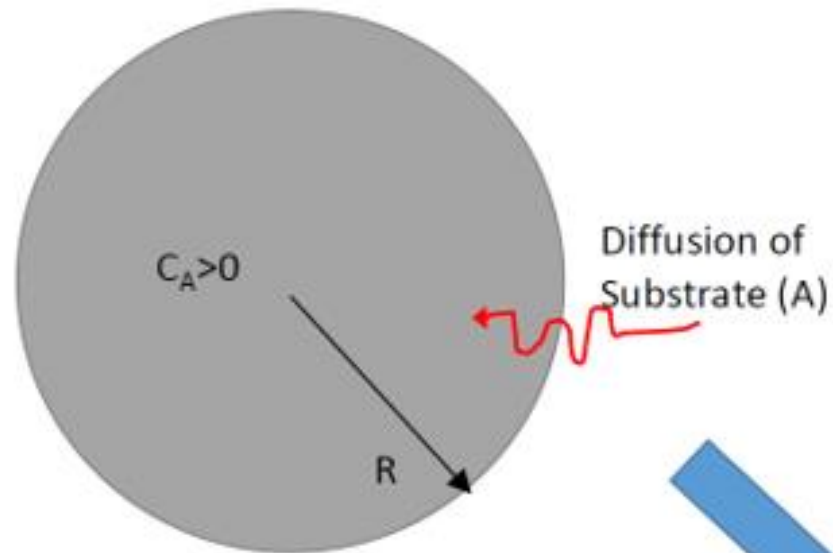
$$C_A = C_{As} + \frac{k_0 R^2}{6\mathcal{D}_{Ae}} \left(\frac{r^2}{R^2} - 1 + \frac{2R_0^3}{rR^2} - \frac{2R_0^3}{R^3} \right)$$

Take, $R_0 = 0$ and at $r = 0$, $C_A = 0$

R is R_{\max}

$$R_{\max} = \sqrt{\frac{6\mathcal{D}_{Ae}C_{As}}{k_0}}$$

Prediction of observed reaction rate: zero Order

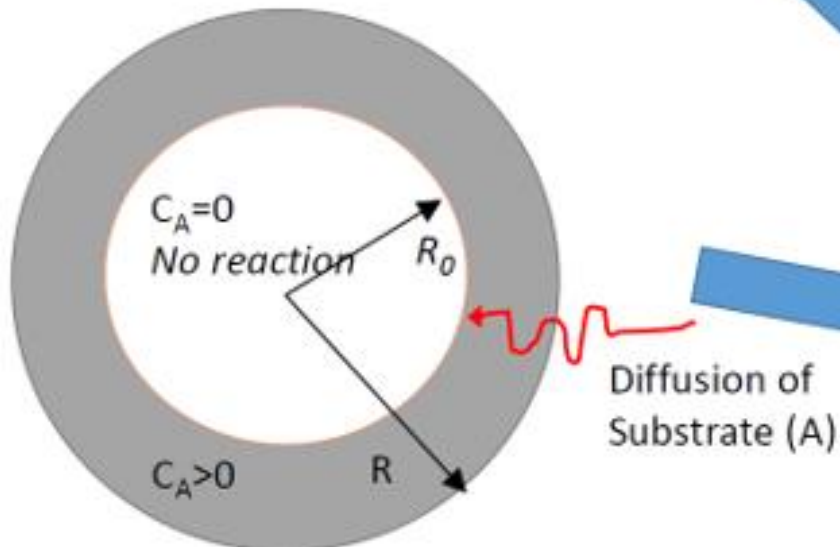


- Concentration is changes across radius (r)
- Rate, $r_A = k_0$, If $C_A > 0$
 $r_A = 0$, If $C_A = 0$

$$r_{A,obs} = \frac{4}{3}\pi R^3 \frac{\int_0^R r_A dV}{V - 0}$$

V : volume

OR, use, total volume x rate of reaction (for this case)



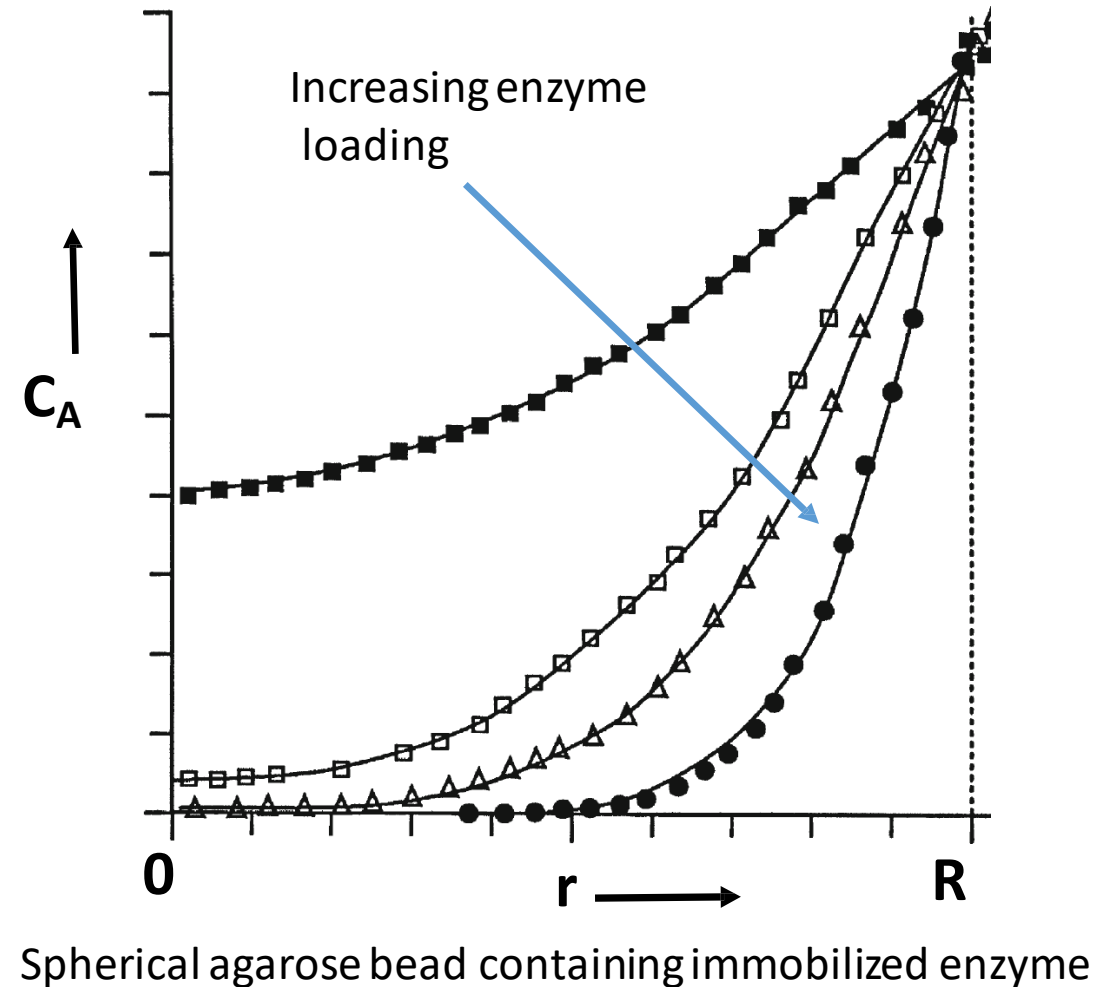
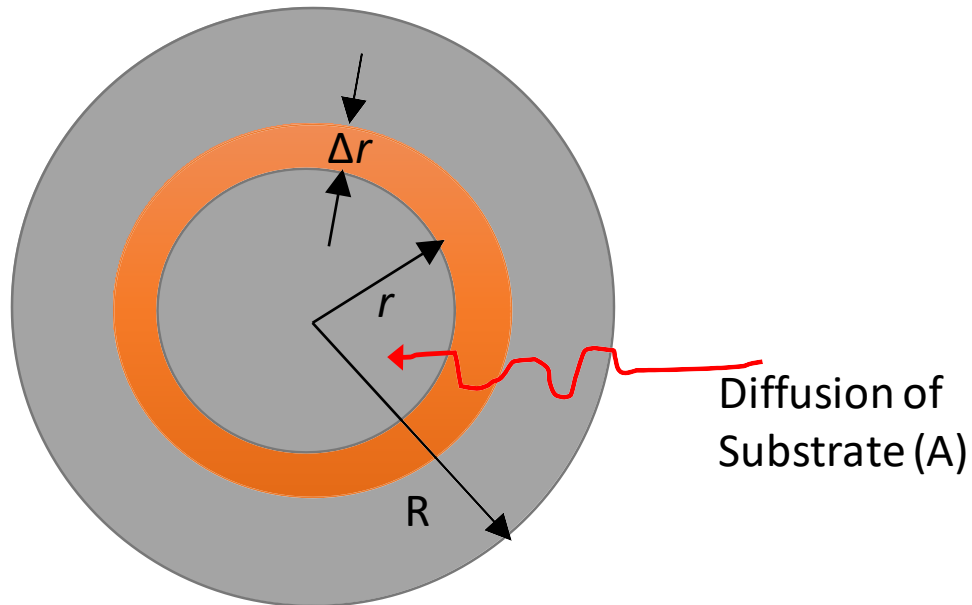
$$r_{A,obs} = \frac{4}{3}\pi R^3 k_0$$

$$r_{A,obs} = \frac{4}{3}\pi (R^3 - R_0^3) k_0$$

Concentration profile: Michaelis Menten Kinetics

$$\mathcal{D}_{Ae} \left(\frac{d^2 C_A}{dr^2} r^2 + 2r \frac{dC_A}{dr} \right) - r_A r^2 = 0$$

→ $\mathcal{D}_{Ae} \left(\frac{d^2 C_A}{dr^2} r^2 + 2r \frac{dC_A}{dr} \right) - \frac{v_{\max} C_A}{K_m + C_A} r^2 = 0$



Prediction of observed reaction rate: Michaelis Menten Kinetics

$$\mathcal{D}_{Ae} \left(\frac{d^2 C_A}{dr^2} r^2 + 2r \frac{dC_A}{dr} \right) - \frac{v_{\max} C_A}{K_m + C_A} r^2 = 0$$

- No analytical solution for C_A
- But numerical can get the C_A profile

$$r_{A,obs} = \frac{4}{3} \pi R^3 \frac{\int_0^R r_A dV}{V - 0}$$

$$r_A = \frac{v_{\max} C_A}{K_m + C_A}$$