BT209

Bioreaction Engineering

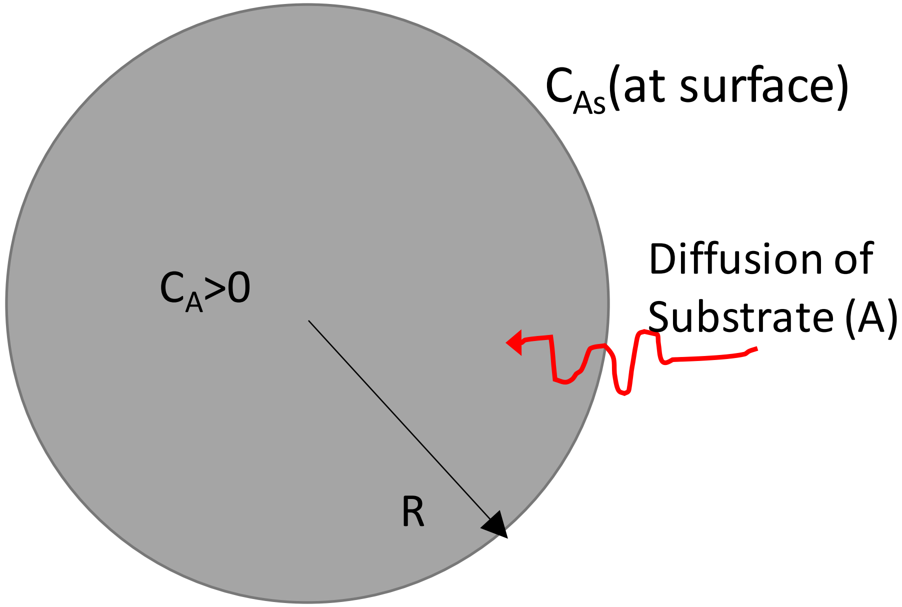
19/04/2023

Heterogeneous reaction

Internal Effectiveness factor (η_i)

- This will give idea the extent to which reaction is affected by the internal mass transfer

$$\eta_i = \frac{\text{observed rate of reaction } (r_{A,obs})}{\text{rate that would occur if } C_A = C_{AS} \text{ everywhere in the particle } (r^*_{AS})}$$



$$r^*_{AS} = \frac{4}{3}\pi R^3 \ (k_1 C_{AS})$$ (maximum rate for 1st order)

if $\eta_i = 1$, there is no mass transfer effect

if $\eta_i \ll 1$, there is large mass transfer effect

Objective: prepared immobilized bead having less mass transfer effect

Predict Internal Effectiveness factor (η_i) for first order

$$\eta_i = \frac{\text{observed rate of reaction } (r_{A,obs})}{\text{rate that would occur if } C_A = C_{AS} \text{ everywhere in the particle } (r^*_{As})}$$

<u>**For first order**</u>

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

$$\eta_i = \frac{4\pi R D_{Ae} C_{AS}\left[R\sqrt{k_1/D_{Ae}}\ coth\left(R\sqrt{k_1/D_{Ae}}\right) - 1\right]}{\frac{4}{3}\pi R^3 \quad k_1\, C_{AS}}$$

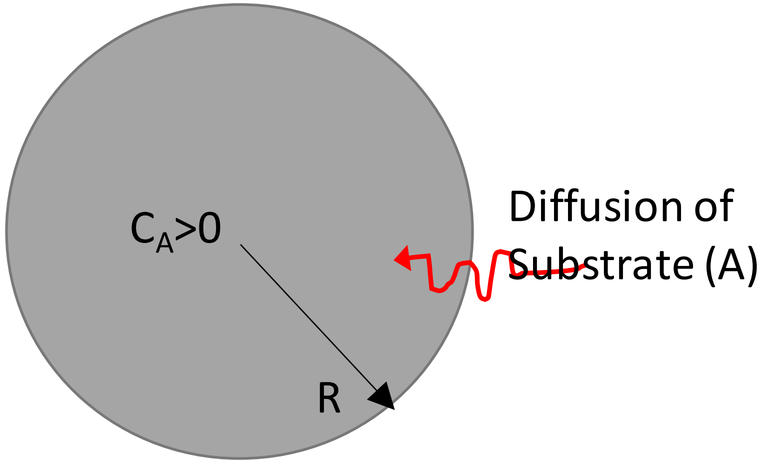
$$\eta_i = \frac{3D_{Ae}}{R^2\, k_1}\left[R\sqrt{k_1/D_{Ae}}\ coth\left(R\sqrt{k_1/D_{Ae}}\right) - 1\right]$$

Predict Internal Effectiveness factor (η_i) for zero order

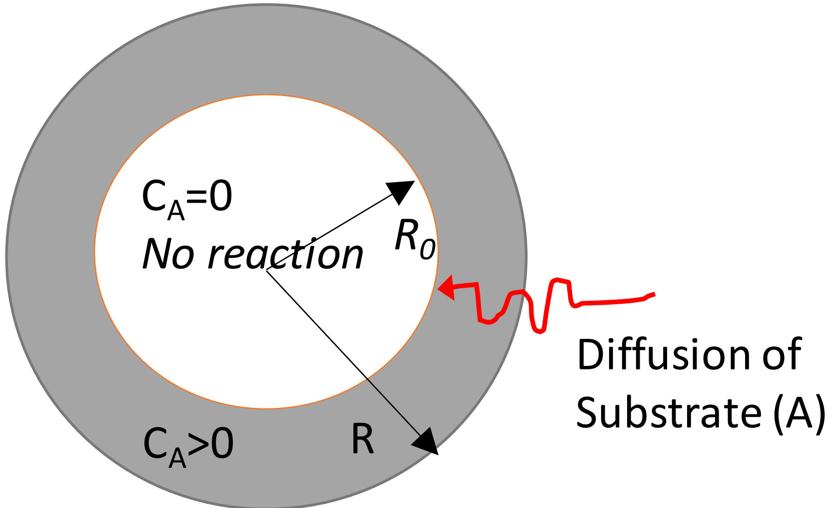
$$\eta_i = \frac{\text{observed rate of reaction } (r_{A,obs})}{\text{rate that would occur if } \mathrm{C_A} = \mathrm{C_{AS}} \text{ everywhere in the particle } (r_{As}^*)}$$

$$\eta_i = \frac{\frac{4}{3}\,\pi\,R^3 \quad k_0}{\frac{4}{3}\,\pi\,R^3 \quad k_0} = 1$$

(Rate independent of concentration)



$$\eta_i = \frac{\frac{4}{3}\pi\,(R^3 - R_0^3)k_0}{\frac{4}{3}\,\pi\,R^3 \quad k_0} = 1 - \left(\frac{R_0}{R}\right)^3$$



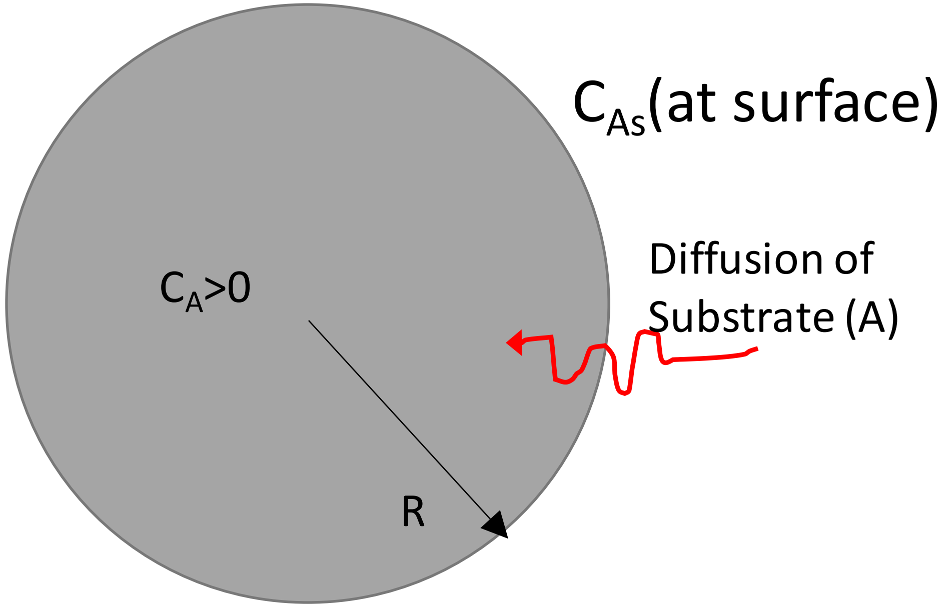
Predict Internal Effectiveness factor (η_i) for Michaelis–Menten kinetics type reaction

$$\eta_i = \frac{\text{observed rate of reaction } (r_{A,obs})}{\text{rate that would occur if } C_A = C_{AS} \text{ everywhere in the particle } (r_{As}^{*})}$$

$$r_{As}^{*} = \frac{4}{3}\,\pi\,R^3\left(\frac{v_{max}\,C_{As}}{K_m + C_{As}}\right) \qquad \text{(maximum rate)}$$

Thiele modulus

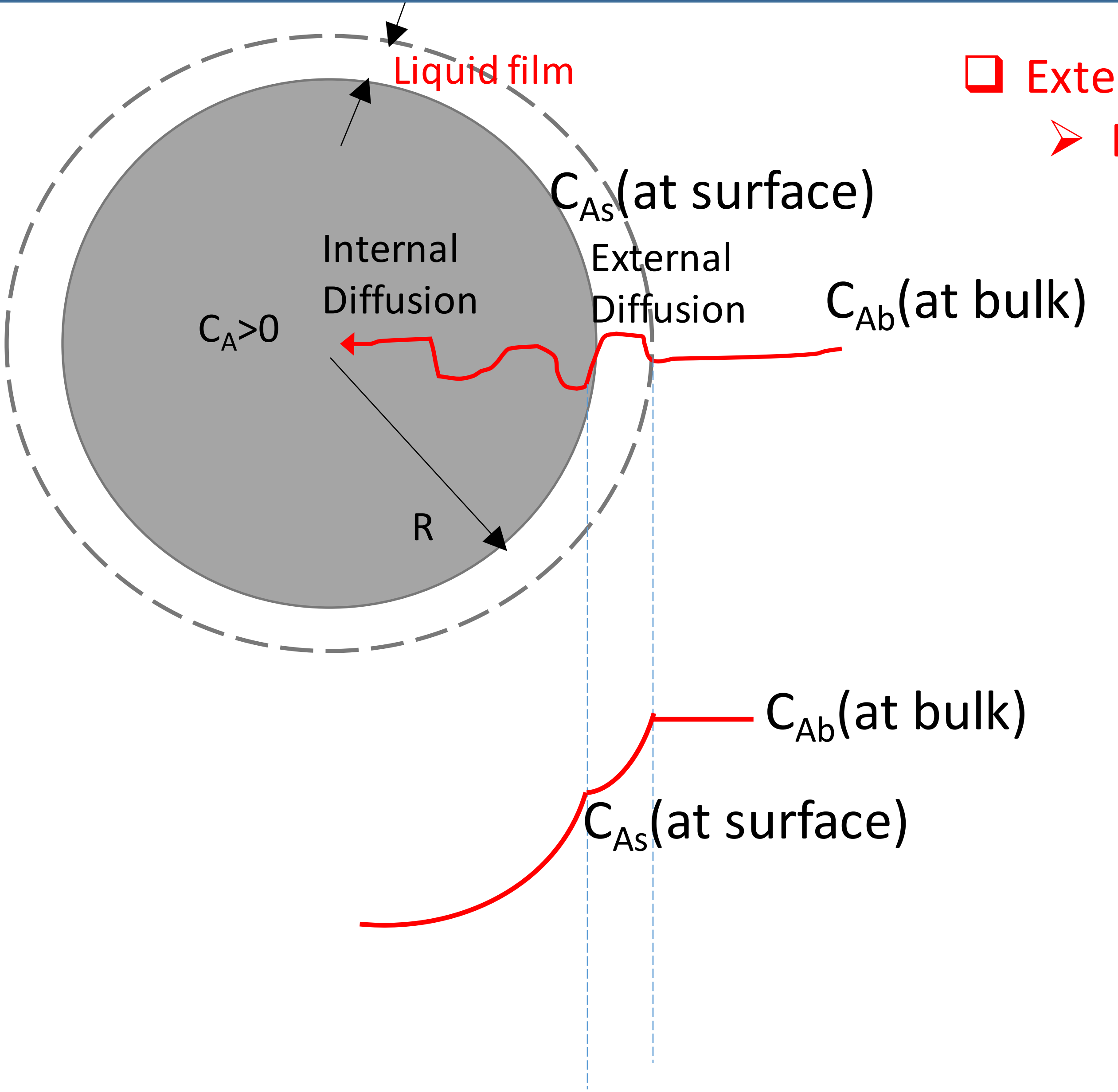
$$\emptyset^2 = \frac{\text{surface reaction rate} \quad (\text{maximum})}{\text{internal diffusion rate}}$$



if $\emptyset$ high, Internal diffusion rate low ,
−process is internal mas transfer control

if $\emptyset$ low, reaction rate low ,
−process is reaction control

External Mass transfer (liquid film mass transfer)



- External barrier/resistance: Liquid film outside the solid
  - External diffusion/External mass transfer

1st order $C_A = C_{As} \frac{R}{r} \frac{\sinh\left(r\sqrt{k_1/\mathscr{D}_{Ae}}\right)}{\sinh\left(R\sqrt{k_1/\mathscr{D}_{Ae}}\right)}$

0th order $C_A = C_{As} + \frac{k_0}{6\mathscr{D}_{Ae}}(r^2 - R^2)$

- Very difficult to measure C_{As}(at surface)

✓ Predict C_{AS}

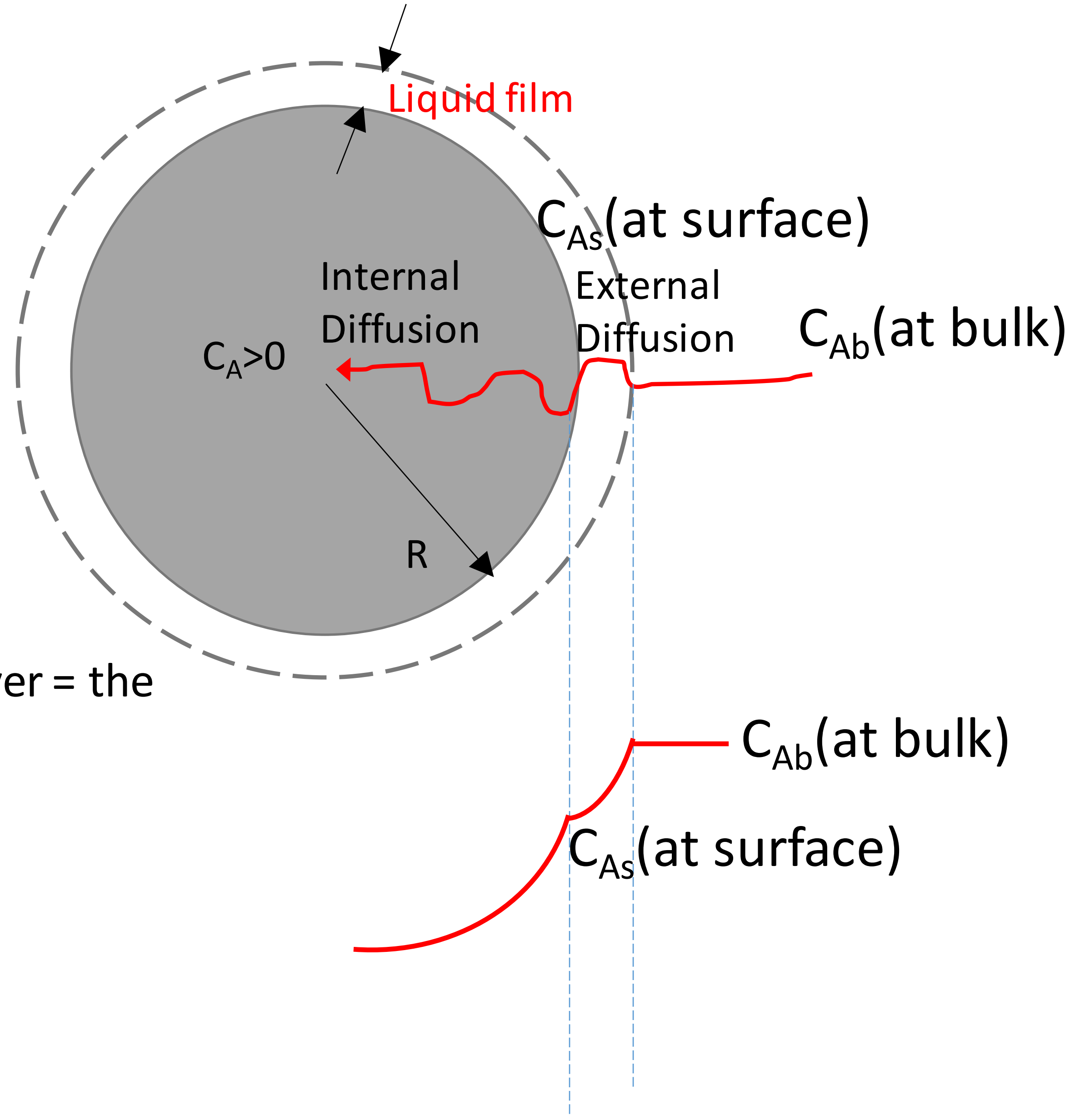
Cont.

The rate of mass transfer across the external film

$$N_A = k_S\, a\,(C_{Ab} - C_{As})$$

k_S : the liquid-phase mass transfer coefficient
a: is the external surface area of the catalyst (some times per unit volume)

$$a = \frac{S_X}{V_P} = \frac{\text{External surface area}}{\text{volume of the particle}}$$



At steady state

the rate of substrate transfer across the boundary layer = the rate of substrate consumption by the catalyst, $r_{A,obs}$.

$$r_{A,obs} = k_S \frac{S_x}{V_p}\,(C_{Ab} - C_{As})$$

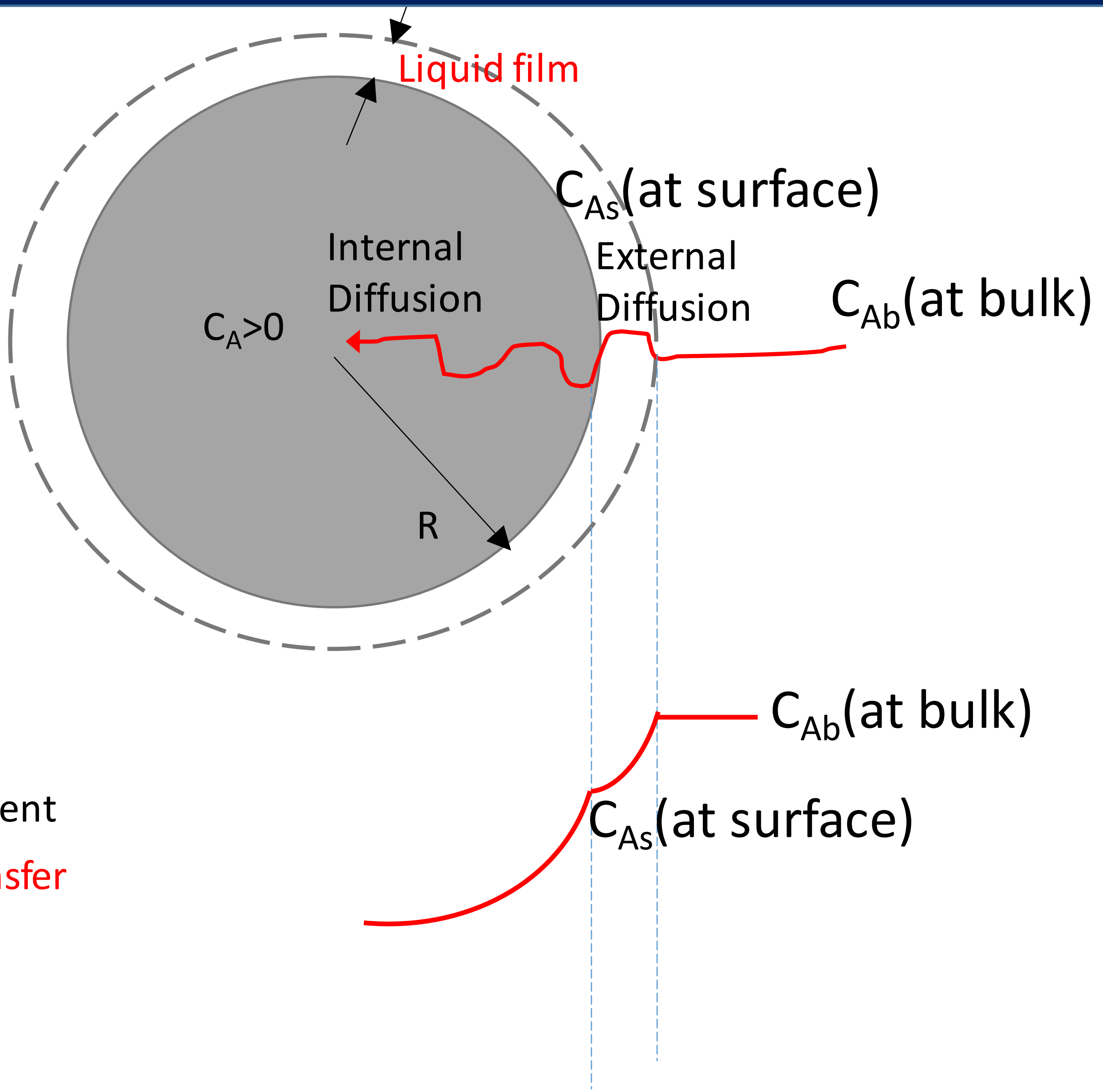
$$\boxed{\frac{C_{As}}{C_{Ab}} = 1 - \frac{V_p}{S_x}\frac{r_{A,obs}}{k_S\, C_{Ab}}}$$

Cont.

$$\boxed{\frac{C_{\mathrm{As}}}{C_{\mathrm{Ab}}} = 1 - \frac{V_{\mathrm{p}}}{S_{\mathrm{x}}} \frac{r_{\mathrm{A,obs}}}{k_{\mathrm{S}}\, C_{\mathrm{Ab}}}}$$

$\frac{C_{As}}{C_{Ab}} \approx 1$, indicates no or negligible external mass transfer limitations, as the substrate concentration at the surface is approximately equal to that in the bulk

$\frac{C_{As}}{C_{Ab}} \ll 1$, indicates a very steep concentration gradient in the boundary layer and severe external mass transfer effects



Total effectiveness factor (η_T)

For reactions affected by both internal and external mass transfer restrictions,

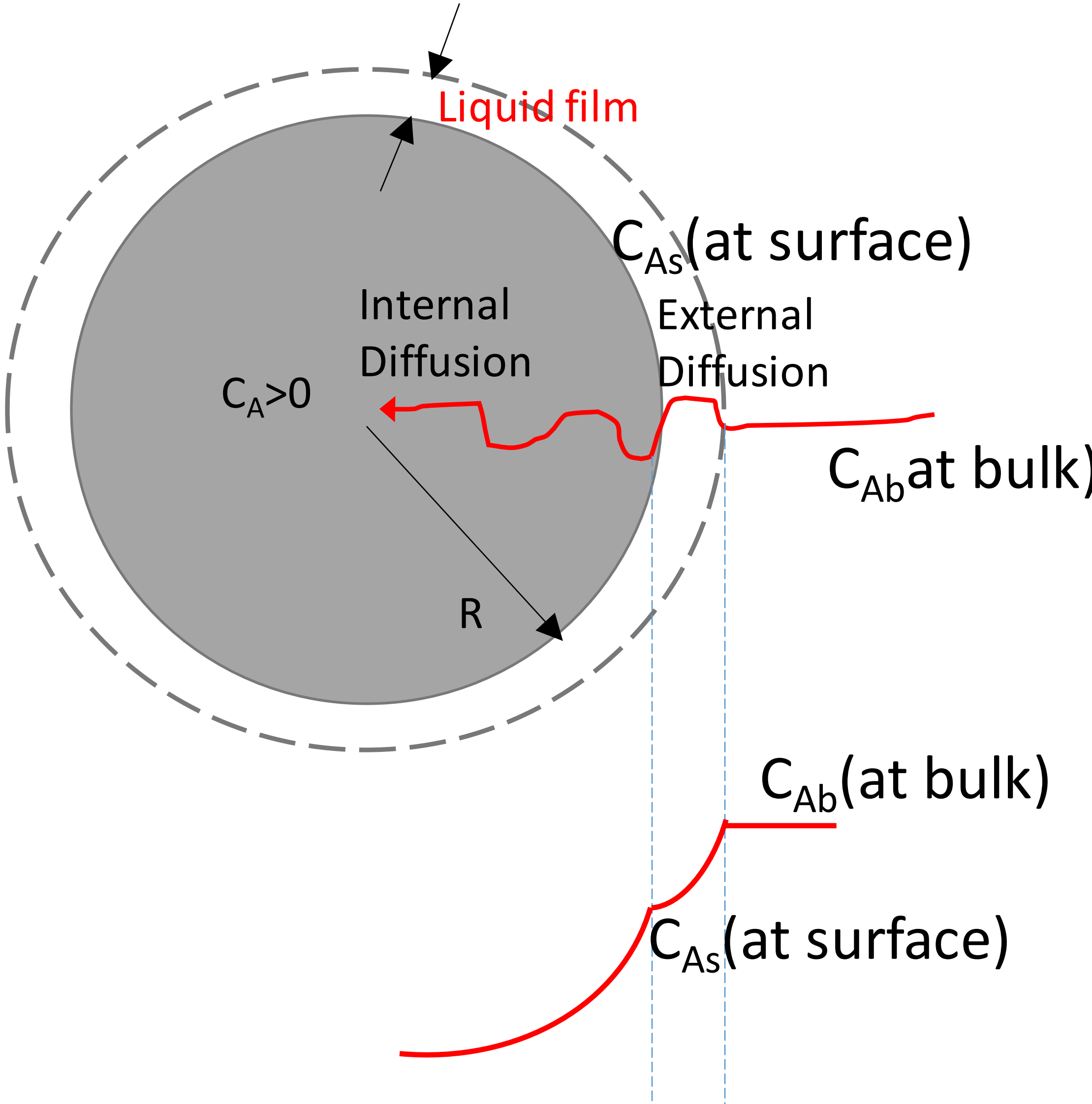
Total effectiveness factor η_T:

$$\eta_T = \frac{r_{A,obs}}{r^*_{Ab}} = \frac{\text{(observed rate)}}{\left(\begin{array}{c}\text{rate that would occur if } C_A = C_{Ab} \\ \text{everywhere in the particle}\end{array}\right)}$$

External effectiveness factor (η_e)

$$\eta_e = \frac{r^*_{As}}{r^*_{Ab}} = \frac{\left(\begin{array}{c}\text{rate that would occur if } C_A = C_{As} \\ \text{everywhere in the particle}\end{array}\right)}{\left(\begin{array}{c}\text{rate that would occur if } C_A = C_{Ab} \\ \text{everywhere in the particle}\end{array}\right)}$$

$$\eta_T = \left(\frac{r_{A,obs}}{r^*_{As}}\right)\left(\frac{r^*_{As}}{r^*_{Ab}}\right) = \eta_i \, \eta_e$$



Special remarks on zero order reaction

- **For zero-order reactions, ($-r_A=k_0$)**

$$\eta_e = \frac{r^*_{As}}{r^*_{Ab}} = \frac{\left(\begin{array}{c}\text{rate that would occur if } C_A = C_{As} \\ \text{everywhere in the particle}\end{array}\right)}{\left(\begin{array}{c}\text{rate that would occur if } C_A = C_{Ab} \\ \text{everywhere in the particle}\end{array}\right)}$$

- η_e = 1 as long as $C_{AS}>0$ and $C_{Ab}>0$

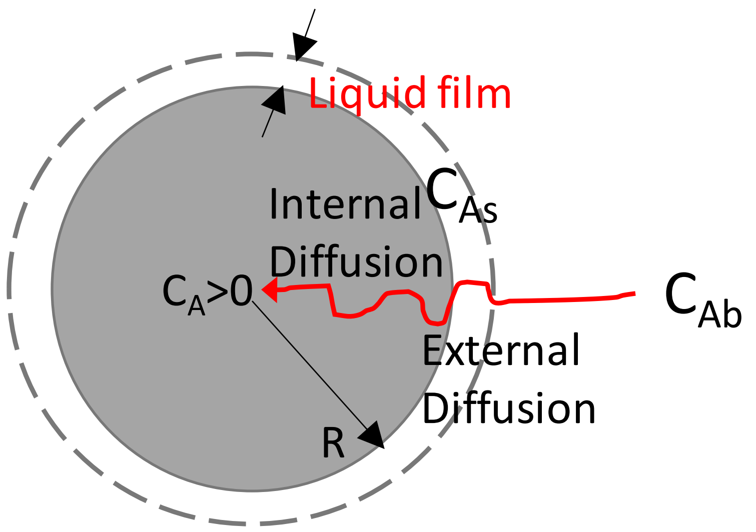
❑ η_e=1 does not imply that an external boundary layer does not exist.

Because r^*_{As} and r^*_{Ab} are independent of C_A

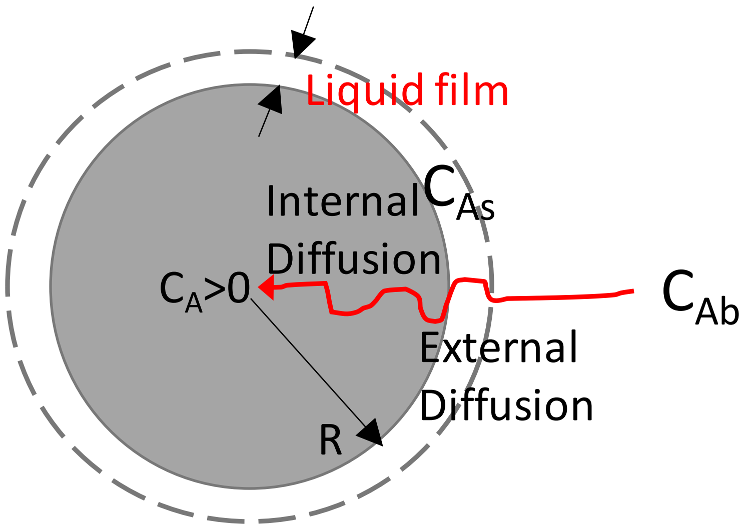
❑ η_e=1 even when there is a reduction in concentration across the external film.

❑Furthermore, η_e=1 does not imply that eliminating the external boundary layer could not improve the observed reaction rate.

➢ Removing the boundary layer would increase the value of C_{As}, thus establishing a greater driving force for internal mass transfer and reducing the likelihood of C_A falling to zero inside the particle.



Minimizing internal mass transfer effects



- Internal mass transfer effects are eliminated when the internal effectiveness factor (η_i) is equal to 1.

  - Reducing the size of the catalyst (travel path length decrease)

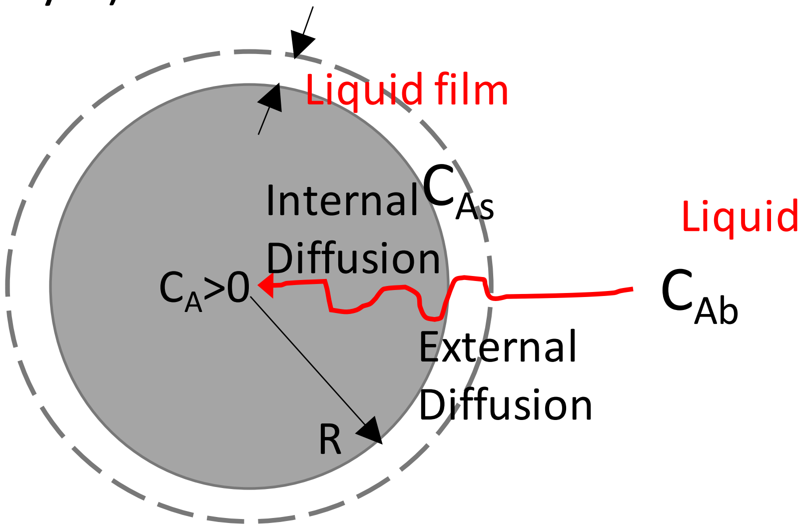
  - Increasing the effective diffusivity D_{Ae} (gel permeability and porosity increase)

  - Increasing the surface substrate concentration CAs

Minimizing external mass transfer effects

The rate of external mass transfer (across the external boundary layer)

$$N_A = k_S\, a\,(C_{Ab} - C_{As})$$



- Increasing the mass transfer coefficient k_S
  - By increasing the bulk liquid velocity

- Increasing the bulk substrate concentration C_{Ab}