Catalysis

Overall effectiveness factor

This lecture presents the effect of external mass transfer resistant, internal mass transfer resistant and surface reaction resistant. The overall effectiveness factor combines these resistances and provides insight of their effects on the catalyst activity.

Overall effectiveness factor, Ω, represents the ratio of actual overall rate of reaction to the rate of reaction if the entire surface is exposed to the bulk concentration of the reactant. It is different from the internal effectiveness factor, η as this is relates the actual rate to the rate if the surface is exposed to surface concentration, C_{As} but not C_{Ab}

Resistances affecting catalytic reaction

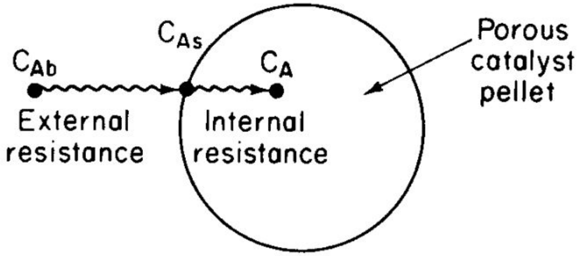
1. Mass transfer (diffusion) of the reactant(s) (e.g., species A) from the bulk fluid to the external surface of the catalyst pellet
2. Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface
3. Adsorption of reactant A onto the catalyst surface
4. Reaction on the surface of the catalyst (e.g., A B)
5. Desorption of the products (e.g., B) from the surface
6. Diffusion of the products from the interior of the pellet to the pore mouth at the external surface
7. Mass transfer of the products from the external pellet surface to the bulk fluid

The overall effectiveness factor Ω is written as:

$$\Omega = \frac{Actual\, rate\, of\, reaction}{Ideal\, rate\, if\, surface\, concentration\, is\, C_{Ab}}$$

Consider the reaction takes place according to the reaction

$$A \rightarrow B$$



Mass transfer and reaction steps.

The external flux of A to the surface is

$$N_A = k_c(C_{Ab} - C_{As})$$

Where k_c is the mass transfer coefficient, C_{Ab} is the bulk concentration of A and C_{As} is the surface concentration of A. The molar rate of external transport, W_A is

$$W_A = N_A a_c\, \Delta V$$

Where ΔV is the differential volume and a_c is the external surface area per volume

The net total reaction rate on and within the catalyst particle is

$$W_A = -r_A'' \times (external\ area + internal\ area)\ of\ the\ particle$$

$$W_A = -r_A''(a_c\,\Delta V + S_a\,\rho_b\,\Delta V)$$

Where S_a is the pore surface area per unit mass, ρ_b is the bulk density.

But internal surface area of the catalyst particle is much greater than its external surface area. Therefore,

$$S_a\rho_b \gg a_c$$

Then, $$W_A = -r_A''(S_a\rho_b\Delta V)$$

But $$-r_A'' = \eta\,k_s\,C_{As}$$

Where from internal effectiveness factor class we had $\eta = \frac{r''_{A-actual}}{k_s\,C_{As}}$

Combine the rate of external molar rate with that of reaction rate as

$$(All\ bulk\ external\ transport\ rate) = \eta\ (That\ gets\ reacted\ ideally\ )$$

$$k_c a_c\, \Delta V (C_{Ab} - C_{As}) = \eta\, S_a\, \rho_b\, \Delta V\, k_1\, C_{As}$$

Where k_1 is the actual rate constant. Rearranging the above relation to get

$$C_{As} = C_{Ab} \frac{k_c a_c}{k_c\, a_c + k_1 \eta\, S_a\, \rho_b}$$

The actual rate of reaction

$$-r_A'' = \eta\, k_1\ C_{As} = \frac{\eta\, k_1\, k_c\, a_c\, C_{Ab}}{k_c\, a_c\ +\ k_1 \eta\, S_a\, \rho_b}$$

However, the diffusion effect appears in the internal diffusion factor (internal effectiveness factor η as

$$\eta = \frac{3\, [\phi \coth \phi\ - 1]}{\phi^2}$$

Where the Thiele Module was

$$\phi^2 = \frac{k_1\, S_a\, \rho_b\, R\, C_{As}^n}{D_e\, (C_{As} - 0)/R}$$

But $-r''_{Ab} = k_1 C_{Ab}$ and $-r''_{A-actual} = k_1\, (-r''_{Ab})$

Therefore, $$-r''_{A-actual} = \frac{\eta\, k_c\, a_c}{k_c\, a_c + \eta k_1 S_a\, \rho_b}(-r''_{Ab})$$ or $$-r''_{A-actual} = \frac{\eta}{1+\frac{\eta k_1 S_a\, \rho_b}{k_c\, a_c}}(-r''_{Ab})$$

Then, the overall effectiveness factor Ω is:

$$\Omega = \frac{-r''_{A-actual}}{-r''_{Ab}} = \frac{\eta}{1+\frac{\eta k_1 S_a\, \rho_b}{k_c\, a_c}}$$

This equation indicates that the overall effectiveness factor Ω is always less than the internal effectiveness factor η due to the effect of external mass transport resistance.

Relation between Ω and η

$$\Omega \leq \eta$$

Special cases

- If $\Omega = \eta$ this indicates there is no resistance to external mass transport
- The internal effectiveness factor is $\eta \leq 1$ therefore, $\Omega \leq 1$

Estimation of Diffusion- and Reaction-Limited Regimes

The following criteria are used to determine the rate limited step(s) for the catalytic reactions

1. Weisz–Prater Criterion for Internal Diffusion

This Weisz–Prater Criterion is used to measure the observed rate of reaction to determine of the internal diffusion is the limiting step.

Recall the equation of internal effectiveness factor for first order reaction, for example,

$$\eta = \frac{3}{\phi_1^2}\left(\phi_1 \coth \phi_1 - 1\right)$$

Rearrange this equation

$$\eta \phi_1^2 = 3\left(\phi_1 \coth \phi_1 - 1\right)$$

$$\boxed{\eta\phi_1^2 = 3(\phi_1 \coth\phi_1 - 1)}$$

The left-hand side of the above equation is the Weisz–Prater parameter:

$$C_{WP} = \eta \times \phi_1^2 = \frac{\text{Observed (actual) reaction rate}}{\text{Reaction rate evaluated at } C_{As}} \times \frac{\text{Reaction rate evaluated at } C_{As}}{\text{A diffusion rate}} = \frac{\text{Actual reaction rate}}{\text{A diffusion rate}}$$

Recall that $\eta = \dfrac{-r'_A(\text{obs})}{-r'_{As}}$ and $\phi_1^2 = \dfrac{-r''_{As} S_a \rho_c R^2}{D_e C_{As}} = \dfrac{-r'_{As} \rho_c R^2}{D_e C_{As}}$

$$\Rightarrow \quad C_{WP} = \eta\phi_1^2 = \frac{-r'_A(\text{obs})\, \rho_c R^2}{D_e C_{As}}$$

Case (1): if $C_{WP} \ll 1$ $\Rightarrow$ there are no diffusion limitations and consequently no concentration gradient exists within the pellet

Case (2): if $C_{WP} \gg 1$ $\Rightarrow$ there is internal diffusion that limits the reaction severely

2. Mears' Criterion for External Diffusion

The Mears criterion uses the measured rate of reaction to learn if mass transfer from the bulk gas phase to the catalyst surface can be neglected. Mears proposed that when

$$\frac{-r'_A \rho_b R n}{k_c C_{Ab}} < 0.15$$

Then external mass transfer effects can be neglected

where n = reaction order
R = catalyst particle radius, m
ρ_b = bulk density of catalyst bed, kg/m^3
$= (1 - \phi)\rho_c \quad (\phi = \text{porosity})$
ρ_c = solid density of catalyst, kg/m^3
C_{Ab} = bulk reactant concentration, mol/dm^3
k_c = mass transfer coefficient, m/s

For non-isothermal system Mears also proposed that the bulk fluid temperature, T, will be virtually the same as the temperature at the external surface of the pellet when

$$\left|\frac{-\Delta H_{\mathrm{Rx}}(-r'_{\mathrm{A}})\,\rho_{\mathrm{b}}\,RE}{hT^{2}R_{\mathrm{g}}}\right| < 0.15$$

where h = heat transfer coefficient between gas and pellet, $\mathrm{kJ/m^2 \cdot s \cdot K}$
R_{g} = gas constant, 8.314 $\mathrm{J/mol \cdot K}$
ΔH_{Rx} = heat of reaction, kJ/mol
E = activation energy, kJ/kmol

Example: Estimating Thiele Modulus and Effectiveness Factor

The first-order reaction $A \longrightarrow B$ was carried out over two different-sized pellets. The results of two experimental runs made under identical conditions are as given in Table bellow.

1. Estimate the Thiele modulus and effectiveness factor for each pellet.
2. How small should the pellets be made to virtually eliminate all internal diffusion resistance?

TABLE E12-3.1 DATA FROM A SPINNING BASKET REACTOR†

	Measured Rate (obs) (mol/g cat · s) × 10^5	*Pellet Radius* (m)
Run 1	3.0	0.01
Run 2	15.0	0.001

Solution

$$\frac{-r'_A(\text{obs})R^2\rho_c}{D_e C_{As}} = \eta\phi_1^2 = 3(\phi_1 \coth\phi_1 - 1)$$

Letting the subscripts 1 and 2 refer to runs 1 and 2, we apply the equation above to runs 1 and 2 and then take the ratio to obtain

$$\frac{-r'_{A2}R_2^2}{-r'_{A1}R_1^2} = \frac{\phi_{12}\coth\phi_{12}-1}{\phi_{11}\coth\phi_{11}-1}$$

The Thiele modulus is

$$\phi_1 = R\sqrt{\frac{-r'_{As}\rho_c}{D_e C_{As}}}$$

Taking the ratio of the Thiele moduli for runs 1 and 2, we obtain

$$\boxed{\frac{\phi_{11}}{\phi_{12}} = \frac{R_1}{R_2}} \quad \Longrightarrow \quad \phi_{11} = \frac{R_1}{R_2}\phi_{12} = \frac{0.01\ \text{m}}{0.001\ \text{m}}\phi_{12} = 10\phi_{12}$$

Substituting for ϕ_{11} and evaluating $-r'_A$ and R for runs 1 and 2 gives us

$$\left(\frac{15\times10^{-5}}{3\times10^{-5}}\right)\frac{(0.001)^2}{(0.01)^2} = \frac{\phi_{12}\coth\phi_{12}-1}{10\phi_{12}\coth(10\phi_{12})-1} \quad \Longrightarrow \quad 0.05 = \frac{\phi_{12}\coth\phi_{12}-1}{10\phi_{12}\coth(10\phi_{12})-1}$$

Solving the obtained Equation yields $\phi_{12} = 1.65$ for $R_2 = 0.001$ m

Then $\phi_{11} = 10\phi_{12} = 16.5$ for $R_1 = 0.01$ m

The corresponding effectiveness factors are

$$\text{For } R_2: \quad \eta_2 = \frac{3(\phi_{12}\coth\phi_{12}-1)}{\phi_{12}^2} = \frac{3(1.65\coth 1.65-1)}{(1.65)^2} = 0.856$$

$$\text{For } R_1: \quad \eta_1 = \frac{3(16.5\coth 16.5-1)}{(16.5)^2} \approx \frac{3}{16.5} = 0.182$$

(b) Next we calculate the particle radius needed to virtually eliminate internal diffusion control (say, $\eta = 0.95$):

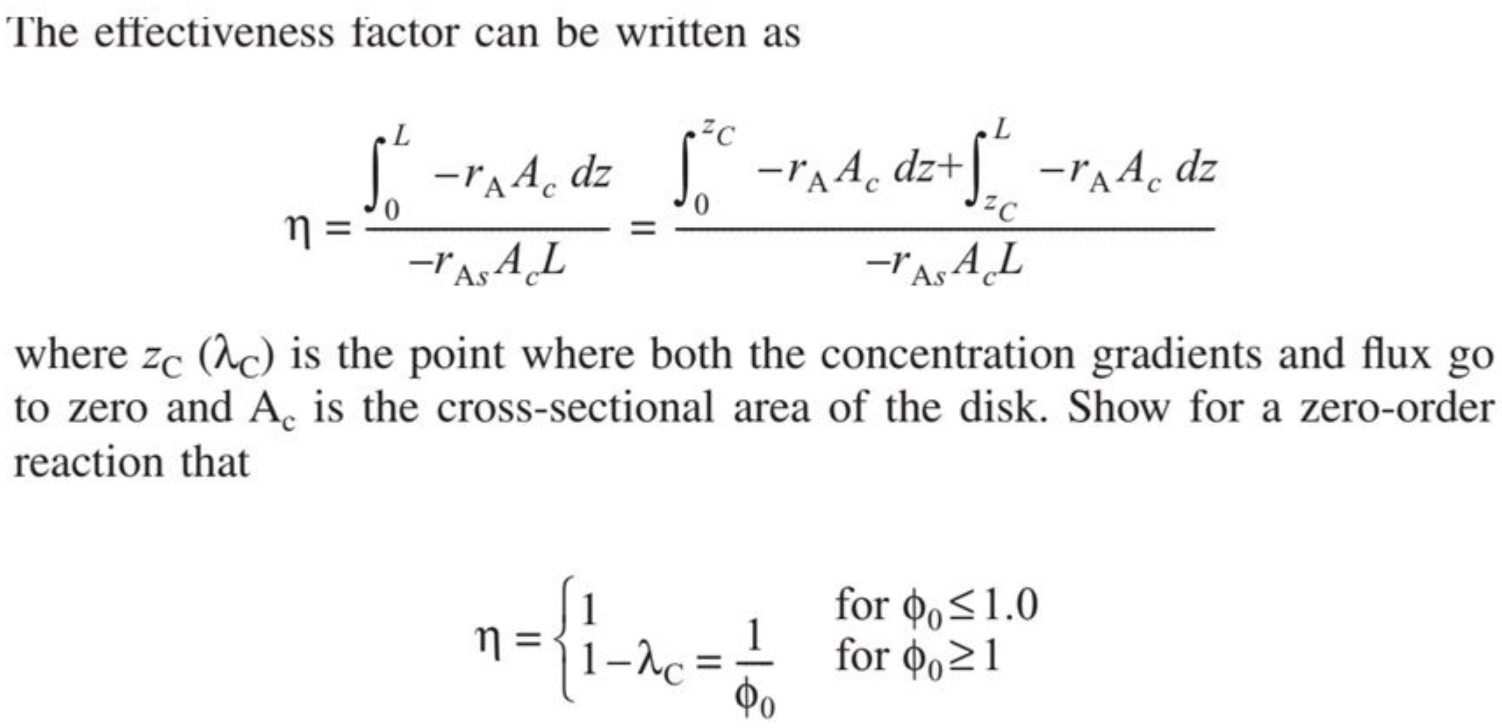
$$0.95 = \frac{3(\phi_{13} \coth \phi_{13} - 1)}{\phi_{13}^2}$$

Solution to the above Equation yields $\phi_{13} = 0.9$:

$$\boxed{R_3 = R_1 \frac{\phi_{13}}{\phi_{11}} = (0.01)\left(\frac{0.9}{16.5}\right) = 5.5 \times 10^{-4} \text{ m}}$$

A particle size of 0.55 mm is necessary to virtually eliminate diffusion control (i.e., $\eta = 0.95$).

Homework **(Due May 4, 2020)**



The effectiveness factor can be written as

$$\eta = \frac{\int_0^L -r_A A_c \, dz}{-r_{As} A_c L} = \frac{\int_0^{z_C} -r_A A_c \, dz + \int_{z_C}^{L} -r_A A_c \, dz}{-r_{As} A_c L}$$

where z_C (λ_C) is the point where both the concentration gradients and flux go to zero and A_c is the cross-sectional area of the disk. Show for a zero-order reaction that

$$\eta = \begin{cases} 1 & \text{for } \phi_0 \leq 1.0 \\ 1 - \lambda_C = \dfrac{1}{\phi_0} & \text{for } \phi_0 \geq 1 \end{cases}$$