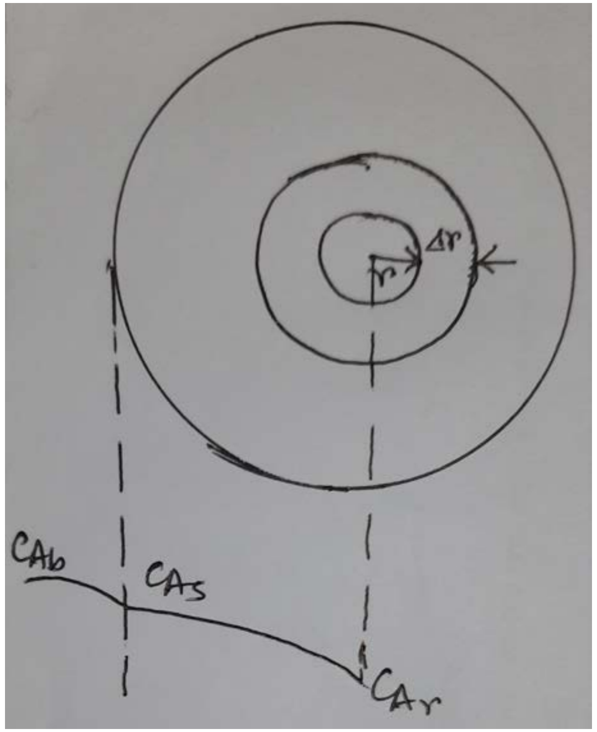
Pore diffusion in a spehericaL pellet: effectiveness factor

Let us take a spherical pellet or particle, where a differential shell of thickness Δr is considered. Pellet is assumed to be isothermal and has uniform properties. Porosity is also uniform.



Mole balance:

Output – input + disappearance= 0

$$-4\pi r^2 D_e\left(\frac{dC_A}{dr_r}\right)-\left(-4\pi r^2 D_e\left(\frac{dC_A}{dr_{r+\Delta r}}\right)\right)=4\pi r^2 \Delta r \rho_p k_1 C_A$$

Where, $k_1 C_A$= rate of the reaction w.r.t. unit mass of the catalyst, kmol/kg-cat.h

It is also assumed that effective diffusivity is independent of concentration. Dividing both sides by $4\pi \Delta r D_e$,

$$\frac{\frac{1}{r^2}}{\Delta r}\left[-r^2\left(\frac{dC_A}{dr_r}\right)+r^2\left(\frac{dC_A}{dr_{r+\Delta r}}\right)\right]=\frac{\rho_p k_1 C_A}{D_e}$$

Taking limit $\Delta r \longrightarrow 0$,

$$\frac{1}{r^2}\left[\frac{d}{dr}\left(r^2\frac{dc_A}{dr}\right)\right] = \frac{\rho_p k_1 C_A}{D_e}$$

Differentiating,

$$\frac{1}{r^2}\left[2r\frac{dC_A}{dr} + r^2\frac{d^2C_A}{dr^2}\right] = \frac{\rho_p k_1 C_A}{D_e}$$

$$\frac{d^2C_A}{dr^2} + \frac{2}{r}\frac{dC_A}{dr} - \frac{\rho_p k_1 C_A}{D_e} = 0$$

The boundary conditions are,

At $r = 0$, $\frac{dC_A}{dr} = 0$ and $r = R$, $C_A = C_{As}$

The differential equation can be solved and after integration, the solution of the equation is,

$$\frac{C_A}{C_{As}} = \frac{C_1}{r} Cosh\sqrt{\frac{\rho_p k_1}{D_e}}.r + \frac{C_2}{r} Sinh\sqrt{\frac{\rho_p k_1}{D_e}}.r,$$

Where C_1 and C_2 are integration constants, whose values can be determined by putting the boundary conditions.

$$C_1=0$$

And,

$$C_2 = \frac{R}{Sinh\sqrt{\frac{\rho_p k_1}{D_e}}.R}$$

Hence,

$$\frac{C_A}{C_{As}} = \frac{R}{r}\frac{Sinh(3\varphi_s \frac{r}{R})}{Sinh3\varphi_s}$$

Where $\varphi_s = \frac{R}{3}\sqrt{\frac{k_1\rho_p}{D_e}}$ This is Thiele Modulus for spherical pellet.

$$[\frac{C_A}{C_{As}} = \frac{C_2}{r} Sinh\sqrt{\frac{\rho_p k_1}{D_e}}.\, r = \frac{R}{r}\frac{Sinh\sqrt{\frac{\rho_p k_1}{D_e}}.\, r}{Sinh\sqrt{\frac{\rho_p k_1}{D_e}}.\, R} = \frac{R}{r}\frac{Sinh(3\varphi_s \frac{r}{R})}{Sinh3\varphi_s}]$$

DETERMINATION OF THE RATE FOR WHOLE PELLET (r_p)

At steady state,

Rate of diffusion= rate of reaction in the catalyst

Rate of diffusion per unit weight of catalyst= rate of reaction per unit weight of catalyst

Rate of diffusion per unit weight of catalyst

$$= \frac{4\pi R^2 D_e \left(\frac{dC_A}{dr_{[r=R]}}\right)}{w} = \frac{4\pi R^2 D_e \left(\frac{dC_A}{dr_{[r=R]}}\right)}{\frac{4}{3}\pi R^3 \rho_p} = \frac{3}{R\rho_p} D_e \left(\frac{dC_A}{dr_{[r=R]}}\right)$$

w=catalyst weight, ρ_p = density of catalyst particle

So, effectiveness factor is,

$$\eta = \frac{r_p}{r_o} = \frac{3D_e}{R\rho_p k_1 C_{As}}\left(\frac{dC_A}{dr_{[r=R]}}\right) = \frac{1}{\varphi_s}\left[\frac{1}{\tanh(3\varphi_s)} - \frac{1}{3\varphi_s}\right]$$

where, $k_1 C_{As}$= r_0= rate of the reaction on the surface of the pellet.

It is observed that, for a particular φ_s , the effectiveness factor η is greater in flat plate than for sphere, i.e., diffusion is more in flat plate than sphere, or in other way, diffusional resistance is less in flat plate than sphere. Hence, flat plate is better than spherical catalyst particle.

For flat plate geometry, Thiele modulus is

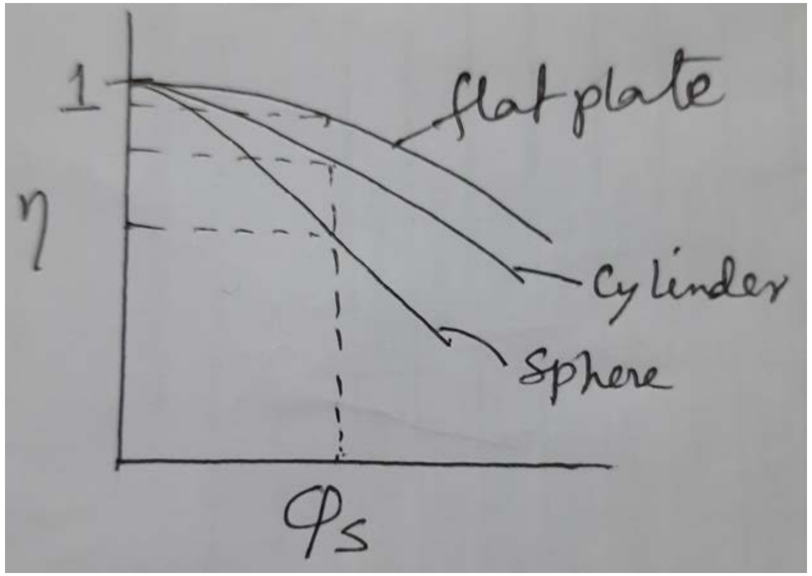
$$\varphi_L = L\sqrt{\frac{k}{D_e}} = L\sqrt{\frac{k\rho_p}{D_e}} \quad \text{for unit mass}$$

Then, effectiveness factor, $\eta = \frac{tanh\varphi_L}{\varphi_L}$

For spherical particle, Thiele modulus is,

$\varphi_S = \frac{R}{3}\sqrt{\frac{k_1\rho_p}{D_e}}$ and effectiveness factor is

$$\eta = \frac{1}{\varphi_S}\left[\frac{1}{\tanh(3\varphi_S)} - \frac{1}{3\varphi_S}\right]$$



For non-spherical particles, $R_{nonsp} = 3\frac{V_p}{S_p} = R,\ \ R$ is equivalent radius

R is the radius of the spherical pellet having the same volume as the non-spherical particle.

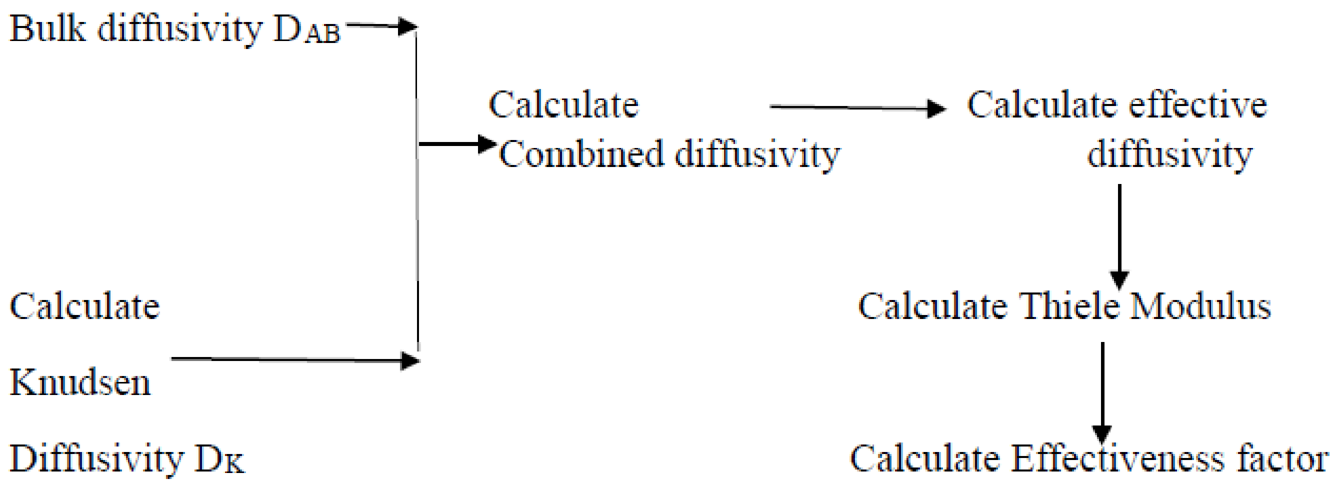
Using R, Thiele modulus and effectiveness factor can be calculated for non-spherical particles

In general, $\varphi = (characteristic\ length)\sqrt{\frac{k_1 \rho_p}{D_e}}$

When, η>0.9, pore diffusion can be neglected and for it, $\varphi < 1$

All the derivations are done assuming first order reaction.

Determination of effectiveness factor for pellet catalyst:-



Physical Significance of Thiele Modulus

The expression of Thiele Modulus is,

$$\varphi = \frac{R}{3}\sqrt{\frac{k_1 \rho_p}{D_e}}$$

Thiele Modulus is directly proportional to reaction rate constant k_1 and inversely proportional to diffusivity D_e. Hence, it can be said that φ gives a measure of the extent of reaction to the extent of diffusion, $\frac{k_1}{D_e}$.

When diffusion is more, the value of D_e is high, and reaction is kinetically controlled. But, when rate of reaction is more than diffusion, k_1 is high, and the reaction is diffusion controlled.

Moreover, φ is also directly dependent on characteristic length of pellet/pore.

DETERMINATION OF EFFECTIVENESS FACTOR FOR REVERSIBLE FIRST ORDER REACTION:

Considering a reversible reaction, $A \rightleftharpoons B$,

Let, $k_1\ and\ k_2$ are the forward and reverse rate constants respectively.

The rate expression is $-\frac{dC_A}{dt} = k_1C_A - k_2C_B$-------(1)

C_B can be expressed in terms of C_A by mass balance. At constant volume, since moles are constant, C_B is equal to the initial concentration value of B, i.e., C_{B_0} and the amount of A which is converted to B.

$\therefore C_B = C_{B_0} + (C_{A_0} - C_A)$---(2)

Putting the value of C_B in eq (1),

$$-\frac{dC_A}{dt} = k_1 C_A - k_2(C_{B_0} + C_{A_0} - C_A)$$

$$= C_A(k_1 + k_2) - k_2(C_{B_0} + C_{A_0}) \text{-----}(3)$$

At equilibrium, forward rate = reverse rate

$$\therefore k_1 C_{A_{eq}} = k_2 C_{B_{eq}}$$

$$\frac{C_{B_{eq}}}{C_{A_{eq}}} = \frac{k_1}{k_2} = K = equlibrium\ constant$$

$$k_2 = \frac{k_1}{K}$$

Putting the value of k_2 in eq (3),

$$-\frac{dC_A}{dt} = k_1 C_A + \frac{k_1}{K} C_A - \frac{k_1}{K} C_{B_0} - \frac{k_1}{K} C_{A_0}$$

$$= k_1 \left[\frac{K+1}{K} C_A - \frac{1}{K}(C_{A_0} + C_{B_0})\right] \text{------}(4)$$

Now, $K = \frac{C_{B_{eq}}}{C_{A_{eq}}} = \frac{C_{B_0} + C_{A_0} - C_{A_{eq}}}{C_{A_{eq}}}$ (from eq (2))

or, $\frac{C_{B_0} + C_{A_0}}{C_{A_{eq}}} - 1 = K$

or, $(C_{B_0} + C_{A_0}) = C_{A_{eq}}(K+1)$-----(5)

The value of $C_{B_0} + C_{A_0}$ is put in eq (4) and we get,

$$-\frac{dC_A}{dt} = k_1\left[\frac{K+1}{K}C_A - \frac{1}{K}.C_{A_{eq}}(K+1)\right]$$

$$= \frac{K+1}{K}.k_1(C_A - C_{A_{eq}})$$

$$= K_R C_A'$$

Where, $K_R = \frac{K+1}{K}.k_1$ and C_A'= $(C_A - C_{A_{eq}})$

Hence, the mass balance of reactant for spherical pellet catalyst and for reversible 1st order reaction is,

$$-4\pi r^2 D_e\left(\frac{dC'_A}{dr_r}\right)-\left(-4\pi r^2 D_e\left(\frac{dC'_A}{dr_{r+\Delta r}}\right)\right)=4\pi r^2\Delta r\rho_p k_1 C'_A$$

Taking limit $\Delta r \longrightarrow 0$,

$$\frac{d^2C'_A}{dr^2}+\frac{2}{r}\frac{dC'_A}{dr}-\frac{\rho_p k_1 C'_A}{D_e}=0$$

Boundary conditions are $\frac{dC'_A}{dr}$=0 at r=0 and C'_A= C'_{As} at r= r_s

Therefore, Thiele Modulus for reversible reaction and spherical pellet can be written as,

$$\varphi'_s=\frac{R}{3}\sqrt{\frac{k_1(K+1)\rho_p}{K.D_e}}$$

As $\frac{K+1}{K}$ is greater than unity, hence, φ'_s is greater than Thiele Modulus of irreversible reaction φ_s and effectiveness factor of the later is more than the former.