Internal Transport Processes – Reaction and Diffusion in Porous Catalysts

Diffusion and Reaction in catalyst pores

An expression is developed for the **rate of reaction for the whole catalyst pellet, r_p** in terms of temperature and concentrations *at the outer surface*

For this, a term known as ***effectiveness factor*** $(\boldsymbol{\eta})$ is defined

$$\boldsymbol{\eta} = \frac{\textbf{actual reaction rate for the whole pellet}}{\textbf{reaction rate evaluated at outer surface conditions}} = \frac{r_p}{r_s}$$

$$r_p = \eta r_s = \eta r_s(C_s, T_s)$$

Unit of rate, r_p is $\left[\dfrac{\text{mols reacted}}{\text{mass of catalyst.time}}\right]$

For isothermal reactions, $r_p = \eta r_s(C_s)$

Evaluation of Effectiveness Factor (η)

- Let us consider an irreversible reaction, $A \rightarrow B$ of the nth order being catalyzed by a spherical pellet of radius R

- In order to evaluate η in terms of D_e and k, it is necessary to determine the concentration profile of reactant A in the pellet

- Mass balance over the spherical volume of thickness Δr gives,

$$\left(-4\pi r^2 D_{e,A} \frac{dC_A}{dr}\right)_r - \left(-4\pi r^2 D_{e,A} \frac{dC_A}{dr}\right)_{r+\Delta r} - (4\pi r^2 \Delta r)\rho_p r_s = 0$$

$$\left[\text{We know that, } \left.\frac{dC_A}{dr}\right|_{r+\Delta r} = \left.\frac{dC_A}{dr}\right|_r + \frac{d}{dr}\left(\frac{dC_A}{dr}\right)\Delta r\right]$$

Dividing the mass balance equation by $4\pi\Delta r$ and taking limits of $\Delta r \rightarrow 0$, we have,

$$\frac{d}{dr}\left(r^2 D_{e.A} \frac{dC_A}{dr}\right) - r^2 \rho_p r_s = 0$$
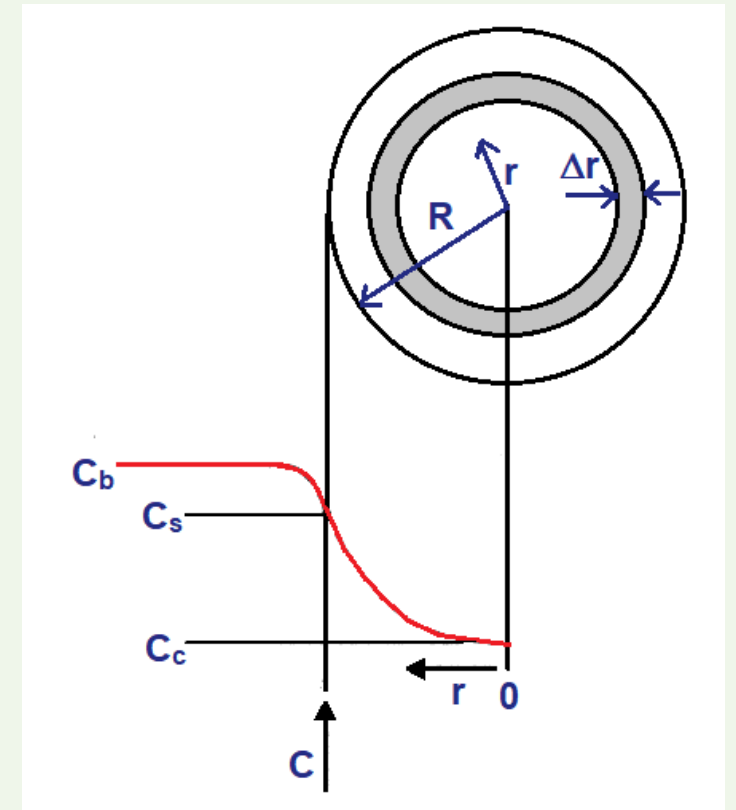
If $D_{e.A}$ is not a function of r and $r_s = kC_A^n$

$$r^2 D_{e.A} \frac{d^2 C_A}{dr^2} + D_{e.A}(2r)\frac{dC_A}{dr} - r^2 \rho_p k C_A^n = 0$$

$$\boxed{\frac{d^2 C_A}{dr^2} + \frac{2}{r}\frac{dC_A}{dr} - \frac{\rho_p k}{D_{e.A}}C_A^n = 0}$$

Boundary conditions for the differential equation is: At $r = R$, $C_A = C_{AS}$ and

At $r = 0$, $\frac{dC_A}{dr} = 0$ or C_A is finite

The above equation can be solved to give the concentration profile

$$\boxed{\frac{C_A}{C_{AS}} = \frac{R}{r}\frac{sinh(3\phi_s{}^r/_R)}{sinh 3\phi_s}}$$

where $\boxed{\phi_s = \frac{R}{3}\sqrt{\frac{k\rho_p C_{As}^{n-1}}{D_{e.A}}}}$ ϕ_s is called the **Thiele modulus**

For a first order reaction, $n = 1$ and Thiele modulus becomes $\phi_s = \frac{R}{3}\sqrt{\frac{k\rho_p}{D_{e.A}}}$ ϕ_s is dimensionless

RHS: $m \times \left(\frac{m^3}{kg.s} \times \frac{kg}{m^3} \times \frac{s}{m^2}\right)^{1/2}$

Significance of Thiele modulus

$$\phi_s = \frac{R}{3}\sqrt{\frac{k\rho_p C_{As}^{n-1}}{D_{e.A}}}$$

$$\phi_s^2 = \frac{R^2}{9} \cdot k\rho_p \cdot \frac{C_{As}^{n-1}}{D_{e.A}} = \frac{R^2}{9} \cdot \frac{k\rho_p C_{As}^n}{D_{e.A}C_{As}} \cdot \frac{\frac{4}{3}\pi R^3}{\frac{4}{3}\pi R^3} = \frac{\left(\frac{4}{3}\pi R^3\right)\rho_p \times kC_{As}^n}{D_{e.A}(4\pi R^2)\frac{(C_{As}-0)}{R/3}}$$

$$\boxed{\phi_s^2 = \frac{\text{chemical reaction rate}}{\text{intraphase diffusion rate}}}$$

- **Small values of ϕ_s** indicate a reaction that is **surface reaction controlled** - concentration nearly uniform throughout the pellet

- **Large values of ϕ_s** indicate a **reaction that is fast** – the reactant is consumed very close to external pellet surface and very little penetrates inside

Concentration profile in a spherical catalyst pellet
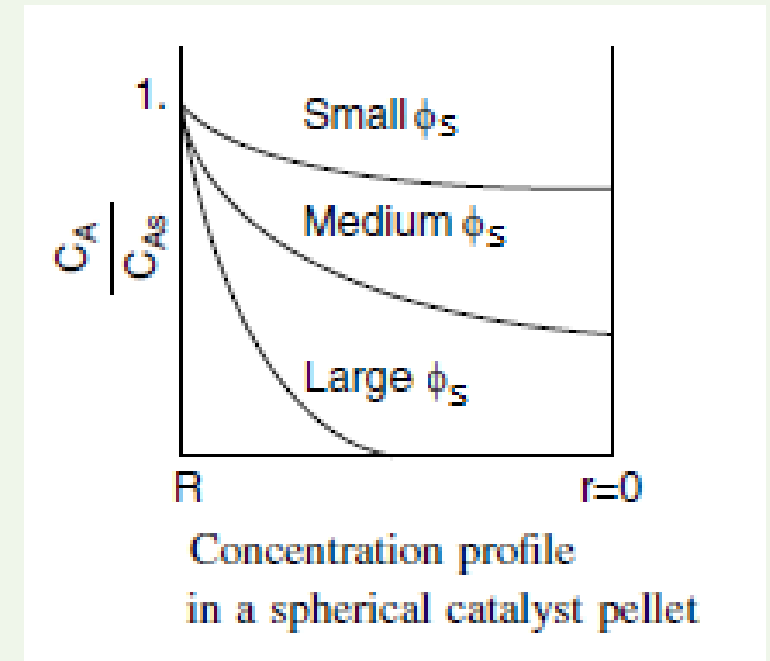
The concentration profile is now used to evaluate effectiveness factor (η)

At steady state,

$$Overall\ rate\ of\ reaction = Rate\ of\ diffusion\ into\ the\ pellet$$

$$\int_0^R \left(4\pi r^2 \rho_p k C_{As}\right)dr = 4\pi R^2\ D_{e.A}\left(\frac{dC_A}{dr}\right)_{r=R}$$

For a first order reaction

The rate of reaction (per pellet) in the absence of pore-diffusional limitations (i.e., when the whole pellet is at the concentration of C_{As}) is given by,

$$Rate = \frac{4}{3}\pi R^3 \rho_p k C_{As}$$

Then the expression for η is,

$$\eta_{sph} = \frac{4\pi R^2\ D_{e.A}\left(\frac{dC_A}{dr}\right)_{r=R}}{\frac{4}{3}\pi R^3 \rho_p k C_{As}}$$

Differentiating the concentration profile and evaluating the derivative at $r = R$ and substituting gives,

$$\eta_{sph} = \frac{1}{\phi_s}\left[\frac{1}{tanh3\phi_s} - \frac{1}{3\phi_s}\right]$$

Using the value of $\eta_{sph} = \frac{1}{\phi_s}\left[\frac{1}{tanh3\phi_s} - \frac{1}{3\phi_s}\right]$ to find the rate of the reaction in the pellet we get,

$$r_p = \frac{1}{\phi_s}\left[\frac{1}{tanh3\phi_s} - \frac{1}{3\phi_s}\right]kC_{As}$$

- From the above equation for estimating η_{sph} , we can see that **for small ϕ_s (ϕ_s < 0.3), $\boldsymbol{\eta_{sph} \approx 1.0}$**

- The intraparticle mass transfer has no effect on the rate of the pellet, the **rate is controlled by the chemical reaction step**

- Since, $\phi_s = \frac{R}{3}\sqrt{\frac{k\rho_p}{D_{e.A}}}$, **small values of $\boldsymbol{\phi_s}$** are obtained when the **pellets are small** (small R) , **diffusivity** ($D_{e.A}$) **is large** or **reaction is intrinsically slow** (small k)

- For **large $\boldsymbol{\phi_s}$ values ($\boldsymbol{\phi_s}$ > 5), $\boldsymbol{\eta_{sph} = \frac{1}{\phi_s}}$**

- For **large $\boldsymbol{\phi_s}$** , **intraparticle diffusion** has a **large effect on the rate**. The diffusion into the pellet is relatively slow, so reaction occurs before the reactant has diffused far into the pellet

- A low η implies that only part of the catalyst interior is utilized

- **Large $\boldsymbol{\phi_s}$ values** are obtained with **large pellets** (large R) , **low diffusivity** ($D_{e.A}$) and **large reaction rate constant** (high k)

η versus ϕ_s plot for $nth\ order$ kinetics in spherical catalyst
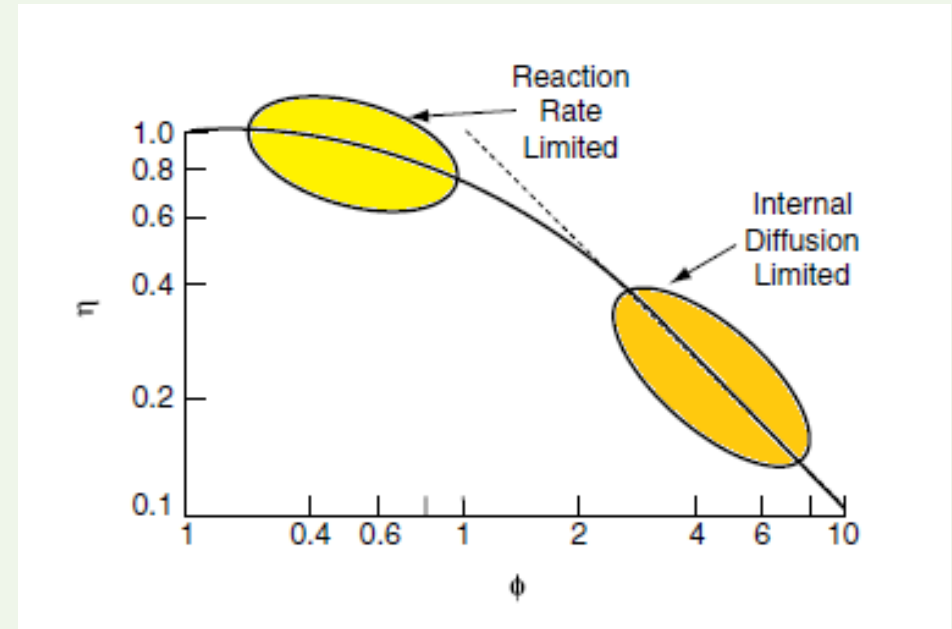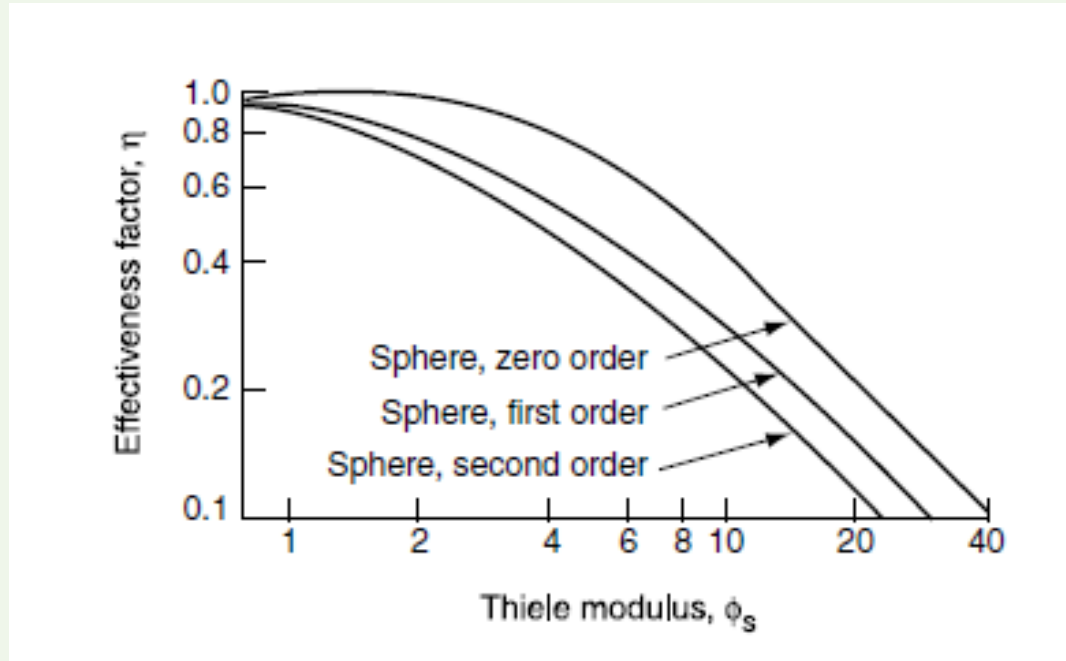
Zero order $\quad \phi_s = \dfrac{R}{3}\sqrt{\dfrac{k\rho_p}{D_{e.A}C_{Ao}}}$

First order $\quad \phi_s = \dfrac{R}{3}\sqrt{\dfrac{k\rho_p}{D_{e.A}}}$

Second order $\phi_s = \dfrac{R}{3}\sqrt{\dfrac{k\rho_p C_{Ao}}{D_{e.A}}}$

For low values of ϕ_s, η is large and diffusional limitations are not important – it is a reaction rate limited condition

For high values of ϕ_s, η is small and intraparticle diffusion in the pellet is slow and important – it is a internal diffusion limited condition

For isothermal pellets, η is always < 1

- The <u>equation derived</u> so far for η is for a <u>spherical pellet</u> and for a <u>first order irreversible reaction</u>

- It is possible to derive expressions for first order reaction using other pellet geometries such a s flat plate and infinite cylinder

- For a **flat plate**, with length and breadth much greater than the thickness, it can be shown that

$$\eta_{fp} = \frac{tanh\phi_{fp}}{\phi_{fp}}$$ where $$\phi_{fp} = L\sqrt{\frac{k\rho_p}{D_{e.A}}}$$ and L = half thickness of flat plate

- For an **infinite cylinder** $\left(\frac{L}{R} \gg 1\right)$, it can be shown that $$\eta_{cyl} = \frac{1}{\phi_{cyl}}\frac{I_1(\phi_{cyl})}{I_0(\phi_{cyl})}$$

where $$\phi_{cyl} = \frac{R}{2}\sqrt{\frac{k\rho_p}{D_{e.A}}}$$ and R = radius of cylindrical pellet of infinite length

I_1, I_0 = modified Bessel functions

- The expressions for ϕ for all three different geometries show that for each case **the square root term** ($\sqrt{\frac{k\rho_p}{D_{e.A}}}$) **is multiplied by the characteristic dimension of the pellet**

- For **flat plate, infinite cylinder and sphere**, these are L, $\frac{R}{2}$ and $\frac{R}{3}$, respectively

- The η versus ϕ values for all three geometries is plotted in the same graph

- The curves for all three geometries are seen to superimpose

- For all three cases, the characteristic dimension is equal to V_p/S_x where V_p is the volume of the pellet and S_x is the external area of the pellet

- The generalized expression for ϕ **for nth order reaction** is

$$\phi = \frac{V_p}{S_x}\sqrt{\frac{k\rho_p C_{As}^{n-1}}{D_{e.A}}}$$

This equation can be used for catalysts of irregular geometries such as extrudates, oblates, finite cylinders
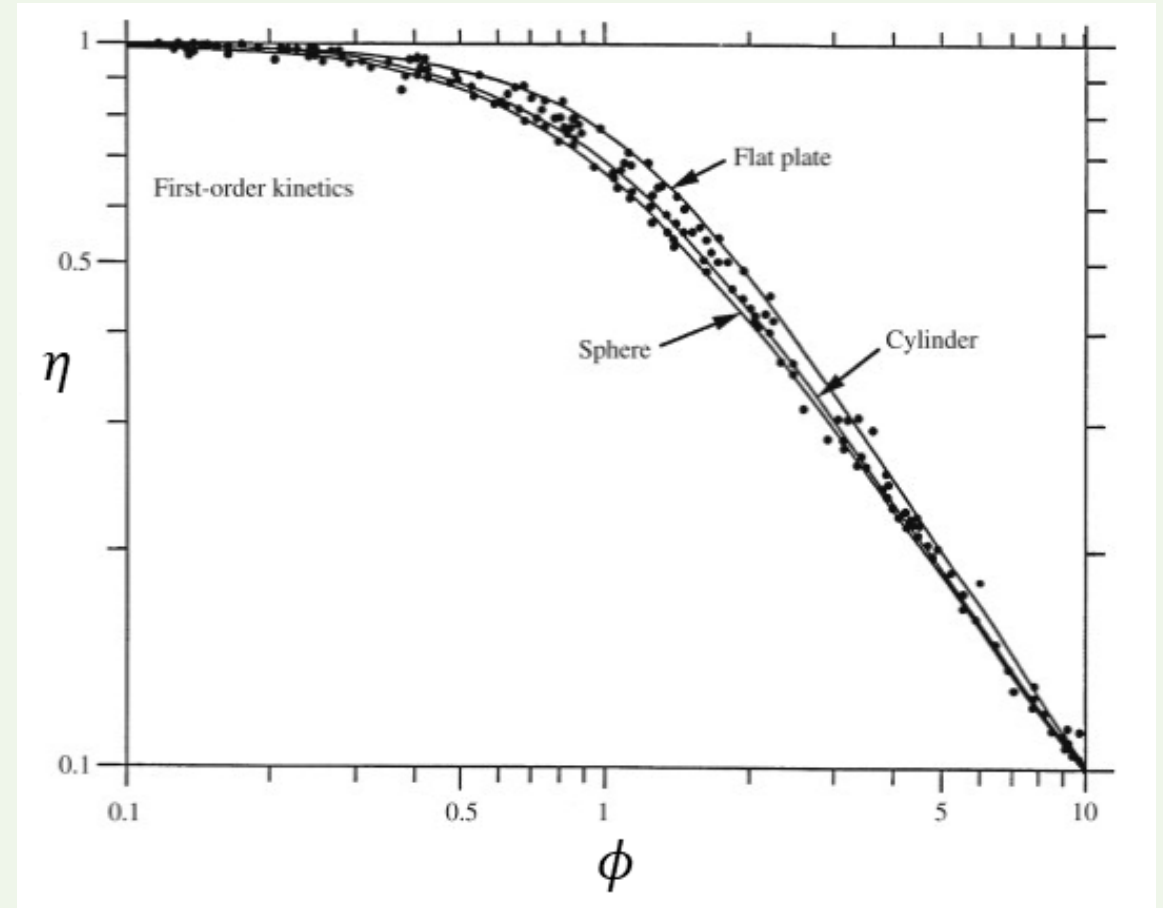

First-order kinetics

Flat plate

Sphere

Cylinder

For a first order reversible reaction $A \rightleftharpoons B$,

$$\phi_s = \frac{R}{3}\sqrt{\frac{k\rho_p(K+1)}{KD_{e.A}}}$$

where K = equilibrium constant

$$r = k_R(C_A - C_{A,eq})$$
$$k_R = \frac{k(K+1)}{K}$$

Example

The isomerization of 1-hexane to form 2- hexane was studied in a laboratory reactor using Rh/Al_2O_3 catalyst at 150°C and 1 atm. The reaction was found to be first order in 1-hexane with a rate constant of $0.14\ s^{-1}$. Find the largest pellet size that can be used in an industrial reactor to achieve 70% of the maximum rate.

The pore radius of Al_2O_3 is 10 nm and D_{AB} is 0.050 cm²/s. Particle porosity can be assumed to be 0.5 and tortuosity as 4

It is necessary to find the particle size that will have η = 0.70

The geometry of the pellet has not been given in the problem. However, we can use the expression for any geometry to determine ϕ knowing η, since it has been seen that the plots of η versus ϕ for different geometries coincide

If the particle is assumed to be spherical,
$$\eta_{sph} = \frac{1}{\phi_s}\left[\frac{1}{tanh3\phi_s} - \frac{1}{3\phi_s}\right]$$

$$0.7 = \frac{1}{\phi_s}\left[\frac{1}{tanh3\phi_s} - \frac{1}{3\phi_s}\right]$$

A trial and error method was used to find the value of ϕ that will give η = 0.7 and the value was found to be 0.925

$$0.7 = \frac{1}{0.925}\left[\frac{1}{tanh(3 \times 0.925)} - \frac{1}{(3 \times 0.925)}\right] = 0.6999$$

In order to find the pellet size or R, we use the expression $\quad \phi_s = \dfrac{R}{3}\sqrt{\dfrac{k\rho_p}{D_{e.A}}}$ where $\phi_s, k\rho_p$ values are known. The unknown $D_{e.A}$, has to be calculated before finding R

Estimation of $D_{e.A}$

D_{AB} = 0.05 cm²/s

Molecular weight (M) of 1-hexane = 84

$$D_K\left(cm^2/s\right) = 9.7 \times 10^3 r \sqrt{\dfrac{T}{M}} = 9.7 \times 10^3 \times (10 \times 10^{-7})\sqrt{\dfrac{423}{84}} = 0.02176 \ cm^2/s$$

Now, $\quad D = \dfrac{1}{\dfrac{1}{D_{AB}}+\dfrac{1}{D_K}} \quad \Rightarrow \quad D = \dfrac{1}{\dfrac{1}{0.05}+\dfrac{1}{0.02176}} \quad \Rightarrow \quad D = 0.01516 \ cm^2/s$

Using the parallel pore model, $D_e = \dfrac{\varepsilon_p D}{\tau} \quad \Rightarrow D_e = \dfrac{0.5\times0.01516}{4} \Rightarrow D_e = 0.001895 \ cm^2/s$

$R = 3\phi_s\sqrt{\dfrac{D_{e.A}}{k}} = 3 \times 0.925\sqrt{\dfrac{0.001895}{0.14}} = 0.32285 \ cm$

The units of given k is s⁻¹ , in order to keep the units consistent, the term inside the

Therefore, spherical particles with diameter = $0.646 \ cm$ will have $\eta = 0.70$

square root is taken as $\sqrt{\dfrac{k}{D_{e.A}}}$ and

not $\sqrt{\dfrac{k\rho_p}{D_{e.A}}}$

Significance of intrapellet diffusion

- For reactor design, it is important to know whether intrapellet diffusion resistance should be considered while evaluating the reaction rate, r_p

- The basic premise made in evaluating the criterion is that if $\phi_s \leq \frac{1}{3}$, the effectiveness factor (η) is not much less than unity ($\eta > 0.9$ for $\phi_s \leq \frac{1}{3}$)

- For first order reactions, $\phi_s = \frac{R}{3}\sqrt{\frac{k\rho_p}{D_{e.A}}} \leq \frac{1}{3}$

$$R\sqrt{\frac{k\rho_p}{D_{e.A}}} \leq 1$$

$$\frac{R^2 k\rho_p}{D_{e,A}} \leq 1$$

Since $\eta \approx 1$, $r_p = \eta k C_s = k C_s$

$$\boxed{W = \frac{R^2 r_p \rho_p}{C_s\ D_{e,A}} \leq 1}$$

This is called the **Weisz Prater criterion**

$\boxed{\textbf{If this criterion holds true, internal diffusion resistance can be neglected}}$

Although this criterion has been derived for a first order reaction, graphs for higher order reactions (for $\phi_s \leq \frac{1}{3}$) are nearly coincidental, and hence this form of the expression can be used for most catalytic reactions