

## SIGNIFICANCE OF INTRAPELLET DIFFUSION: EVALUATION OF EFFECTIVENESS FACTOR

Isothermal effectiveness factor for practical reaction covers a wide range.

With normal pellet sizes ( $\frac{1}{8}$  to  $\frac{1}{2}$  inch),  $\eta$  is 0.7 to 1 for intrinsically slow reactions. For fast reactions,  $\eta \approx 0.1$ . Hence, for the case of intrapellet diffusion,  $\eta$  can be evaluated for different reactions, temperatures and pellet sizes.

Should we consider intrapellet diffusion for evaluating global rate i.e., whether  $\eta$  is significantly less than unity?

Suppose that, the rate  $r_p$  is measured at a given bulk concentration of reactant.

Also suppose that, either the external resistance to mass transfer is negligible i.e.,  $C_{Ab} = C_s$  or the surface concentration can be evaluated from the bulk value.

Weitz has provided a criterion for deciding from these measurements and  $D_e$ , whether intrapellet diffusion resistance can be disregarded.

It is seen that, if  $\varphi_s \leq \frac{1}{3}$  then  $\eta$  is not much less than unity.

So, the criterion can be written as,

$$r_s \sqrt{\frac{k_1 \rho_p}{D_e}} \leq 1 \quad \text{or} \quad r_s^2 \frac{k_1 \rho_p}{D_e} \leq 1 \quad \text{where, } r_s \text{ is the radius of the catalyst particle}$$

The unknown rate constant  $k_1$  can be eliminated by measuring the rate  $r_p$ , when  $\eta \rightarrow 1$ . Then the rate equation becomes,

$$r_s^2 \frac{r_p \rho_p}{C_s D_e} \leq 1, \text{ considering 1}^{\text{st}} \text{ order reaction}$$

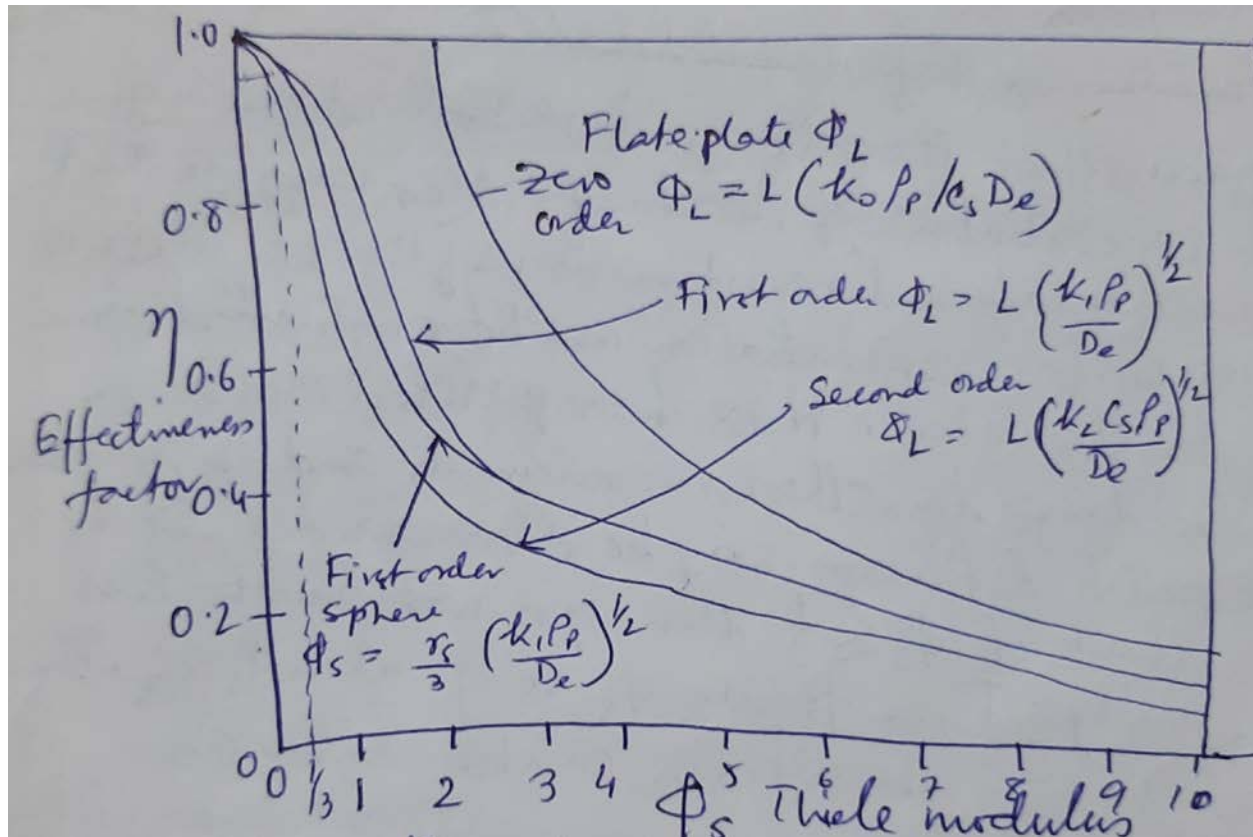
And  $C_{wp} = r_s^2 \frac{r_p \rho_p}{C_s D_e}$  = Weitz-Prater criterion

Therefore if  $C_{wp} \leq 1$ , then the reaction is not internal diffusion controlled.

And when  $C_{wp} \geq 1$ , then the reaction is influenced by intrapellet diffusion.

$$\begin{aligned} C_{wp} = \eta \times \varphi^2 &= \frac{\text{Observed (actual) reaction rate}}{\text{reaction rate evaluated at } C_s} \times \frac{\text{reaction rate evaluated at } C_s}{\text{diffusion rate}} \\ &= \frac{\text{Observed (actual) reaction rate}}{\text{diffusion rate}} \end{aligned}$$

Plot of  $\varphi_s$  vs.  $\eta$  shows that the curves of first or and higher order reactions are nearly co-incident at  $\varphi_s \leq \frac{1}{3}$ .



Hence, the usefulness of the Weitz-Prater criterion is that, it becomes satisfactory as an approximate criterion for most solid catalytic reaction kinetics, even though it is derived for a first order case.

Problem.

Dehydrogenation of butane at atmospheric pressure using a chromia-alumina catalyst at 530°C is done with catalyst size,  $d_p=0.32$  cm. The experimental data suggests a first order reaction rate constant of 0.94 cm<sup>3</sup>/s.g of cat. The pore radius of the catalyst is given as 110 Å. Assuming Knudsen diffusivity at this low pressure and estimating the pore volume as 0.35 cm<sup>3</sup>/g, predict the effectiveness factor for the catalyst. Use parallel pore model with a tortuosity factor 3.0.

Given, Particle diameter  $d_p=0.32$  cm,  $\therefore R=0.16$  cm

$T=(530+273)$  K= 803 K, Butane ( $C_4H_{10}$ ) molecular weight  $M=58$

Pore volume( $v_g$ )= 0.35 cm<sup>3</sup>/g, tortuosity  $\tau = 3.0$ ,  $k_1=0.94$  cm<sup>3</sup>/s.g of cat

Pore radius  $a= 110$  Å=  $110 \times 10^{-8}$  cm

$$\begin{aligned}\text{Knudsen diffusivity } D_K &= 9.7 \times 10^3 \times (110 \times 10^{-8}) \times \left(\frac{803}{58}\right)^{\frac{1}{2}} \\ &= 0.01067 \times 3.72 = 0.0392 \text{ cm}^2/\text{s}\end{aligned}$$

Now, Combined diffusivity

$$D = \frac{1}{\frac{1}{D_{AB}} + \frac{1}{D_K}}$$

Here,  $D_{AB}$  is not considered, hence,  $D = D_K$ .

The effective diffusivity,

$$D_e = \frac{\varphi_p D}{\tau}, \quad \text{where, } \varphi_p \text{ is pellet porosity}$$

$$\varphi_p = \rho_p v_g = \rho_p \times 0.35, \quad \rho_p = \text{pellet density}$$

$$\text{Thiele Modulus, } \varphi_s = \frac{R}{3} \sqrt{\frac{k_1 \rho_p}{D_e}} = \frac{R}{3} \sqrt{\frac{k_1 \rho_p \tau}{D \varphi_p}} = \frac{R}{3} \sqrt{\frac{k_1 \rho_p \tau}{D \rho_p \times 0.35}} = \frac{R}{3} \sqrt{\frac{k_1 \tau}{D \times 0.35}}$$

$$\text{Hence, } \varphi_s = \frac{0.16}{3} \sqrt{\frac{0.94 \times 3}{0.35 \times 0.0397}} = 0.0533 \sqrt{202.9} = 0.7593$$

$$\begin{aligned} \text{Now, effectiveness factor, } \eta &= \frac{1}{\varphi_s} \left[ \frac{1}{\tanh(3\varphi_s)} - \frac{1}{3\varphi_s} \right] \\ &= \frac{1}{0.7593} \left[ \frac{1}{\tanh(3 \times 0.7593)} - \frac{1}{3 \times 0.7593} \right] \\ &= \frac{1}{0.7593} [1.043 - 0.4578] \\ &= 0.77 \end{aligned}$$

Therefore, the effectiveness factor for the reaction is 0.77.

# MASS AND HEAT TRANSFER WITH REACTION

When a reaction takes place, heat of reaction makes a difference in temperature between the surface of the catalyst and the core.

The rate of the reaction in a catalyst pellet is largely dependent on this temperature gradient.

The combined effect of mass and heat transfer can be expressed by the effectiveness factor,

$$\eta = \frac{\text{Actual rate of reaction in the catalyst pellet}}{\text{Rate at the surface of the pellet}}$$
$$= \frac{r_p}{r_s}$$

$r_p = \eta \times r_s = \eta f(T_s, C_s)$  For heat transfer taken into consideration,  $\eta$  is called non-isothermal effectiveness factor.



# NON-ISOTHERMAL EFFECTIVENESS FACTOR

$C_b$  = Concentration at the bulk

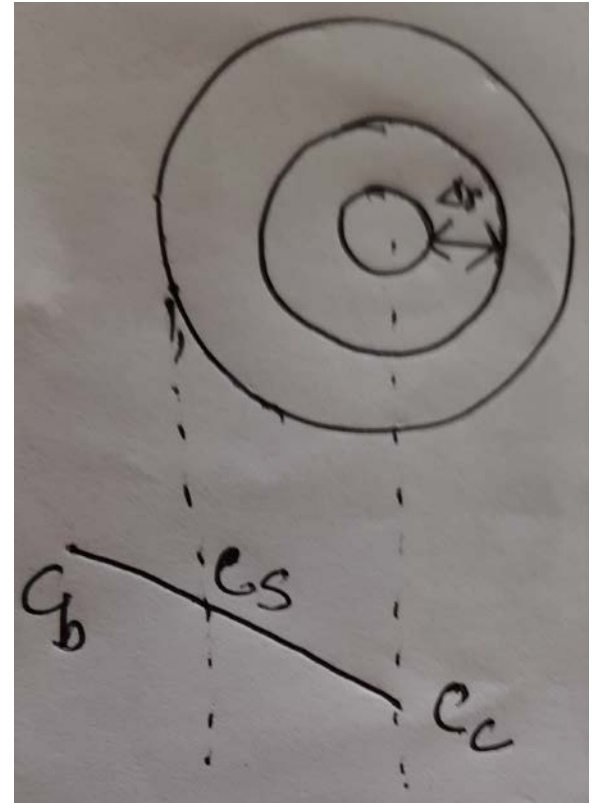
$C_s$  = Concentration at the surface

$C_c$  = Concentration at the core

$\Delta r$  = Thickness of a differential volume

For isothermal effectiveness factor, where heat effect is neglected, only mass transfer is considered, the mole balance is written as,

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



After differentiating, the equation can be transformed into,

$$\frac{d^2 C_A}{dr^2} + \frac{2}{r} \frac{dC_A}{dr} - \frac{\rho_p k_1 C_A}{D_e} = 0 \text{----(1)}$$

Similarly for heat transfer, the energy balance can be written as,

$$-4\pi r^2 K_e \left( \frac{dT}{dr_r} \right) - \left( -4\pi r^2 K_e \left( \frac{dT}{dr_{r+\Delta r}} \right) \right) = 4\pi r^2 \Delta r \rho_p k_1 C \Delta H$$

Where,  $K_e$  = effective thermal diffusivity

$\Delta H$  = Heat of reaction

Taking limit  $\Delta r \rightarrow 0$ ,  $K_e$  is independent of temperature and dividing both sides by  $4\pi\Delta r K_e$ ,

$$\frac{d^2T}{dr^2} + \frac{2}{r} \frac{dT}{dr} - \frac{\rho_p k_1 C}{K_e} \Delta H = 0 \text{ ----(2)}$$

With boundary conditions,

$\frac{dT}{dr} = 0$  at  $r = 0$  i.e. there is no change in temperature at the centre

And,  $T = T_s$  at  $r = r_s$

Again, comparing eq (2) with similar equation of mass transfer (eq 1) and equating both sides,

$$D_e \left( \frac{d^2C}{dr^2} + \frac{2}{r} \frac{dC}{dr} \right) = \frac{K_e}{\Delta H} \left( \frac{d^2T}{dr^2} + \frac{2}{r} \frac{dT}{dr} \right)$$

Taking integration twice and putting boundary conditions,

$$T - T_s = \frac{-\Delta H D_e}{K_e} (C - C_s)$$

This was derived by Damkoehler and is applicable to any form of rate expressions.

The maximum temperature rise in a pellet will occur when the rate of consumption of the reactant will be equal to the rate of diffusion of the reactant.

So, for  $C=0$ ,

$$T - T_s = \frac{\Delta H D_e}{K_e} C_s$$

Hence, the maximum temperature rise depends on  $\Delta H$ .

$\eta$  is dependent on three dimensionless parameters,

1. Thiele modulus

$$\phi_s = r_s \sqrt{\frac{(k_1)_s \rho_p}{D_e}}$$

Here,  $\phi_s$  = Thiele modulus evaluated at surface temperature

2. Arrhenius number

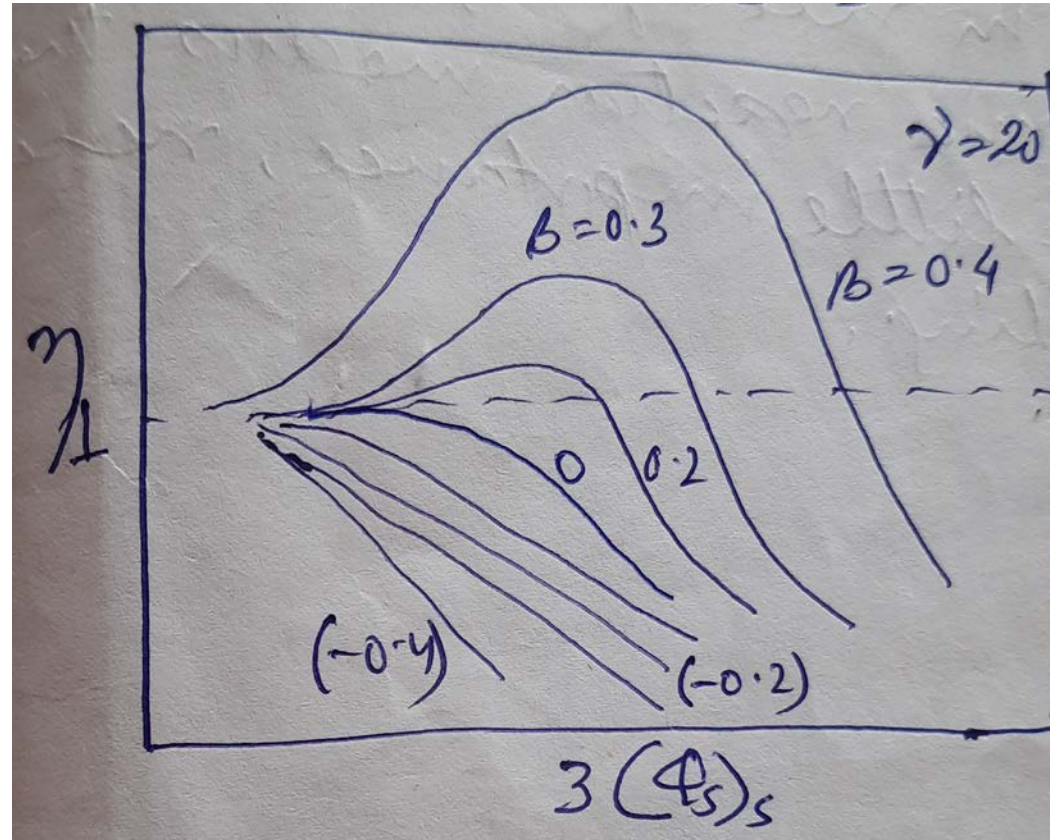
$$\gamma = \frac{E}{R_g T_s}$$

3. Heat of reaction parameter

$$\beta = \frac{(-\Delta H) D_e C_s}{K_e T_s}$$

This is a set of curves of  $\eta$  versus  $\varphi_s$  at fixed  $\gamma=20$ .

This type of sets can be obtained at different  $\gamma$ . The curve  $\beta=0$  corresponds to isothermal reaction. For positive  $\beta$ , the reaction is exothermic and for negative  $\beta$  the reaction is endothermic.



For an exothermic reaction, (positive  $\beta$ ), the temperature rise goes into the pellet. The increase in rate of reaction accompanying the temperature rise can more than offset the decrease in rate due to drop in concentration. Then  $\eta$  value is greater than unity.

While  $\eta > 1$ , the rate of the reaction per pellet increases, which increases production per unit mass of catalyst.

But the disadvantages associated are that, with large  $\eta$ ,

- There will be a large increase in temperature towards the centre of the pellet, resulting in sintering and catalyst deactivation.
- The desired product may subject to further reaction to unwanted product or undesirable side reactions may occur.
- If these undesirable reactions have higher activation energy, rise in temperature may reduce selectivity of desired product.

For an endothermic reaction, the temperature decreases with the progress of the reaction and rate decreases. Hence,  $\eta$  is always less than unity.

As rate decreases with decrease in temperature, the heat transfer resistance is also diminished. Actually, decrease in rate going into the pellet for endothermic reaction means that mass transfer is of little importance, reaction resistance is rate controlling.