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Mass and heat transfer in catalytic reactions

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Abstract

When a porous solid catalyst is added to a fluid reactant, the reaction process becomes immediately much more complex with respect to the homogeneous single-phase process. Indeed, since the reaction now takes place essentially at the surface of the porous solid, diffusional heat and mass transfer intrusions may intervene. Then the kinetic analysis of heterogeneous catalytic reactions cannot neglect the effect of such intrusions, since the rate of the reaction now corresponds to the slowest step of the overall catalytic process, the so-called rate-determining step, and the heat and mass transfer intrusions may affect considerably the relative rate of such steps.

Keywords: Catalyst; Mass transfer; Heat transfer

1. Introduction

In reactions catalysed by porous solids the molecules of the fluid reactant may come in contact with the active sites of the catalyst only by diffusing first through the fluid layer, surrounding the catalyst particle (*external diffusion*), and then through the pore network within the particle (*internal diffusion*). Since the internal surface is usually by far larger than the external one, the overall reaction rate can be strongly affected by the ability of reactant in attaining the active sites, i.e. by the rate of diffusion.

Furthermore, porous solid catalysts are usually made of poorly heat-conductive materials. Hence, for relatively highly exothermal or endothermal reactions, a considerable temperature gradient may be found along the particle radius. As a consequence, since heat and mass transfer coefficients and mainly the reaction rate constant depend on temperature, different reaction conditions may be found along the particle radius, so affecting considerably the kinetics of the overall process.

2. Mass and heat transfer from the reacting fluid to porous particles

The rate N (mol cm^{-2} s^{-1}) of mass transfer of a given reacting species from a fluid flowing through a bed of porous particles to the external surface of the latter is given by

$$N = k_c(c_0 - c_s). \tag{1}$$

In case of a gaseous reactant, Eq. (1) can be written as

$$N = k_g(p_0 - p_s). \tag{2}$$

c (mol cm^{-3}) and p (Pa=N m^{-2}) being the concentration and the partial pressure of the reactant and the subscripts 0 and s representing the bulk fluid phase

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and the external surface of the particle, respectively. The relationship between the two mass transfer coefficients (k_c and k_g) is

$$k_g = \frac{k_c}{RT}. \tag{3}$$

The value of k_c and k_g can be calculated by means of correlations, determined experimentally [1], between the Sherwood ($Sh = k_c D_p / D$), Schmidt ($Sc = \mu / \rho D$) and Reynolds ($Re = D_p \rho u_s / \mu$) numbers, D_p (cm) being the catalyst particle diameter, D (cm^2 s^{-1}) the diffusion coefficient of the reactant, ρ (g cm^{-3}) and μ (Pa s) the density and viscosity of the fluid and u_s (cm s^{-1}) the superficial flow rate of the fluid, referred to the overall cross section of the catalyst bed, calculated in the absence of catalyst.

The correlations are of the form

$$j_D = \frac{Sh}{Re\, Sc^{1/3}} = f(Re). \tag{4}$$

More explicitly we have

$$j_D = \frac{k_c}{u_s}\left(\frac{\mu}{\rho D}\right)^{0.67} = \frac{k_g P}{u_s c}\left(\frac{\mu}{\rho D}\right)^{0.67} = \frac{k_g P}{G_{ms}}\left(\frac{\mu}{\rho D}\right)^{0.67}, \tag{5}$$

where P (Pa) is the total pressure and $G_{ms} = u_s c$ the molar superficial flow rate (mol cm^{-2} s^{-1}) of the reactant.

As for heat transfer, through a similar reasoning involving the Nusselt ($Nu = h D_p / k$), Prandtl ($Pr = c_p \mu / k$) and Reynolds numbers, we have

$$j_H = \frac{h}{c_p \rho u_s}\left(\frac{c_p \mu}{k}\right)^{0.67}, \tag{6}$$

where h (J s^{-1} cm^{-2} K^{-1}), c_p (J g^{-1} K^{-1}) and k (J s^{-1} cm^{-1} K^{-1}) are the laminar coefficient for the fluid–solid heat transfer, the heat capacity and the thermal conductivity of the reacting fluid, respectively.

The previously mentioned experimental relationships are the following:

- for gaseous reactants, $3 < Re < 2000$ and $0.416 < \epsilon < 0.788$

$$j_D \epsilon = 0.357\, Re^{-0.359}, \tag{7}$$

- for liquid reactants, $55 < Re < 1500$ and $0.35 < \epsilon < 0.75$

$$j_D \epsilon = 0.25\, Re^{-0.31}, \tag{8}$$

- for liquid reactants and $0.0016 < Re < 55$

$$j_D \epsilon = 1.09\, Re^{-0.67}, \tag{9}$$

where ϵ is the interparticle void fraction of the bed of particles.

Finally, the relationship between j_D and j_H is

$$j_H \cong 1.08 j_D. \tag{10}$$

3. Mass transfer within porous particles

Three diffusion modes can be observed, depending on the catalyst pore size. When the pore diameter d_p is much larger than the mean free path λ of diffusing molecules, the diffusion takes place in the usual (*Maxwellian*) way, as observed outside the pores (bulk or molecular diffusion). When $d_p \cong \lambda$ the diffusing molecules hit upon the pore walls more frequently than upon other molecules (*Knudsen diffusion*). In microporous solids, such as zeolites, the pore diameter of which is close to the size of the reactants' molecule, the latter can diffuse within the pores only by remaining constantly in contact with the pore walls (*surface* or *configurational diffusion*).

It is generally accepted [2] that surface diffusion can affect considerably the overall reaction rate only for low-temperature processes. At high temperature a total pressure difference across the pore is usually present, generating a forced flow in pores.

The internal diffusion rate N_i (mol cm^{-2} s^{-1}) can be described by Fick's law ($N_i = -D_e(\partial c/\partial z)$, z being the diffusion coordinate), in which an effective diffusion coefficient D_e (cm^2 s^{-1}) is inserted, given by

$$\frac{1}{D_e} = \frac{1}{D_{b,e}} + \frac{1}{D_{k,e}}, \tag{11}$$

where $D_{b,e}$ and $D_{k,e}$ are the effective diffusion coefficients for bulk and Knudsen diffusion, respectively. They can be calculated by the following equations [1]:

$$D_{b,e} = \frac{D_b \theta}{\tau}, \tag{12}$$

$$D_{k,e} = 1.94 \times 10^4 \frac{\theta^2}{\tau S_g \rho_p} \sqrt{\frac{T}{M}}, \tag{13}$$

where D_b (cm^2 s^{-1}) is the bulk diffusion coefficient, θ the internal void fraction of the solid particle, τ the

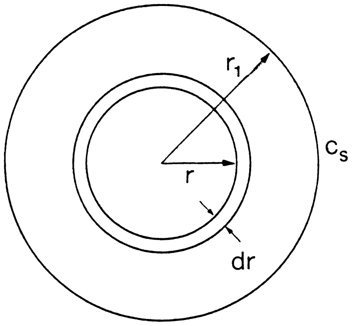

Fig. 1. Scheme of a spherical catalyst particle.

tortuosity factor of the pores, S_g (cm^2 g^{-1}) the specific surface area of the catalyst, ρ_p (g cm^{-3}) the particle density, T (K) the reaction temperature and M (g mol^{-1}) the molecular mass of the diffusing species. In the absence of specific experimental data, a value of ca. 0.5 and of ca. 4 can be attributed to θ and τ, respectively [3].

For a spherical particle of radius r_1 (cm) (Fig. 1) the profile of reactant concentration as a function of particle radius may be calculated by means of a mass balance referred to a spherical shell of thickness dr and radius r. Putting c and c+(dc/dr) dr the concentration of the reactant at r=r and r=r+dr, respectively, we have

$$4\pi(r+\mathrm{d}r)^2\frac{\mathrm{d}}{\mathrm{d}r}\left(c+\frac{\mathrm{d}c}{\mathrm{d}r}\,\mathrm{d}r\right)D_\mathrm{e}-4\pi r^2\frac{\mathrm{d}c}{\mathrm{d}r}D_\mathrm{e} = r_\mathrm{a}\,4\pi r^2\,\mathrm{d}r. \qquad (14)$$

For a first-order chemical reaction, the reaction rate r_a (mol cm^{-3} s^{-1}), referred to the unit volume of catalyst particle, is given by

$$r_\mathrm{a}=k_\mathrm{s}\,S_v\,c. \qquad (15)$$

k_s (cm s^{-1}) being the reaction rate constant and S_v (cm^2 cm^{-3}) the surface area per unit particle volume. Developing Eq. (14) and neglecting the higher-order infinitesimals, we have

$$D_\mathrm{e}\left(\frac{\mathrm{d}^2c}{\mathrm{d}r^2}+\frac{2}{r}\frac{\mathrm{d}c}{\mathrm{d}r}\right)=k_\mathrm{s}\,S_v\,c, \qquad (16)$$

the integration of which allows one to obtain the reactant concentration profile within the particle.

The integration can be made easier by introducing a dimensionless parameter Φ, known as Thiele modulus

$$\Phi=r_1\sqrt{\frac{k_\mathrm{s}\,S_v\,c_\mathrm{s}^{\nu-1}}{D_\mathrm{e}}}, \qquad (17)$$

where c_s is the reactants' concentration at the external particle surface and ν the reaction order. Φ represents the ratio of reactivity over diffusivity of the reacting species and, for first-order reactions, Φ is independent of reactants' concentration.

The result of the integration is

$$c=\frac{c_\mathrm{s}\,r_1}{r\sin h\,\Phi}\sin h\left(\frac{r\Phi}{r_1}\right). \qquad (18)$$

The profile is shown in Fig. 2, together with the drop in concentration within the fluid film surrounding the particle, according to the boundary-layer theory [4].

4. Catalyst effectiveness

Under steady-state conditions and in the absence of reverse reaction, the rate of reaction (mol s^{-1}) of a reactant A equals the rate of diffusion of A from the bulk fluid to the external surface of the catalyst particle. For a spherical particle we have

$$\frac{4}{3}\pi r_1^3\,r_\mathrm{a}=4\pi r_1^2 N_\mathrm{A}=4\pi r_1^2 D_\mathrm{e}\left(\frac{\mathrm{d}c}{\mathrm{d}r}\right)_{r=r_1}. \qquad (19)$$

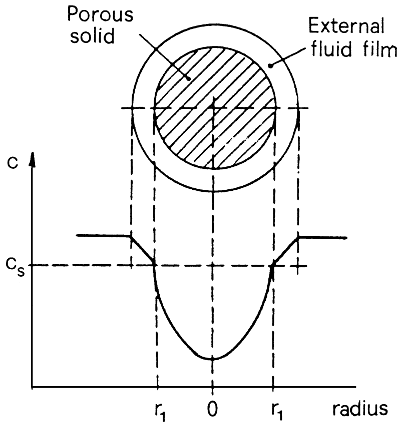

Fig. 2. Concentration profile of reactant close to the external surface and within a spherical catalyst particle. First-order reaction kinetics.

Combining with Eq. (18) and solving

$$\frac{4}{3}\,\pi\,r_1^3\,r_a = 4\,\pi\,r_1^2\,D_e\left[\frac{c_s\,\Phi}{r_1}\left(\frac{1}{T\,g\,h\,\Phi}-\frac{1}{\Phi}\right)\right]. \tag{20}$$

In the absence of any diffusional resistance, i.e. if the overall surface of the catalyst were exposed uniformly to the concentration c_s of reactant, existing at the external surface of the particle, the rate of consumption of A would be

$$\tfrac{4}{3}\pi\,r_1^3\,r_a = \tfrac{4}{3}\pi\,r_1^3\,c_s\,k_s\,S_v. \tag{21}$$

The *effectiveness* or *effectiveness factor* η of the catalyst is then defined by the ratio of Eq. (20) over Eq. (21)

$$\eta = \frac{3\,D_e\,\Phi}{r_1^2\,k_s\,S_v}\left(\frac{1}{Tgh\,\Phi}-\frac{1}{\Phi}\right). \tag{22}$$

Remembering the definition of Φ (Eq. (17)), we have

$$\eta = \frac{3}{\Phi}\left(\frac{1}{Tgh\,\Phi}-\frac{1}{\Phi}\right). \tag{23}$$

The dependence of η on Φ is shown in Fig. 3.

5. Non-isothermal catalyst particles

For a spherical particle and under steady-state reaction conditions, the heat released or absorbed by the reaction may be calculated by means of a heat balance similar to the previously discussed mass balance, referred to the same spherical shell (Fig. 1)

$$\frac{4}{3}\,\pi(r+\mathrm{d}r)^2 k_T\,\frac{\mathrm{d}}{\mathrm{d}r}\left(T+\frac{\mathrm{d}T}{\mathrm{d}r}\,\mathrm{d}r\right) - 4\,\pi\,r^2\,k_T\,\frac{\mathrm{d}T}{\mathrm{d}r} = 4\,\pi\,r^2\,\mathrm{d}r\,r_a(-\Delta H). \tag{24}$$

Developing Eq. (24) and neglecting the higher-order infinitesimals, we get

$$k_T\left(\frac{\mathrm{d}^2T}{\mathrm{d}r^2}+\frac{2}{r}\,\frac{\mathrm{d}T}{\mathrm{d}r}\right) = r_a(-\Delta H). \tag{25}$$

k_T (J s^{-1} cm^{-1} K^{-1}) and $-\Delta H$ (J mol^{-1}) being the thermal conductivity of the solid and the enthalpy change connected with the reaction, respectively. The temperature change within the particle may be calculated by integrating simultaneously Eqs. (16) and (25) and by expressing the dependence on temperature of the reaction rate constant k_s by means of the Arrhenius equation

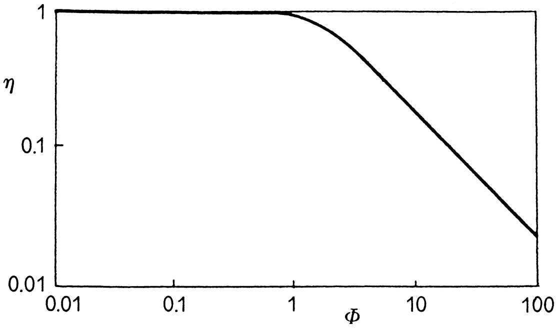

Fig. 3. Effectiveness of a catalyst as a function of Thiele modulus Φ. Spherical particles, first-order reaction.

$$k_s = A\,\mathrm{e}^{-E_a/RT}. \tag{26}$$

A (cm s^{-1}) and E_a (J mol^{-1}) being the so-called *pre-exponential factor* and the apparent *activation energy* of the reaction, respectively.

Two dimensionless parameters can be introduced to classify the kinetic data of a given reaction in terms of E_a, ΔH, and k_T. Such parameters are the Prater number

$$\beta = \frac{c_s(-\Delta H)D_e}{k_T\,T_s} = \frac{T_{\max}-T_s}{T_s}, \tag{27}$$

and the Arrhenius number

$$\gamma = \frac{E_a}{R\,T_s}, \tag{28}$$

where T_s is the temperature at the external surface and $T_{\max}$ the maximum temperature detected along the radius of the particle.

It may be noticed that $\beta=0$, $\beta<0$ and $\beta>0$ for isothermal, endothermal and exothermal reactions, respectively. As for γ, a common value for most catalytic reactions is $\gamma=20$, corresponding to $E_a=100$ kJ mol^{-1} and reaction temperature of ca. 600 K. The result of the integration is usually reported as a set of curves of η versus Φ (Fig. 4). Similar sets of curves can be calculated for different reaction orders and catalyst particles of different shape [1,2]. It may be observed that for exothermal reactions ($\beta>0$) η can become higher than unity. Indeed, in this case the effect of decreasing of reactants' concentration within the particle is more than counterbalanced by the effect

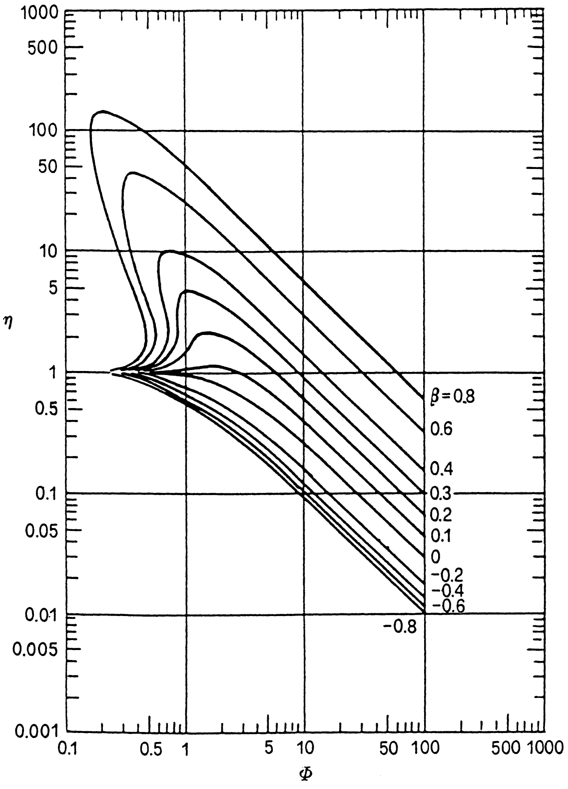

Fig. 4. Effectiveness factor η versus Thiele modulus $\Phi = r_1\sqrt{k_s S_v/D_e}$. $\beta = c_s(-\Delta H)D_e/k_T T_s)$, $\gamma = E_a/RT_s = 20$. First-order reaction over spherical catalyst particles.

of increasing temperature on the kinetic constant of the reaction. Furthermore, it may be noted that for highly exothermal reactions and $\Phi<1$, up to three values of η may correspond to a given set of values of Φ, β and γ. Every one of these values of η represents a steady state, in which the heat generated by the reaction equals the heat carried away by the refrigerating system. Only the upper and lower situations however represent an autostabilising state, the intermediate one being intrinsically unstable. For a detailed discussion of these aspects see e.g. [5,6].

6. Simultaneous effect of external and internal diffusion on the kinetics of heterogeneous catalytic reactions

For a catalyst particle immersed in a flowing gas in which a reactant A is present, the rate r_{ed} of external diffusion and the rate r_r of reaction of A in the presence of internal diffusion effects may be expressed in terms of partial pressure of A (p_A). For a first-order kinetics we have

$$r_{ed} = k_g\,a(p_A - p_{As}), \tag{29}$$

$$r_r = \eta\,k_r\,p_{As}, \tag{30}$$

where the subscript s refers to the external surface of the particle, k_g is the mass transfer coefficient of A, a ($\mathrm{cm}^2\,\mathrm{cm}^{-3}$) the specific surface area of catalyst and k_r the reaction rate constant. r_{ed}, r_r, a and k_r are referred to unit volume of bed.

Under steady-state conditions $r_{ed}=r_r$, so that, by combining Eqs. (29) and (30), the overall reaction rate r_t of the process can be written as

$$r_t = \frac{\eta\,k_r\,p_A}{1 + (\eta\,k_r/k_g\,a)} = \frac{\eta\,k_r\,p_A}{1 + \eta\,Da}. \tag{31}$$

$Da=k_r/k_g\,a$ being the Damkohler number, expressing the ratio of the rate of chemical reaction over the rate of external diffusion of the reactant.

The following significant cases may then occur:

1. When $\Phi<1$, and therefore $\eta\cong1$, i.e. when internal diffusion has no significant effect, Eq. (31) becomes

$$r_t \cong \frac{k_r\,p_A}{1 + (k_r/k_g\,a)} = \frac{k_r\,p_A}{1 + Da}. \tag{32}$$

But k_g and k_r depend on temperature as shown in Fig. 5. Hence, for low temperature ($T<600$ K) $k_g\,a \gg k_r$, so that

$$r_t \cong k_r\,p_A. \tag{33}$$

This means that the rate of the overall catalytic process is governed by the chemical reaction (*chemical regime*). On the other hand, at high temperature $k_r \gg k_g\,a$, so that

$$r_t \cong k_g\,a\,p_A. \tag{34}$$

i.e. the overall rate is governed by the external diffusion (*external diffusional regime*).

2. When $\Phi>3$, so that $\eta\cong3/\Phi$, Eq. (31), by recalling the definition of the Thiele modulus (Eq. (17)) becomes

$$r_t = \frac{p_A\,a\sqrt{k_r D_e}}{(r_1\,a/3) + (\sqrt{k_r D_e}/k_g)}. \tag{35}$$

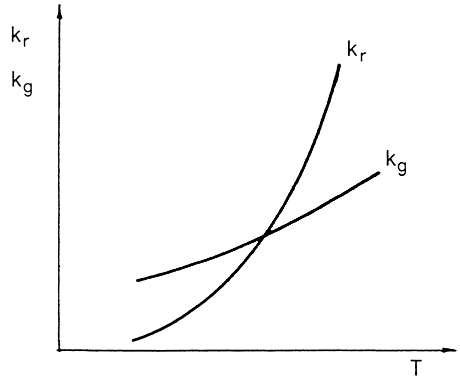

Fig. 5. Dependence on temperature of $k_r = A\,e^{-E_a/RT}$ and $k_g \propto T^2$.

However, if the value of the effective diffusion coefficient D_e is low, so to have $\sqrt{k_r D_e}/k_g \ll r_1\, a/3$, Eq. (35) becomes

$$r_t = \sqrt{k_r D_e}\, p_A \frac{3}{r_1}. \qquad (36)$$

i.e. the overall rate is governed by internal diffusion (*internal diffusional regime*).

Analogous considerations lead to similar, though more complex, expressions in case of chemical reaction of higher reaction orders [1].

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