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Overall Effectiveness Factor for Gas–Solid Reactions

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An expression for the effectiveness factor is developed which takes into account the contribution of the internal and external surface areas of the solid. The development is done for a catalyst with its boundary layer and for a solid reactant with its boundary layer and its product layer of variable thickness. The influence of the internal and external surface areas contribution is computed by different terms. The overall effectiveness factor is expressed as a function of the internal effectiveness factor and the result obtained is of general validity for any kind of geometry, kinetics, thermal conditions, etc., provided the boundary and ash layers are not taken into account.

NOMENCLATURE

A, B, C, D	reaction components
a_e	outer surface area of solid B per unit volume, $a_e = S'_e/V$, L^2/L^3
a_i	internal surface area of solid B per unit volume, L^2/L^3
b, d	stoichiometric coefficients
Bi_D	biot number for mass transfer in gas phase based upon diffusion in porous solid, $\mathrm{Bi}_D = Lk_{A_g}/D$
Bi_k	Biot number for mass transfer in gas phase based upon chemical reaction, $\mathrm{Bi}_k = k_{A_g}K/k'(K+1)\epsilon_B f$
Bi_p	Biot number for mass transfer through ash layer based upon chemical reaction, $\mathrm{Bi}_p = D'/k'R_e\epsilon_B f$
C_A	molar concentration of A, moles/L^3
C_B	molar concentration of B, moles/L^3
C_p	specific heat at constant pressure, $Q/m\cdot T$
D'	effective diffusivity of A in ash layer, L^2/θ
D	effective diffusivity of A in reaction zone, L^2/θ
E	activation energy, Q/mole
f	roughness factor at boundary between reaction zone and ash layer or at gas–solid interface
h	Thiele modulus, $h = L[k(K+1)/KD]^{1/2}$ for first-order reversible reaction
h^+	correction factor to the Thiele modulus, defined in Eq. (19)
ΔH	enthalpy of reaction, Q/mole
k	reaction rate coefficient per unit volume, θ^{-1}
k'	reaction rate coefficient per unit surface area, L/θ
k_{A_g}	mass transfer coefficient, L/θ
K	equilibrium constant
L	characteristic length, $L = V/S$, L
R	radius, L
R^*	dimensionless radius, $R^* = R/R_0$
r	reaction rate per unit volume, moles/$\theta\cdot L^3$
r'	reaction rate per unit surface area, moles/$\theta\cdot L^2$
S'	surface area of solid B, L^2
S	geometrical area, L^2
S'_e	external surface area of solid B for reaction at boundary between reaction zone and gas film

S_i	internal surface area of solid B for reaction, L^2
t	time, θ
T	temperature, T
V	volume, L^3
z	distance, L

Subscripts

app	apparent
e	solid–gas interface
g	bulk gas
0	initial value
obs	observed
s	boundary between reaction zone and product layer

Superscripts

0	reference value

Greek Letters

α	dimensionless surface area, $\alpha = S_e/(S_e + S_i)$
γ	reaction order
ϵ	porosity
ϵ_B	surface fraction of solid B at boundary between reaction zone and gas film or product layer
η	overall effectiveness factor
η_i	internal effectiveness factor
λ	effective thermal conductivity, $Q/L\theta T$
ϕ	modulus defined by Eq. (25)

INTRODUCTION

There are many examples of reactions which involve a solid and a gaseous phase. The solid can be a true reactant, as it is in the case of the gas–solid reactions, or can be merely a catalyst.

When the solid is nonporous, the reaction takes place on its outer surface area. This case has been studied extensively, and good examples of those studies are given in several references (*1*, *6*, *9*, *10*, *12*, *16*, *17*, and *18*), which, for a gas–solid reaction, represent the well-known moving boundary model (MBM), shrinking core model, or shell progressive model.

On the other hand, when the solid is porous, the gaseous reactant is able to penetrate inside its pores by diffusion; hence, the reaction would also take place on the internal surface area of the solid with a concentration gradient of the gaseous reactant. Furthermore, this picture can be seen as the general case from which particular cases arise. Thus, when the reaction rate is large compared with that of diffusion, the reaction will take place in an external shell. In the limit, when the reaction rate is very high, the reaction will take place on the external surface area of the solid and so the system will reach the MBM. On the other hand, when the reaction rate is very small in comparison with that of diffusion, the reaction will take place without concentration gradients, namely, uniformly inside the porous solid.

It is seen that this picture makes no distinction between a solid which is a true reactant and one which is a catalyst. In both cases, the objective will be to relate the consumption rate of the reactants to the reaction parameters. So, mass balances for the reactants and the thermal energy equation will be necessary to determine the composition and temperature fields inside the porous solid. If A is the gaseous component and B the solid,

$$\epsilon \frac{\partial C_A}{\partial t} = \nabla \cdot D \nabla C_A - r_A, \qquad (1)$$

$$-\frac{\partial C_B}{\partial t} = b r_A, \qquad (2)$$

$$\frac{\partial(\rho_B C_p T)}{\partial t} = \nabla \cdot \lambda \nabla T - r_A(\Delta H), \qquad (3)$$

where $r_A = k' a_i F(C_A)$ (the symbols are defined in the Nomenclature section). Equations 1 to 3 have to be solved together with their boundary and initial conditions.

It is useful to express the final solution by means of the well-known effectiveness factor used extensively in heterogeneous catalysis since the pioneer solutions (*13*, *19*). However, the contribution of the external solid surface to the reaction has not been usually taken into account in the effectiveness factor. Some authors have dealt with this problem (*7*, *8*, *9*), but no application has been made in the solid reactive field from a general point of view. We shall use the term internal effectiveness factor (IEF) when the external surface contribution is not taken into account, and the overall effectiveness factor (OEF) will be defined by the relationship

$$\eta = \frac{r_{\mathrm{A_{obs}}}}{r_{\mathrm{A}}^{0}}, \tag{4}$$

where $r_{\mathrm{A_{obs}}}$ is the experimentally observed reaction rate and r_{A}^{0} is a reference reaction rate.

It is now convenient to deal separately with the solid catalyst and the solid reactant.

SOLID CATALYST

When the solid phase is a catalyst, only Eqs. (1) and (3) are necessary to solve the problem, and the external surface or bulk gaseous phase conditions can be used to define the reference reaction rate. At the same time, the steady state continuity equation for the reactant A through the external solid surface yields

$$\begin{aligned} r_{\mathrm{A_{obs}}}V &= \int_{S_\mathrm{e}} D\nabla C_{\mathrm{A}}|_{\mathrm{e}}\, dS_{\mathrm{e}} + \int_{S'_\mathrm{e}} r'_{\mathrm{A_e}}\, dS'_{\mathrm{e}} \\ &= k_{\mathrm{A_g}}(C_{\mathrm{A_g}} - C_{\mathrm{A_s}})S_{\mathrm{e}}, \end{aligned} \tag{5}$$

where S_e is the geometrical external surface of the solid and S'_e is the external surface area of the solid at the solid–gas boundary. This is the area on which the reaction would take place if its rate approached infinity.

S_e is related to S'_e through

$$S'_{\mathrm{e}} = S_{\mathrm{e}}\epsilon_{\mathrm{B}}f, \tag{6}$$

where ϵ_B and f account for the effect of porosity and roughness on the actual external surface area, respectively.

If the bulk gas phase conditions are taken as reference, from Eqs. (4) and (5) it follows that:

$$\eta = \frac{\int_S D\nabla C_{\mathrm{A}}|_{\mathrm{e}}\, dS + \int_{S'_\mathrm{e}} r_{\mathrm{A_e}}'\, dS'_{\mathrm{e}}}{r_{\mathrm{A_g}}V}. \tag{7}$$

Hence, for the reaction A = C, the isothermal effectiveness factor for a first-order reversible catalytic reaction in a solid with slab geometry and a kinetic expression of the type,

$$r_{\mathrm{A}} = k\left(C_{\mathrm{A}} - \frac{C_{\mathrm{C}}}{K}\right), \tag{8}$$

will be:

$$\eta = \frac{(1-\alpha)\{[\alpha/(1-\alpha)] + (\tanh h/h)\}}{1 + \left\{\frac{1}{\mathrm{Bi}_k}\left[1 + \frac{1-\alpha}{\alpha}\frac{\tanh h}{h}\right]\right\}}, \tag{9}$$

where $\mathrm{Bi}_k = k_{\mathrm{A_g}}K/k'(K+1)\epsilon_{\mathrm{B}}f$, and $h = L[k(K+1)/DK]^{1/2}$ provided the effective diffusivities of A and C are equal and constant.

It is to be observed from Eq. (9) that when $\alpha \to 0$, namely when the solid has a very high internal surface area, Eq. (9) reduces to that obtained by Carberry (*5*) for a catalyst in which the outer surface area was neglected. To perform such comparison it is necessary to take into account that:

$$\frac{1}{\mathrm{Bi}_k} = \frac{h^2}{\mathrm{Bi}_D}\frac{a_{\mathrm{e}}}{a_{\mathrm{i}}}. \tag{10}$$

Nevertheless, when $\mathrm{Bi}_k \to \infty$ the OEF [Eq. (7)] can be written in a more general way as:

$$\eta = (1-\alpha)\left[\frac{\alpha}{1-\alpha} + \eta_{\mathrm{i}}\right], \tag{11}$$

where:

$$\eta_{\mathrm{i}} = \frac{D\nabla C_{\mathrm{A}}|_{\mathrm{e}}\, S_{\mathrm{e}}}{r_{\mathrm{A_e}}'\, S_{\mathrm{i}}}. \tag{12}$$

Equation 11 is very important because from Eq. (12), η_i is the internal effectiveness factor no matter what the reaction conditions are; in other words, this result is also valid for nonisothermal conditions, any kind of reaction kinetics, any shape of solid, etc. Obviously, it depends upon the existence of a solution for η_i under such conditions.

Equation (11) is plotted in Fig. 1 for a first-order isothermal reaction in slab geometry. The plot is still valid in the asymptotic region (*11*) for any irreversible reaction and some reversible ones provided the Thiele modulus is defined in a general fashion (*3*). In the same way it is valid for different geometries provided a correct characteristic length is defined (*2*).

Figure 1 shows that the traditional solution for the effectiveness factor corresponds to a value of $\alpha = 0$. On the other hand, a value of $\alpha = 1$ represents the nonporous solid in which the reaction always takes place on its external surface area for any value of the Thiele modulus.

For a porous solid with a value $0 < \alpha < 1$ it is observed that there are two regions in which the OEF is independent of the Thiele modulus. The first one, at low values of the

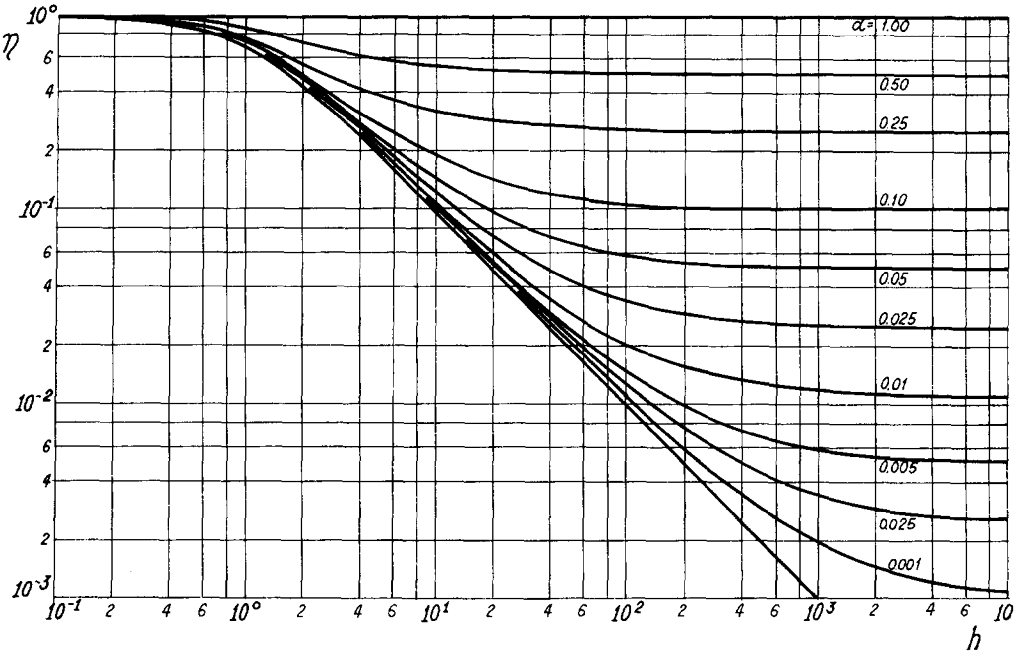

FIG. 1. Overall effectiveness factor as a function of Thiele modulus and fractional outer surface area.

Thiele modulus, corresponds to the case of an OEF equal to one and with a reaction taking place without concentration gradients inside the porous solid. The second region is reached at high Thiele modulus values and $\eta = \alpha$, with the reaction taking place on the external surface area of the solid. In the intermediate region the reaction takes place in a shell whose thickness decreases as the Thiele modulus increases.

REACTANT SOLID

Let us consider the isothermal reaction

$$A_{(g)} + bB_{(s)} = C_{(g)} + dD_{(s)}, \tag{13}$$

in which the solid D remains as a porous ash layer around B.

It is necessary to remember that now the porous structure of B is changing because of the reaction. Hence, the internal surface area of B and its porosity will be variable. Furthermore, the ash layer thickness will increase as reaction progresses.

The pore structure variation has to be taken into account when defining the reference reaction rate. So, the reference conditions will be defined as those of the bulk gaseous phase for A and initial solid condition for B.

Consequently, for an isothermal, irreversible first-order reaction with respect to A:

$$r_A{}^0 = k' C_{A_g} S_{B_0}. \tag{14}$$

If the solid is spherical and the pseudo-steady-state assumption is made, the concentration of A in the bulk gas phase can be related to the kinetic parameters of the reaction in the following way:

$$C_{A_g} = C_{A_s} + \frac{D\nabla C_A|_s + r'_{A_s}S'_s}{k_{A_g}S_e} + \frac{D\nabla C_A|_s S_s + r'_{A_s}S'_s}{D'R_eS_s/R(R_e - R)}. \tag{15}$$

A picture of the system is given in Fig. 2.

If Eq. (15) is introduced in Eq. (14) and then Eqs. (5) and (14) are introduced in Eq. (4), the following result is obtained:

$$\eta = \frac{r'_{A_s}S'_s + D\nabla C_A|_s S_s}{k'S_{B_0}\{C_{A_s} + [(D\nabla C_A|_s S_s + r'_{A_s}S'_s)/k_{A_g}S_e] + [(D\nabla C_A|_s S_s + r'_{A_s}S'_s)/D'R_eS_s/R(R_e - R)]\}}. \tag{16}$$

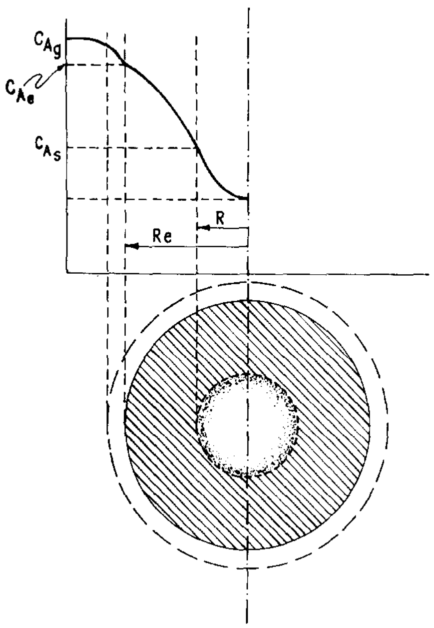

FIG. 2. General picture of the reacting system.

And if the IEF is defined as:

$$\eta_i = \frac{D\nabla C_A|_s S_s}{r'_{As} S_{i0}}, \tag{17}$$

Eq. (16) can finally be written as:

$$\eta = \frac{\alpha}{\dfrac{1}{1 + [(1 - \alpha)/\alpha]\eta_i} + \dfrac{R^{*2}}{\mathrm{Bi}_k} + \dfrac{R^*(1 - R^*)}{\mathrm{Bi}_p}}, \tag{18}$$

where $\alpha = S_e/(S_e + S_i)$, and η_i is the instantaneous IEF for the radius R^*. Equation (18) shows the series connection resistances of film diffusion–ash layer diffusion, and diffusion with simultaneous reaction in solid.

It should be observed that provided the system reacts isothermally, following an irreversible first-order kinetic law with respect to A, Eq. (18) holds no matter what the expression for the IEF. This IEF must take into account the pore structure variation of B.

In order to obtain η_i for a solid reactant, it is necessary to include in the system of differential equations, the mass balance for the consumption of B (Eq. 2), and to take into account D and a_i as variables in Eq. (1). This problem is analyzed elsewhere (*4*) by introducing a factor h^+ that modifies the Thiele modulus (due to the existence of D and a_i profiles in the solid reactant) in such a way that:

$$\eta_i = \frac{h^+}{h} \tag{19}$$

in the asymptotic region of the IEF. In Eq. (19), h is the Thiele modulus for initial a_i and D.

Obviously, Eq. (18) must imply all the different particular cases of a first-order irreversible reaction:

1. If the reaction rate is infinitely fast compared with that of diffusion, then $\eta_i \rightarrow 0$ and Eq. (18) reduces to:

$$\eta = \frac{\alpha}{1 + \dfrac{R^{*2}}{\mathrm{Bi}_k} + \dfrac{R^*(1 - R^*)}{\mathrm{Bi}_p}}, \tag{20}$$

which is the effectiveness factor for a porous solid when the MBM is assumed.

If the solid is nonporous, $\alpha = 1$ and Eq. (18) will reduce also to Eq. (20) which is that obtained by Ishida (*6*).

In turn, Eq. (18) can be simplified even more when the two biot numbers approach infinity.

2. If there is no ash layer, then $\mathrm{Bi}_p \rightarrow \infty$; in such a case Eq. (18) will reduce to an equation similar to Eq. (9) but with an instantaneous IEF. This can in turn reduce to Eq. (11).

3. If the reaction rate is infinitely slow compared with that of diffusion, then both biot numbers approach infinity and $\eta_i \rightarrow 1$; hence Eq. (18) will reduce to:

$$\eta = 1, \tag{21}$$

and reaction takes place at uniform composition inside the solid.

FALSIFICATION OF KINETIC PARAMETERS

It is well known that the diffusional effects falsify the kinetic parameters of a reaction. This falsification has been studied by taking into account only the internal surface area of the solid and neglecting the external one. Hence, the results obtained were of the form:

$$E_{\mathrm{app}}/E = f_1(h) \tag{22}$$

$$\gamma_{app}/\gamma = f_2(h). \qquad (23)$$

Now, we will include the influence of the parameter α in Eqs. (22) and (23).

Activation Energy. It has been demonstrated that the falsified activation energy E_{app} is related to the true chemical one E (*14*) by the following relationship

$$E_{app}/E = 1 + (1/2)d \ln \eta / d \ln h. \qquad (24)$$

(In fact, that development has been done for the IEF, but it is also valid for the OEF.)

As the Thiele modulus contains the parameter k, let us replace it by another modulus which contains the observed reaction rate (*15*)

$$\phi = L^2 r_{A_{obs}}(1 - \alpha)/DC_A, \qquad (25)$$

or

$$\phi = \eta h^2. \qquad (26)$$

Hence, introducing Eq. (26) in (24) it follows that

$$E_{app}/E = d \ln \phi / d \ln h^2. \qquad (27)$$

Equation (26) can also be written in the following way

$$\phi = \alpha h^2 + (1 - \alpha) h \tanh h, \qquad (28)$$

for a first-order isothermal reaction.

Consequently, with Eqs. (27) and (28), the ratio E_{app}/E can be calculated as a function of the parameters ϕ and α. The results are plotted in Fig. 3.

As would be expected, the falsified activation energy decreases as a function of ϕ and falls to one half of the true value when α is very low ($\alpha < 10^{-4}$). For values of $\alpha > 10^{-4}$, the falsified activation energy decreases to a value which is always higher than one half of the true chemical one. It is also seen that the ratio E_{app}/E goes through a minimum and that for low and high enough values of ϕ approaches to one corresponding to $\eta = 1$ and $\eta = \alpha$, respectively.

Reaction order. For a reaction rate expression of the type

$$r_A = kC_A{}^{\gamma}, \qquad (29)$$

the apparent reaction order γ_{app} is related to the true one by (*14*)

$$\gamma_{app} = \gamma(E_{app}/E) \quad \text{if} \quad D = D^0/C_{A_s}, \qquad (30)$$

$$\gamma_{app} = 1 + (E_{app}/E)(\gamma - 1) \quad \text{if} \quad D = \text{constant}. \qquad (31)$$

Since E_{app}/E in turn depends upon h and α it is seen from Eqs. (30) and (31) that, for a given value of γ, γ_{app} goes through

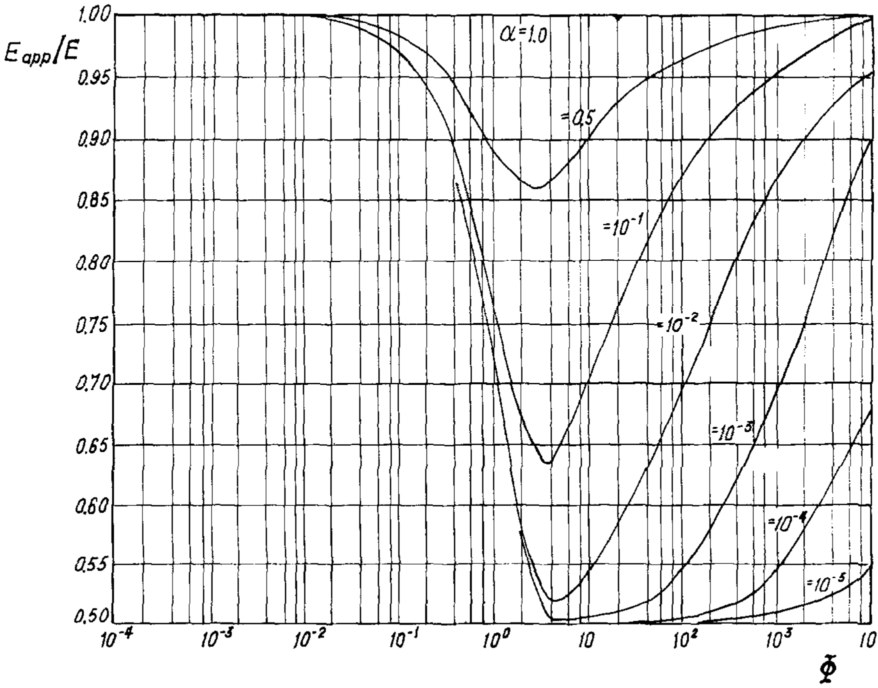

FIG. 3. Influence of fractional outer surface area upon the falsification of activation energy.

a minimum which corresponds to the minimum in E_{app}/E. Furthermore, and as it is the case for E_{app}, the falsified reaction order equals that of the true one when ϕ is sufficiently low or sufficiently high.

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