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Criterion of Applicability of the Moving Boundary Model

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A criterion was developed to check the validity of the moving boundary model. The criterion is based upon the expression of the overall effectiveness factor for a gas–solid reaction obtained by computing the effective diffusivity and surface area profiles inside the reactant solid. The criterion can be expressed as a function of the initial parameters of the reaction. On the other hand, the validity of the arguments usually applied to check the assumption of the moving boundary model is discussed. It is concluded that for most practical situations, in the absence of previous diffusional steps, the moving boundary model assumption is almost completely restricted to a nonporous solid reactant.

NOMENCLATURE

a	surface area of solid B per unit volume, L^2/L^3
a_e	outer surface of solid B per unit volume, $a_e = a\epsilon_B f$, L^2/L^3
a_i	internal surface of solid B per unit volume, L^2/L^3
b	stoichiometric coefficient
Bi_k	Biot number for mass transfer in boundary layer, $\mathrm{Bi}_k = \mathrm{k}_{Ag}/\mathrm{k}'\epsilon_B f$
Bi_p	Biot number for mass transfer in ash layer, $\mathrm{Bi}_p = D'R_0k'\epsilon_B f$
C_A	molar concentration of A, moles$/L^3$
C_A^*	dimensionless concentration of A, $C_A^* = C_A/C_{Ag}$
C_B	molar concentration of B, moles$/L^3$
C_B^*	dimensionless concentration of B, $C_B^* = C_B/C_{B_0}$
D	effective diffusivity of A in solid B, L^2/θ
D'	effective diffusivity of A in solid D, L^2/θ
e	coefficient, $e = (\epsilon_s - \epsilon_0)/\epsilon_0$
E	activation energy, Q/mole
f	roughness factor at boundary between product layer and reaction zone
h	Thiele modulus, $h = L\ (k'\ a_i/D)^{1/2}$
h^+	correction factor for Thiele modulus
I	integral defined in Eq. (23)
k	reaction rate coefficient per unit volume, $1/\theta$
k'	reaction rate coefficient per unit surface area, L/θ
k_{A_g}	mass transfer coefficient, L/θ
L	characteristic length ($3/R_s$ for spherical geometry), L
n	number of moles
R	pellet radius, L
R^*	dimensionless radius, $R^* = R/R_0$
r_A	reaction rate per unit volume, moles$/L^3\theta$
r_A'	reaction rate per unit surface area, moles$/L^2\theta$
t	time, θ
t^*	dimensionless time, $t^* = br'_{A_g}\epsilon_B ft/R_0C_{B_0}$
V	volume, L^3
x	conversion
z	distance, L

Subscripts

app	apparent
g	bulk gas
MB	moving boundary model
0	initial value
s	boundary between product layer and reaction zone

Greek letters

α	dimensionless surface area $\alpha = a_e/(a_e + a_i)$
β	dimensionless surface area $\beta = (1 - \alpha)/\alpha$

δ	reaction layer thickness, L
δ^*	dimensionless reaction layer thickness, $\delta^* = \delta/L$
ϵ	porosity
ϵ_B	solid B surface fraction at boundary between product layer and reaction zone
ξ	tolerance
η_i	internal effectiveness factor (IEF)
η	overall effectiveness factor (OEF)
ϕ	modulus, $\phi = \eta h^2$

INTRODUCTION

The moving boundary model (MBM) (also known as the shrinking core model in the literature) for a solid–gas reaction states that the gaseous reactant is consumed completely on the outer surface of the solid reactant. This model has been widely studied (*1, 6–8, 12, 15, 16*) and it has been stated that many reactions obey it (*4, 5, 9–11, 13, 17*). Actually, from a rigorous point of view, the MBM only will be satisfactory when the solid is nonporous. Obviously, the case is different when the solid involved is porous. In such a case the gaseous reactant will penetrate inside the porous solid. This penetration will depend upon the relative rates between intrapellet diffusion and chemical reaction. The faster the kinetic step is in relation to the intrapellet diffusion, the thinner will be the shell in which the reaction takes place.

In this way it is possible to distinguish two contributions to the overall reaction rate in the pellet; namely the reation which takes place on the outer surface and that which proceeds on the internal one. However, it is difficult to imagine a sharp separation between the two types of surface area of the solid reactant, and the outer surface must be considered not only as a geometric concept but also as a kinetic one. Due to the large number of papers in which the MBM has been applied, it becomes important to state precisely the conditions under which the model is actually achieved.

Consequently, the criterion to be developed must be supplied from the general solution of the mass transfer equations for the system, provided it is isothermal. If the reaction takes place isothermally between the porous solid B and the gas A, the mass balance for both components will be

$$\epsilon \frac{\partial C_A}{\partial_t} = \nabla \cdot D \nabla C_A - r_A, \tag{1}$$

$$-\frac{\partial C_B}{\partial_t} = b r_A, \tag{2}$$

where b is the number of moles of B which react with 1 mole of A.

Equations (1) and (2) have been analyzed elsewhere (*2*) in connection with the overall effectiveness factor (OEF) given by

$$\eta = \frac{(1-\alpha)\{[\alpha/(1-\alpha)] + \eta_i\}}{1 + \left\{\left[\frac{R^{*2}}{\mathrm{Bi}_k} + \frac{R^*(1-R^*)}{\mathrm{Bi}_p}\right]\left[1 + \frac{1-\alpha}{\alpha}\eta_i\right]\right\}}. \tag{3}$$

In this equation η_i is the internal effectiveness factor (IEF), α the fractional external surface area, and R^* the dimensionless radius of the reaction front; Eq. (3) takes into account the diffusional resistance of the boundary layer by means of the biot number (Bi_k) and also the diffusional resistance of the ash layer of solid product by means of Bi_p.

THE MOVING BOUNDARY MODEL CRITERION

It is seen from Eq. (3) that whenever

$$\eta_i(1-\alpha)/\alpha \rightarrow 0, \tag{4}$$

Eq. (3) will reduce to

$$\eta = \frac{\alpha}{1 + (R^{*2}/\mathrm{Bi}_k) + [R^*(1-R^*)/\mathrm{Bi}_p]}, \tag{5}$$

and the reaction will take place only on the outer surface of the solid. In this case the MBM will certainly be valid.

As a matter of fact the evaluation of α presents a problem in itself, because it involves not only the geometrical outer surface area, but also a factor accounting for the effect of porosity and roughness, such as $(1-\epsilon)f$. Only in the case of a nonporous, smooth solid is the value of α obviously defined by means of the geometrical external surface area of the pellet.

In order to state a precise condition for the validity of the MBM, we shall throw the limiting condition of Eq. (4) into a form that has physical meaning. The rate of reaction on the internal surface is proportional to η_i and that on the external surface to $\alpha/(1-\alpha)$ with the same constant of proportionality. Thus if we set

$$\eta_i \frac{1-\alpha}{\alpha} \leq \xi, \tag{6}$$

the fraction of the reaction taking place internally is less than ξ and we may say that Eq. (5) holds with a tolerance of ξ.

The common picture of the MBM represents it as a step function in C_A at the outer surface of B; in other words, the gaseous reactant A does not penetrate at all inside the solid B. But it is important to emphasize that once a value of ξ has been adopted, the the MBM will be assumed with this tolerance, no matter how much A penetrates inside B. The C_A profile could be very far from being a true step function and the MBM would hold, provided ξ is the required tolerance. In this way a criterion can be established; it will be more general than, for example, that quoted by White (*14*), who states $h \geqslant 200$ to achieve the MBM.

A reasonable value for ξ would be 0.01, which means that we accept the MBM whenever the reaction that takes place on the internal surface is less than 1% of that produced on the outer surface area of the solid. It is also possible to observe that with such a tolerance and with a very low value of $\beta = (1-\alpha)/\alpha$ (there are actual systems for which it is 0.1) the MBM will hold if $\eta_i \leqslant 0.1$. This means that for porous solids the IEF necessary for the achievement of the MBM lies on the asymptotic region of the IEF, and this represents an important characteristic because it is in that region where an analytic solution of the IEF is available (*3*).

Hence, for an isothermal, first order with respect to A, irreversible solid–gas reaction with diffusivity and surface area profiles inside the spherical porous solid, Eq. (6) can be expressed as

$$\eta_i = \frac{h^+}{h} \leqslant \frac{0.01}{\beta}, \tag{7}$$

where h^+ is the correction factor for the distribution of diffusivity and surface area that has been obtained elsewhere (*3*).

Equation (7) shows that this criterion is not dependent upon the characteristic length (L) of the reactant solid; hence, Eq. (7) can be written as

$$h_0 \geqslant 100 h^+ \beta_0, \tag{8}$$

where the characteristic length in h_0 and β_0 is the original for the solid at $t = 0$.

Nevertheless, in the general case in which a solid is reacting with a gas to produce another solid, additional resistances can arise in the system, and it is possible to take this into consideration in the criterion that has just been established. Equation (3) shows that the physical picture of no mass transfer resistance in film and product layer around the reacting core will be obtained with an accuracy of 1% whenever

$$\frac{1}{1 + (\beta_0 h^+/h_0)} \geqslant 100 \frac{R^{*2}}{\mathrm{Bi}_k} \tag{9}$$

and

$$\frac{1}{1 + (\beta_0 h^+/h_0)} \geqslant \frac{100 R^*(1-R^*)}{\mathrm{Bi}_p}. \tag{10}$$

However, it is interesting to analyze the possibility of achieving the MBM under this situation. By introducing Eq. (8), a condition to validate the MBM without film concentration gradients is obtained;

$$\frac{100 R^{*2}}{\mathrm{Bi}_k} \leqslant 1. \tag{11}$$

From Eq. (11) it can be seen that Bi_k must be extremely high in order to satisfy both conditions given by Eqs. (8) and (9). In addition, as k' must be high enough to accomplish the MBM, the possibility of achieving the MBM without mass transfer resistance in gas film around the pellet is virtually restricted to nonporous solids.

In a similar way but working with Eqs. (8) and (10), we obtain

$$\frac{100 R^*(1-R^*)}{\mathrm{Bi}_p} \leqslant 1, \tag{12}$$

which implies a very high value of Bi_p except at initial stages of reaction, when the thickness of the product layer is very small. In other words, this situation implies such a relationship between the diffusivity of the original solid and that of the product, that it is very difficult to have the MBM without a simultaneous resistance in product layer, when it exists, or a gas film when there are no solid products.

ANALYSIS OF OTHER CRITERIA

The validity of the MBM has very often been claimed on the basis of experimental results in which there is some agreement between the data and relationships derived from the MBM itself. For example, the relationship between conversion and size or between size and time in a given geometry has been used. A cross-sectional photograph of a partially reacted sample showing a sharp transition between the ash layer and the reactive solid is sometimes given in evidence. Another criterion that has been used is the identity of the observed and the true activation energy.

Relationship between reactive solid size and conversion. It has been shown elsewhere (*3*) that the number of moles of reactant solid B present at a given time can be expressed by

$$n_B = C_{B_0} V(1 - \eta_i). \tag{13}$$

Writing Eq. (13) in terms of the conversion x_B for a spherical solid, the following expression is obtained:

$$\begin{aligned} x_B &= 1 - (1 - \eta_i) R^{*^3} \\ &= 1 - \left(1 - \frac{h^+}{h_0 K^*}\right) R^{*^3}. \end{aligned} \tag{14}$$

The same relationship, but for the MBM, is

$$x_B = 1 - R^{*^3}. \tag{15}$$

It is then observed, from the comparison of Eqs. (14) and (15) that for high values of the Thiele modulus the difference between both expressions will be negligible except for $R^* \rightarrow 0$.

Hence, unless the conversion-size relationship is determined with a high accuracy, it would be impossible to decide whether the MBM was achieved or not.

Relationship between reactive solid size and time. The relationship between size and time for a spherical isothermal solid with diffusional and surface area profiles and an irreversible, first-order reaction with respect to A has been obtained elsewhere (*3*). Let us compare this relationship with that obtained for the MBM when there is no influence of diffusional steps surrounding the reactive core. In this case the relationship is

$$t = \left[\frac{(1 - R^*)}{1 + [(\beta_0 h^+ / h_0)]} + \frac{2 \ln R^*}{3[(h_0/h^+) + \beta_0]} \right] \frac{R_0 C_{B_0}}{b r_{A_s} \epsilon_B f} \tag{16}$$

and that for the MBM is

$$t = (1 - R^*) \frac{R_0 C_{B_0}}{b r_{A_s} \epsilon_B f}. \tag{17}$$

The linear relationship between t and R^* is usually quoted to verify the achievement of the MBM. However, Eq. (16) also gives, in practice, a closely linear relationship between t and R^*. Nevertheless, the most important fact is that the coefficient of $(1 - R^*)$ in Eq. (16) can be much smaller than 1. Consequently, even though a linear relationship between t and R^* still holds, the slope of such a relationship could be quite different from that given by the MBM. This is extremely important in the case in which a kinetic measurement is analyzed, as well as when a design calculation is performed. Hence, a linear relationship between size and time cannot be used as a criterion to check the achievement of the MBM, and, in addition, the use of the MBM relationship leads to serious errors in the evaluation of constants when it is not achieved.

Reaction thickness. We have already said that another criterion that has been used to validate the MBM is to observe a cross-sectional cut in the solid showing a sharp transition between ash layer and solid reactant. In such a situation the reaction takes place in a layer so thin that its thickness can be considered negligible. Let us analyze what is meant by a "thin" layer from our present standpoint. We will refer to the case in which the reaction is not affected by the mass transfer through ash and boundary layers, namely, when the C_A profile is flat through them.

When the reaction is not described by the MBM, there are C_A and C_B profiles inside the solid B. If the reaction is taking place near the MBM condition, the concentration of A will fall to zero (or almost zero) in some part of B. Hence, it is possible to define a reaction thickness (δ) given by the distance between $C^*_B = 0$ and $C^*_A = 0.01$ where the reaction takes place. Working with high Thiele modulus, the mass balance for component A in spherical coordinates can be simplified to that of slab geometry, which, under the pseudo-steady-state assumption, will yield

$$\frac{d}{dz} D \frac{dC_A}{dz} = k' a_i C_A. \tag{18}$$

This equation has been integrated once to get the IEF. In doing so, it was necessary to use different pore models to establish a relationship between a_i and C_B and between C_A and C_B. This has been analyzed in detail elsewhere (*3*). Performing the first integration between $C_A = 0$ and $C_A = C_A$, it is possible to calculate dC_A/dz as a function of C_A, and doing a second integration between $C_A = 0.01 C_{A_s}$ and $C_A = C_{A_s}$, the reaction layer thickness (δ) is obtained as

$$\delta = \int_{0.01\, C_{A_s}}^{C_{A_s}} \frac{L(C_A) dC_A}{\left[2 \int_0^{C_A} D(C_A) r_A(a_i, C_A)\, dC_A \right]^{0.5}}. \tag{19}$$

At the same time, the effective diffusivity and the reaction rate can be written as follows (*3*):

$$D(C_A) = D_0(1 + eC^*_A)^2, \tag{20}$$

where $e = (\epsilon_s - \epsilon_0)/\epsilon_0$,

and

$$\begin{aligned} r_A(a_i, C_A) &= k' a_{i_0} C_{As} a^*_i C^*_A \\ &= k' a_{i_0} C_A\, f(C^*_A), \end{aligned} \tag{21}$$

where $a^*_i = a_i / a_{i_0}$.

Finally, if Eq. (21) is taken into account, Eq. (19) can be rewritten as

$$\delta^* = I/h_0, \tag{22}$$

where

$$I = \int_{0.01}^{1} \frac{(1 + eC^*_A)^2\, dC^*_A}{\left[2 \int_0^{C_A^*} (1 + eC^*_A)^2 f(C^*_A)\, dC^*_A \right]^{0.5}}. \tag{23}$$

It is necessary to evaluate I by a numerical method. The value of I will depend upon the function $f(C^*_A)$, which is given by the pore structure model selected, and also upon the value of e, which measures the influence of the effective diffusivity profile. The pore structure models used, dispersed solid model and Petersen model, are those already analyzed (*3*).

At the same time it will be interesting to compare the results from Eq. (22) with that which corresponds to a solid with uniform effective diffusivity and surface area (such as a catalyst). That is to say, when

$$D = D_0 \quad \text{and} \quad a_i = a_{i_0}. \tag{24}$$

In such a case Eq. (2) reduces to

$$\delta^* = 4.606/h_0. \tag{25}$$

The numerical integration of Eq. (22) for the dispersed solid and Petersen models shows very little difference from the value given by Eq. (25). Hence, by introducing Eq. (25) into Eq. (8) it is possible to obtain the criterion in terms of the reaction layer thickness:

$$\delta^* \leqslant \frac{4.606 \times 10^{-2}}{h^+ \beta_0}. \tag{26}$$

Equation (26) shows that for a 1-cm-diameter spherical solid with $h^+\beta_0 = 765$, δ must be $\leqslant 0.1\mu$ in order to achieve the MBM. In addition, if $h_0 = 765$, Eq. (8) shows that the criterion will not be satisfied and that the reaction thickness from Eq. (25) will be $\delta = 10\mu$ approximately.

Obviously, such a thickness will induce one to believe that the MBM is achieved. Since h^+ does not differ appreciably from unity (*3*), we have $\eta_i = 1/\beta_0$, and the reaction which takes on the outer surface area represents half of the total. Hence, from Eq. (16) it is seen that the relationship between $(1 - R^*)$ and t will be twice that of the MBM, leading to a falsification of the evaluated kinetic constant. Then, it is concluded that a "sharp" transition between the reactive solid core and the product is not a useful criterion for deciding whether or not the MBM is achieved.

Activation energy falsification. Let us analyze again the case in which the overall

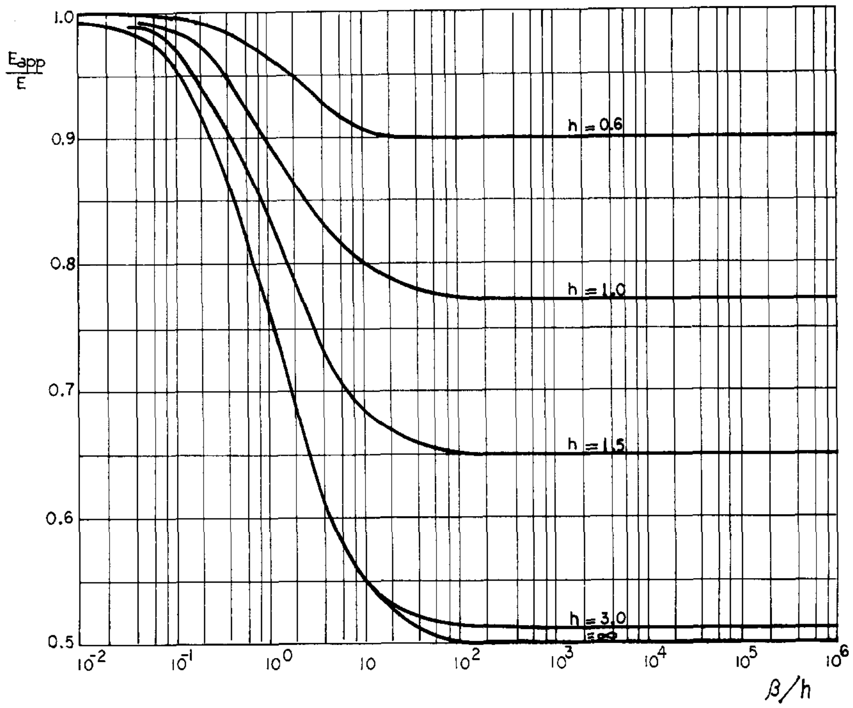

FIG. 1. Influence of Thiele modulus upon the falsification of the activition energy.

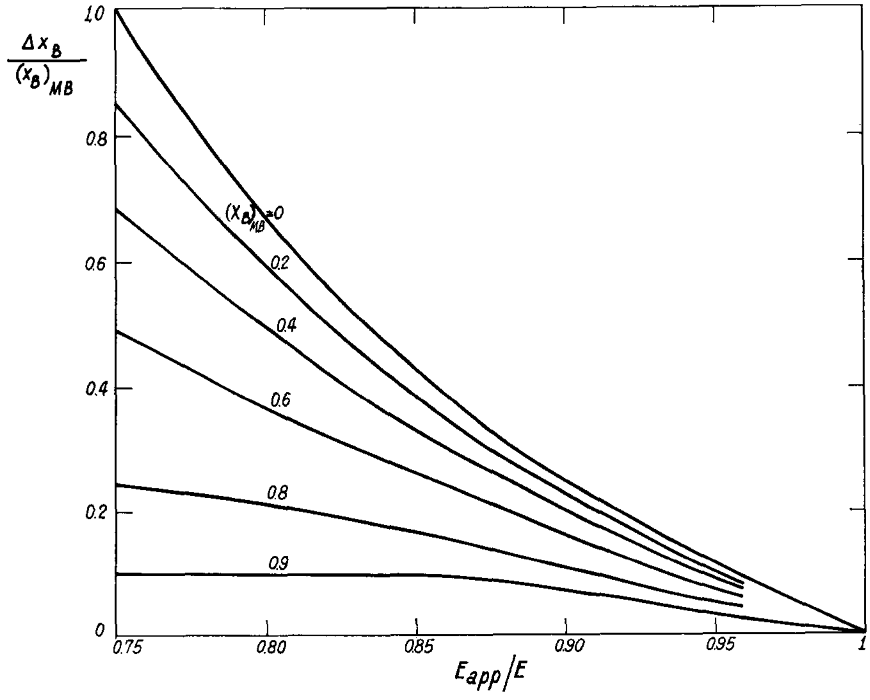

FIG. 2. Influence of the falsification of activation energy upon the error in conversion with respect to the moving boundary model.

reaction rate is not affected by the diffusion through ash or boundary layers. It is well known that the intrapellet diffusional effects modify the observed activation energy. It has been demonstrated (*2*) that the falsified or apparent activation energy E_{app} is related to the true one by

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

Applying Eq. (27) to a gas–solid reaction when $m = h/h^+$ is high enough to lie in the asymptotic region of the IEF and taking into account that $\phi = \eta m^2$, the following relationship is obtained:

$$\frac{E_{\mathrm{app}}}{E} = 1 + \frac{d \ln [1 + (\beta/m)]}{d \ln m^2}. \qquad (28)$$

From Eq. (28) it can be seen that once a value of β/m is proposed, there is one value of E_{app}/E. Since the ratio β/m is not dependent upon the characteristic length, it is possible to use β_0/m_0 to evaluate E_{app}/E from Eq. (28). Fig. 1 shows the monoparametric behavior of the asymptote.

On the other hand, for values of m_0 higher than 50 and conversion smaller than 98%, the logarithmic term of Eq. (16) can be neglected and the same can be said for the $1/m_0R^*$ term of Eq. (14).

Under such conditions Eqs. (14) and (16) can be rewritten as

$$x_{\mathrm{B}} = 1 - R^{*^3}, \qquad (29)$$

$$t^* = \frac{1 - R^*}{1 + (\beta_0 h^+/h_0)}, \qquad (30)$$

showing that the x_{B}–t^* relationship depends upon β_0/m_0. Hence, for the conditions mentioned, by giving a value to β_0/m_0 or to E_{app}/E, the relative error in the conversion can be obtained by taking the MBM as reference.

This ratio is shown in Fig. 2 as a function of E_{app}/E, with the conversion for the MBM $(x_{\mathrm{B}})_{\mathrm{MB}}$, as a parameter. Fig. 2 shows that the relative error in conversion increases as the conversion and E_{app}/E decrease. As shown by Fig. 2, only a rigorous measurement of E_{app}/E could be a criterion to verify the MBM assumption. However, taking into account the usual experimental error in the evaluation of the activation energy (at least ±10%), from Fig. 2 it is concluded that the use of E_{app}/E as a criterion can lead to a high error in the conversion-time relationship.

CONCLUSIONS

From the analysis of the criteria usually applied to check the MBM accomplishment, it can be concluded that Eq. (8) is the necessary and sufficient condition to check the achievement of the MBM in a reacting system under isothermal conditions. The criterion is expressed in terms of basic kinetic parameters and predicts whether or not a serious error will arise from the application of the model. In addition, when there is no influence of previous diffusional steps, it is shown that the possibility of obtaining the MBM is almost completely restricted to nonporous solids. The analysis also shows the extreme inaccuracy that could be introduced, either in the evaluation of kinetic constants or in the conversion-time relationship predictions, by using the MBM assumption in porous solids.

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