Effectiveness Factors in Gas-Liquid Reactions

The concept of the effectiveness factor, commonly used as a means of accounting for diffusional effects in gas-solid catalytic and noncatalytic reactions, is extended to gas-liquid reactions. The relevant differential equations for an isothermal system with appropriate boundary conditions are solved for the case of (1) a simple first-order irreversible reaction, (2) a consecutive reaction, and (3) a parallel reaction. The results are presented in terms of effectiveness factor plots, and methods of delineating the controlling regimes are discussed. It is shown that gas-liquid reactions represent perhaps the most general case which reduces to gas-solid reactions under appropriate limiting conditions.

B. D. KULKARNI
and
L. K. DORAISWAMY
National Chemical Laboratory
Poona-8, India

SCOPE

Very few attempts to extend the concept of the effectiveness factor to gas-liquid reactions have been reported in the literature. This concept has been widely used in gas-solid catalytic and noncatalytic systems to account for diffusion. Rony (1968) applied it to a simple gas-liquid catalyzed system and Shah and Kenney (1973) to another simple reaction scheme. A general analysis similar to that for gas-solid systems is still lacking, and the purpose of this paper is to analyze gas-liquid systems in terms of the effectiveness factor. A first-order irreversible isothermal reaction is first considered, and the basic equation for the effectiveness factor is obtained for reaction in the diffusion regime (that is, restricted to the bulk) as well as for the case where part of the reaction occurs in the film and the rest in the bulk. The treatment is then extended to consecutive and parallel reaction schemes. As with the simple reaction, in these cases also the object is to show that the gas-liquid system provides a general framework within which the gas-solid catalytic reaction fits under certain conditions.

Although the application of this concept to gas-liquid reactions has been hinted in the book by Astarita (1967), the present paper provides perhaps the first comprehensive analysis of the effectiveness factor concept as applied to gas-liquid reactions. In view of the work being done in this laboratory on gas-solid catalytic and noncatalytic reactions as well as on gas-liquid reactions, the use of a generalized approach based on a single concept—the effectiveness factor—arose as a distinct possibility.

The chief objective of an analysis of this kind is to enable the determination of the true kinetic parameters of a reaction as well as to predict the performance of industrial contactors under specific condition of operation. Thus, as part of this paper, an analysis of the various regimes of control and the bounds within which they lie is also made. The entire gamut of controlling regimes can be depicted on a single effectiveness factor plot as distinct regions in the plot. Under certain conditions these regions degenerate into a line which represents the usual effectiveness factor plot for a gas-solid reaction.

CONCLUSIONS AND SIGNIFICANCE

The results are presented in terms of a plot of the effectiveness factor as a function of the Thiele modulus with a new quantity β as parameter. β represents the ratio of the area per unit volume in the film $1/\delta$ to that in the liquid a and is therefore a measure of the participation of the bulk in the overall process. Thus when $\beta = 0$ there is no contribution from the bulk. The use of this parameter β generalizes the application of the effectiveness factor concept to gas-solid as well as gas-liquid reactions.

In the effectiveness factor plot for gas-liquid reactions, therefore, several curves are obtained with β as parameter. With these curves as the basis the controlling regime for a reaction can be easily determined. Upper and lower bounds can be drawn so that the entire region bounded by the effectiveness factor axis, Thiele modules axis, and the curve for $\beta = 0$ is divided into distinct regimes of control. Principally four regimes can be identified: (1) in which the effectiveness factor is greater than 0.95 and therefore corresponds to the kinetic regime, (2) in which the reaction occurs in the bulk (as in the kinetic regime) but is controlled by pure diffusion through the film, (3) in which part of the reaction occurs in the film and part in the bulk, and (4) in which reaction is restricted to the film. The boundary between the last two can only be fixed approximately by neglecting the reaction in the bulk at an assumed low value of the effectiveness factor. Although in general the effectiveness factor for reaction in the film is quite low, the exact regime of control depends also on the value of β.

For a known value of the parameter β, the effectiveness factor determined experimentally under a given set of conditions can be used to determine the regime of control. The appropriate equation can then be used for design or for obtaining the kinetic parameters of the reaction. The concept of the effectiveness factor as applied to gas-liquid reactions is more complicated and involves a region as against a line in gas-solid reactions. The common effectiveness factor expression for reaction in a catalyst slab is merely a special case of gas-liquid reactions when $\beta = 0$,

namely, when the reaction is complete in the catalyst (which, in gas-liquid phraseology, may be called a *film*).

The effectiveness factor concept can also be applied to consecutive as well as parallel reaction schemes. In both the cases the equations reduce to those for gas-solid catalytic reaction in a slab when β approaches zero. It would therefore appear that the effectiveness factor concept can be usefully employed for all reaction systems, namely, gas-solid catalytic, gas-solid noncatalytic, and gas-liquid, as well as for simple and complex reactions.

In the analysis of chemical reactions occurring in fluid-fluid and fluid-solid systems, two entirely different approaches have been employed. In the case of fluid-fluid reactions, particularly gas-liquid reactions, it is customary to regard chemical reaction as an accelerator of the absorption process and to define an enhancement factor which is the ratio of the absorption rate with chemical reaction to that under conditions of no reaction. On the other hand, for fluid-solid reactions, particularly solid catalyzed gas phase reactions, chemical reaction is regarded as the main process with diffusion acting as a retarding influence; thus an effectiveness factor is defined which is the ratio of chemical reaction in the presence of diffusion to that in the absence of any diffusional effect.

As long as one is designing equipment with the object of carrying out a chemical reaction in it, it is logical to regard chemical reaction as the principal process. Thus, irrespective of the type of system employed (namely, gas-liquid, gas-solid catalytic, gas-solid noncatalytic, liquid-liquid, etc.), it seems reasonable to use a single concept of the effectiveness factor as a common means of accounting for diffusion. This concept has been widely employed for gas-solid catalytic and gas-solid noncatalytic systems, but there is hardly any reported attempt to extend it to other systems. The purpose of this paper is to present an analysis of gas-liquid systems in terms of the effectiveness factor and to propose methods of delineating the controlling regimes based on this concept.

Based on the film theory four distinct regimes can be identified in gas-liquid reactions: (1) very slow reaction where the reaction occurs entirely in the bulk; (2) slow reaction where there is a diffusional resistance in the film, but the reaction still occurs only in the bulk; (3) the reaction is complete in the film, and (4) the reaction is so fast that the active species from the liquid diffuses partly into the film and the reaction occurs on a plane within the film. In the first case the reaction is completely kinetically controlled, in the second diffusion controlled, in the third controlled both by diffusion and chemical reaction, and in the fourth instantaneous. Since the concept of the effectiveness factor can be conveniently applied to the first three cases, the present treatment will be restricted to the analysis of a first-order irreversible isothermal reaction under two conditions: (1) reaction is confined to the bulk with film diffusion controlling, and (2) reaction occurs both in the film and bulk. Case (1) corresponds to regime 2, and case (2) to regime 3 and the regime between 2 and 3.

REACTION COMPLETE IN BULK

This regime is characterized by a pure diffusional resistance in the film, with reaction confined exclusively to the bulk. The reaction is not so fast as to occur in the film simultaneously with diffusion, but is fast enough to offer less resistance than pure diffusion in the film. The concentration gradients for this regime are shown in Figure 1a.

Considering the reaction

$$A \rightarrow \text{Products}$$

the following mass balance equation can be written for A:

$$-D_A \frac{d\,C_A}{d\,y}\Big|_{y=\delta} = k_L\,[C_A{}^* - C_{A0}] \tag{1}$$

or, in dimensionless form,

$$-\frac{d\,w_A}{d\,x}\Big|_{x=1} = [1 - w_{A0}] \tag{2}$$

where

$$w_A = \frac{C_A}{C_A{}^*},\quad w_{A0} = \frac{C_{A0}}{C_A{}^*},\quad x = \frac{y}{\delta}\quad \text{and}\quad \delta = \frac{D}{k_L} \tag{3}$$

The rate of reaction in the bulk is given by

$$r_B = k_1\,C_{A0} = k_1\,C_A{}^*\,w_{A0} \tag{4}$$

which, when combined with Equation (2), leads to

$$r_B = k_1\,C_A{}^*\left[1 + \frac{d\,w_A}{d\,x}\Big|_{x=1}\right] \tag{5}$$

$\frac{d\,w_A}{d\,x}\Big|_{x=1}$ may be evaluated in terms of a Thiele modulus m and another dimensionless number β obtained from the relationship

$$-D_A \frac{d\,C_A}{d\,y}\Big|_{y=\delta} = \frac{k_1\,C_{A0}}{a} \tag{6}$$

Thus, in dimensionless form, this can be written as

$$-\frac{d\,w_A}{d\,x}\Big|_{x=1} = \frac{k_1\,\delta^2}{D_A}\,\frac{1}{a\delta}\,\frac{C_{A0}}{C_A{}^*} = m^2\,\beta\,w_{A0} \tag{7}$$

where β represents the ratio of the volume per unit area of the bulk $[1/a]$ to the volume per unit area of the film δ.

Substitution of Equation (7) in (5) leads to

$$r_B = \frac{k_1\,C_A{}^*}{1 + m^2\,\beta} \tag{8}$$

The rate of reaction in the absence of any diffusional resistance will be given by $k_1\,C_A{}^*$; hence the following expression for the effectiveness factor can be written

$$\eta = \frac{k_1\,C_A{}^*}{k_1\,C_A{}^*[1 + m^2\,\beta]} = \frac{1}{1 + m^2\,\beta} \tag{9}$$

From Equation (9) it can be seen that the effectiveness factor is not only a function of the modulus m but also of the dimensionless ratio β. Since this analysis is restricted to control by pure diffusion in the film and it is assumed that chemical reaction is reasonably fast, the effectiveness factor should necessarily be less than one. This can happen only when β has a finite value. For a value of β close to zero (namely, the interfacial area $a \rightarrow \alpha$), the physical situation would be that no liquid bulk exists. This situation is clearly impossible for a gas-liquid reaction so that η can never be equal to unity in the diffusion regime. It may be noted that there is no counterpart to this regime in gas-solid catalytic reactions. For such a hypothetical situation $\beta = 0$ (as explained later in the paper) so that $\eta = 1$. Thus this regime merges with the kinetic regime.

Equation (9) for gas-liquid reactions is therefore strictly valid only up to a certain finite value of β. If, as in the case of catalytic reactions, it is stipulated that the reaction can be assumed to be diffusion influenced if η is $\lesssim 0.95$, the following condition can be written for the applicability of Equation (9):

$$\left.\begin{array}{c} \dfrac{1}{1 + m^2 \beta} \lesssim 0.95 \\ \text{or} \qquad \\ m^2 \beta \gtrsim 0.05 \end{array}\right\} \qquad (10)$$

η is plotted as a function of the modulus m for various values of β in Figure 2. For β equal to zero, that is, when the interfacial area a tends to infinity, practically no liquid bulk exists, and hence for a system under diffusion control no reaction can occur.

REACTION BOTH IN THE FILM AND BULK

Let us now consider the more general case where a part of the reaction occurs in the film and the rest in the bulk. The concentration profile for this situation will be as shown in Figure 1b. This should be distinguished from regime 3 in which the reaction is complete in the film. The situation considered is thus a more general one which reduces to regime 3 when there is no reaction in the bulk. In this analysis a simple irreversible first-order reaction will first be considered and the treatment then extended to a consecutive reaction.

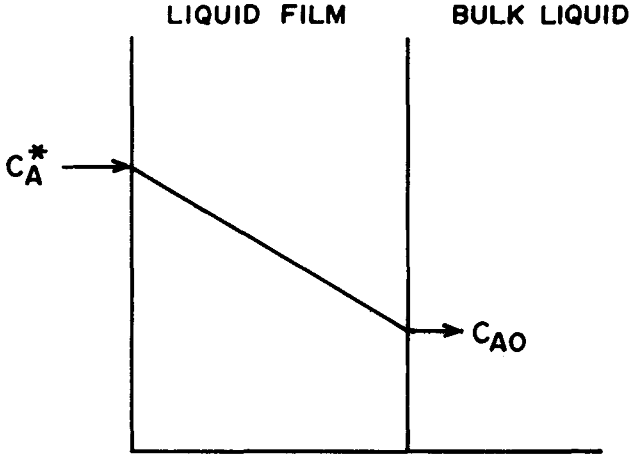

Fig. 1a. Concentration profiles in the film: Diffusional resistance.

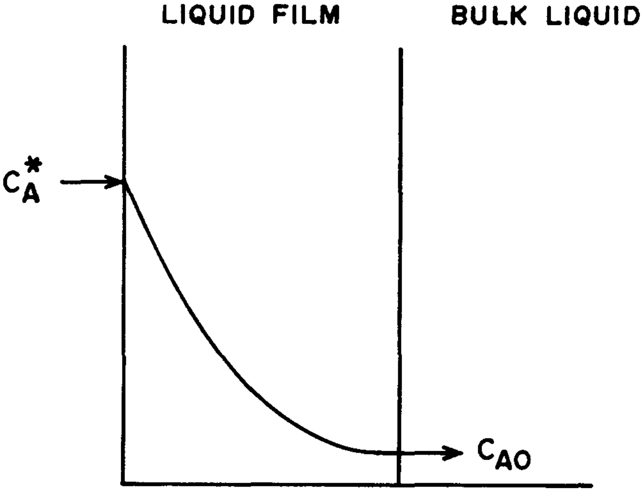

Fig. 1b. Concentration profiles in the film: Part of reaction in film and rest in bulk.

Simple Reaction

Considering a first-order isothermal reaction, the mass balance equation for the film is given by

$$D_A \frac{d^2 C_A}{d y^2} = k_1 C_A \qquad (11)$$

or, in dimensionless form, by

$$\frac{d^2 w_A}{d x^2} = m^2 w_A \qquad (12)$$

The initial and final boundary conditions are

$$x = 0, \quad w_A = 1 \qquad (13a)$$

$$x = 1, \quad -\frac{d w_A}{d x} = m^2 \beta w_{A0} \qquad (13b)$$

Boundary condition (13b) represents the mass flux at the $x = 1$ plane (end of film) equated to that consumed in the bulk. In other words, it represents the kinetic boundary condition and is applicable both to the film and the bulk. The usual Danckwerts boundary condition, which demands that the flux be zero, is not applicable in this case. This constitutes the major difference between solid catalyzed gas-phase reactions and gas-liquid reactions. In the former the entire reaction is completed in the solid (that is, the *film*) and there is thus neither a positive nor negative flux at the end of the pore, namely, $\dfrac{d w_A}{d x} = 0$. There is no such restriction in the general kinetic boundary condition represented by (13b).

Equation (12) may be solved through boundary condition (13) to give the following equation for the concentration profile:

$$w_A = \frac{- m \beta w_{A0} [\sinh mx] + \cosh m [1 - x]}{\cosh m} \qquad (14)$$

The total mass flux at $y = 0$ is then calculated as

$$-D_A \frac{d C_A}{d y}\bigg|_{y=0} = \frac{D_A C_A^*}{\delta} \left[\frac{m^2 \beta w_{A0}}{\cosh m} + m \tanh m \right] \qquad (15)$$

Equation (15) represents the total mass flux consumed by reaction in the film plus that in the bulk. The total reaction flux under ideal conditions (that is, with no diffusional influence) will be given by reaction occurring in the film (usually a very small quantity) plus the reaction occurring in the bulk:

$$\begin{aligned} r_A &= k_1 C_A^* \delta + \frac{k_1 C_A^*}{a} \\ &= k_1 C_A^* \left[\frac{1 + a \delta}{a} \right] \end{aligned} \qquad (16)$$

In writing Equation (16), the assumption has been made that at the film-bulk interface the conditions existing in the bulk and the film are both operative. Actually in the kinetic regime the only difference between the two is in respect to the area available for the reaction, the concentration of A in both being equal to C_A^* (as there is no diffusional resistance). In reality, in a situation of this kind, the film can be ignored. But in order to maintain similarity with the developments that follow, the total intrinsic reaction is hypothetically divided into film and bulk contributions.

The effectiveness factor for the system is given by

$$\eta = \frac{1}{1+\beta}\left[\frac{\beta\, w_{A0}}{\cosh m} + \frac{\tanh m}{m}\right] \tag{17}$$

w_{A0}, the dimensionless concentration in the bulk, may be expressed in terms of the modulus m using Equation (14) with the condition that at $x = 1$, $w_A = w_{A0}$; thus

$$w_{A0} = \frac{1}{\cosh m}\left[\frac{1}{1 + m\,\beta \tanh m}\right] \tag{18}$$

Substituting Equation (18) in (17)

$$\eta = \frac{1}{1+\beta}\left[\frac{\beta}{[\cosh m]^2\,[1 + m\,\beta\tanh m]} + \frac{\tanh m}{m}\right] \tag{19}$$

This equation is also plotted in Figure 2, and the main features of the plot are discussed in the section on Controlling Regimes.

Consecutive Reactions

A first-order consecutive chemical reaction of the gaseous species A dissolved in a liquid is considered here in order to bring out the applicability of the effectiveness factor concept to gas absorption followed by a complex reaction. Thus, for the scheme

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

the following differential mass balance can be written for each species:

$$D_A \frac{d^2 C_A}{d y^2} = k_1 C_A \tag{20}$$

$$D_B \frac{d^2 C_B}{a y^2} = - k_1 C_A + k_2 C_B \tag{21}$$

with the initial and boundary conditions:

$$\left.\begin{aligned} C_A &= C_A^* \\ C_B &= C_B^* \end{aligned}\right\} \quad \text{at } y = 0, \text{ and} \tag{22}$$

$$\begin{aligned} -D_A \frac{d C_A}{d y}\bigg|_{y=\delta} &= \frac{k_1 C_{A0}}{a} \\ -D_B \frac{d C_B}{d y}\bigg|_{y=\delta} &= \frac{k_2 C_{B0}}{a} - \frac{k_1 C_{A0}}{a} \end{aligned} \tag{23}$$

These equations can be arranged in dimensionless form using the transformation

$$w_i = \frac{D_i C_i}{\Sigma D_i C_i^*}, \quad i \text{ species } A, B \tag{24}$$

which reduces to $w_A = C_A/C_B^*$ where only A is involved.

Thus we have

$$\frac{d^2 w_A}{d x^2} = m_1^2 w_A \tag{25}$$

and

$$\frac{d^2 w_B}{d x^2} = - m_1^2 w_A + m_2^2 w_B \tag{26}$$

with the transformed boundary conditions:

$$w_A^* = \frac{D_A C_A^*}{\Sigma D_i C_i^*}, \quad w_B^* = \frac{D_B C_B^*}{\Sigma D_i C_i^*}, \quad \text{at} \quad x = 0 \tag{27}$$

$$-\frac{d w_A}{d x}\bigg|_{x=1} = m_1^2 \beta w_{A0}, \quad -\frac{d w_B}{d x}\bigg|_{x=1} = [m_2^2 w_B - m_1^2 w_{A0}]\,\beta \tag{28}$$

In writing Equations (28) and (23) the kinetic boundary condition explained earlier has been used.

Equation (25) under boundary conditions (27) and (28) can be solved to give the concentration profile for A:

$$w_A = \left[\frac{D_A C_A^*}{\Sigma D_i C_i^*}\,\frac{\cosh m_1 [1-x]}{\cosh m_1} - \frac{m_1 \beta w_{A0} \sinh m_1 x}{\cosh m_1}\right] \tag{29}$$

With this concentration profile, Equation (26) becomes

$$\frac{d^2 w_B}{d x^2} = - m_1^2 \left[\frac{D_A C_A^*}{\Sigma D_i C_i^*}\,\frac{\cosh m_1 [1-x]}{\cosh m_1} - \frac{m_1 \beta w_{A0}\sinh m_1 x}{\cosh m_1}\right] + m_2^2 w_B \tag{30}$$

This is a second-order differential equation, which can be solved to get the concentration profile for the species B:

$$w_B = \left(w_B^* + \frac{\Delta^2}{\Delta^2 - 1} w_A^*\right)\frac{\cosh m_2 [1-x]}{\cosh m_2} + m_2\left[(w_{B0} - \Delta^2 w_{A0}) - \frac{\Delta^2}{\Delta^2-1}\,\frac{m_1^2 \beta w_{A0}}{m_2}\right]\frac{\sinh m_2 x}{\cosh m_2} - \frac{\Delta^2}{\Delta^2-1} w_A \tag{31}$$

where Δ represents the ratio of the moduli, m_1 and m_2.

From Equations (29) and (31), the ratio of the rates of production of B and reaction of A can be obtained as

$$\frac{\left.\dfrac{d w_B}{d x}\right|_{x=0}}{\left.\dfrac{d w_A}{d x}\right|_{x=0}} = \frac{\text{rate of production of } B}{\text{rate of reaction of } A} = \gamma \tag{32}$$

Hence

$$\gamma = \left[\frac{m_2 \tanh m_2\left(w_B^* + \dfrac{\Delta^2}{\Delta^2-1} w_A^*\right) - \left[m_2^2 (w_{B0} - \Delta^2 w_{A0}) - \dfrac{\Delta^2}{\Delta^2-1} m_1^2 \beta w_{A0}\right]\dfrac{1}{\cosh m_1}}{m_1 \tanh m_1 w_A^* + \dfrac{m_1^2 \beta w_{A0}}{\cosh m_1}}\right] + \frac{\Delta^2}{\Delta^2-1} \tag{33}$$

For the case where the reaction of both B and A is complete in the film, w_{B0} and w_{A0} are zero. Further, m_1 and m_2 being high (for a fast reaction), tanh m_1 and tanh m_2 approach unity. Thus

$$\gamma = \left[\frac{\Delta}{\Delta+1} - \frac{w_B^*}{\Delta w_A^*}\right] \tag{34}$$

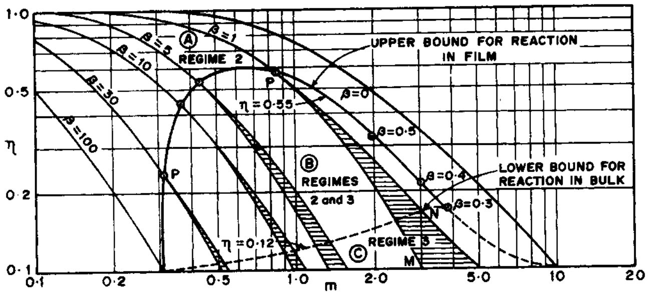

Fig. 2. Determination of the lower and upper bounds for reaction in the bulk.

Equation (34) is the well known equation for a first-order consecutive reaction scheme in an isothermal catalyst where the reaction is considered to be complete in the film. Thus Equation (33) represents the most general solution for a first-order consecutive chemical reaction under isothermal conditions.

Parallel Reactions

The effectiveness factor concept can also be used to define the selectivity of a product in a parallel reaction scheme in gas-liquid reactions. Let us consider a general pth qth order reaction,

$$\begin{array}{c} B \\ \nearrow \\ A \\ \searrow \\ C \end{array}$$

The mass balance equation for this scheme may be written as

$$D_A \frac{d^2 C_A}{d y^2} = k_1 C_A{}^p + k_2 C_A{}^q \tag{35}$$

with the initial and final boundary conditions:

$$y = 0, \quad C_A = C_A{}^* \tag{36a}$$

$$y = \delta, \quad -D_A \frac{d C_A}{d y} = [k_1 C_{A0}{}^p + k_2 C_{A0}{}^q] \frac{1}{a} \tag{36b}$$

Equation (36b) represents the kinetic boundary condition explained earlier.

Equation (35) can be integrated once to give

$$\frac{d C_A}{d y} = \left\{ \frac{2}{D_A} \left[\frac{k_1}{p+1} (C_A{}^{p+1} - C_{A0}{}^{p+1}) + \frac{k_2}{q+1} (C_A{}^{q+1} - C_{A0}{}^{q+1}) \right] - \left(\frac{1}{a D_A} \right)^2 (k_1 C_{A0}{}^p + k_2 C_{A0}{}^q)^2 \right\}^{1/2} \tag{37}$$

which, in dimensionless form, becomes

$$\frac{d w_A}{d x} = \sqrt{2} m \left\{ \frac{(w_A{}^{p+1} - w_{A0}{}^{p+1})}{p+1} + \frac{M^* (w_A{}^{q+1} - w_{A0}{}^{q+1})}{q+1} - \frac{[m \beta w_{A0}{}^p (1 + M^0)]^2}{2} \right\}^{1/2} \tag{38}$$

where

M^* = ratio of the true rates of reaction

$$\frac{k_2 C_A{}^{*q+1}}{k_1 C_A{}^{*p+1}}$$

M^0 = ratio of the rates of reaction in the bulk

$$\frac{k_2 C_{A0}{}^{q+1}}{k_1 C_{A0}{}^{p+1}}$$

The selectivity for the component B can then be obtained from Equation (32) which becomes

$$\gamma = \frac{\int_0^1 w_A{}^p \, d x + \beta w_{A0}{}^p}{[1 + M^*][\beta + 1]} \tag{39}$$

For the specific case of $\beta = 0$ this reduces to

$$\gamma = \frac{\int_0^1 w_A{}^p \, d x}{[1 + M^*]} \tag{40}$$

which is the equation for a gas-solid catalytic reaction derived recently by Roberts (1972). Thus Equation (39) is of the correct form and represents the situation for the more general case where β has finite positive values.

For specific orders [p, q], Equation (37) can be cast into standard forms of integration and evaluated to obtain the concentration profile. Equation (40) can then be used to calculate the selectivity of the reaction. The procedure is similar to that followed in the case of gas-solid reactions (Roberts, 1972) and is not repeated in this paper. The important point to stress here is that by changing the usual Danckwerts boundary condition at the end of the film to the kinetic boundary condition [Equation (36b)] it is possible to derive an expression for gas-liquid reactions of which gas-solid reactions (flat plate geometry) constitute a special case ($\beta = 0$). Thus it seems reasonable to use the single concept of effectiveness factor irrespective of the type of system involved to represent the selectivity in the case of parallel reactions also. Onda et al. (1970) analyzed this system in terms of the enhancement factor usually employed for gas-liquid reactions.

CONTROLLING REGIMES

An examination of Figure 2 reveals some interesting features, based on which certain generalized conclusions can be drawn with respect to regimes 1, 2, and 3 for simple first-order reactions.

In preparing this plot for gas-liquid reactions, the effectiveness factor η is plotted against the modulus m for various values of the parameter β with the curve for $\beta = 0$ (for gas-solid catalytic reactions) representing the upper limit. Three separate regions A, B, and C can be identified. In region A (which corresponds to regime 2) the reaction is confined to the bulk; in region C (which corresponds to regime 3) the reaction is confined to the film; while in region B (intermediate between regimes 2 and 3) the reaction occurs both in the bulk and the film. The bounds for these regions can be fixed from the following considerations.

Let us take the curves for, say, $\beta = 1$. The upper curve represents the case where a part or whole of the reaction occurs in the film (regimes 2 and 3), while the lower curve represents the case where there is a pure diffusional resistance and the reaction is confined to the bulk (regime 2). P represents the point of separation between these curves. The locus of all such points for various values of β will give the lower bound for region A, above which the reaction is confined to the bulk and below which a part of the reaction occurs in the film also. If an upper bound for region C can be fixed, then all the three regions can be clearly demarkated. Unfortunately, it is not possible to precisely fix the boundary between regions B and C. If, however, it is assumed that reaction in the bulk is negligible at $\eta < 0.1$ (which is a reasonable assumption), then an approximate upper bound can be prescribed for region C. Thus let us again consider the case, $\beta = 1$. The lower curve (corresponding to reaction in the bulk) intersects the m-axis at the point M. Since this point corresponds to $\eta = 0.1$, it will be assumed that any reaction occurring will be restricted to the film and this will correspond to the point N on the upper curve (located by drawing an ordinate from M). The locus of all such points for various values of β will give the upper bound for the reaction to be confined to the film, namely, for region C. Since this is not a true bound and is only an approximate one, this is shown in the figure by a broken curve.

For a given value of m, therefore, the region A represents the fast reaction regime where only the film is involved. The region B represents the case where a part of the reaction occurs in the film and the rest in the bulk. The region C represents the case where only diffusion in the film is predominant and the reaction occurs wholly in the bulk. The region $0.95 < \eta < 1.0$ represent the kinetic regime. These various regimes are clearly brought out in Figure 2.

Having defined the regions A, B and C, some interesting conclusions can be drawn from a study of these regions.

1. For a given value of m, several values of the effectiveness factor η are possible depending on the value of β. The value of η also determines the regime in which the reaction occurs. For $m = 1$, for instance, if η is less than 0.12 the reaction occurs in regime 3 (remembering always the assumption involved in prescribing the upper bound for this regime). If η is between 0.12 and 0.55, the reaction occurs in a region between regimes 2 and 3. For η between 0.55 and 1.0, regime 2 alone is involved. It will thus be noticed that for the same value of m several regimes of control are possible. This is distinctly different from solid catalyzed reactions where a unique value of η exists for a given value of m. If an analogy is to be drawn between gas-liquid and gas-solid catalytic reactions, it can be stated that any diffusional limitation in the latter will always place it in an expanded version of regime 3 in which the reaction need not be complete in the film. There is nothing like a bulk in catalytic reactions so that the reaction must be confined to the catalyst which may be regarded as equivalent to the film in gas-liquid reactions. It is interesting to note that for a gas-liquid system where the reaction is complete in the film the effectiveness factor is very much lower than for a gas-solid system (in which case the reaction need not be complete in the solid, that is, the film), being represented by a point in region A.

2. In view of the fact that the upper bound for regime 3 is much lower than the lower bound for regime 2, it might appear that the effectiveness factor for regime 3 should always be less than for regime 2 or for the region between regimes 2 and 3. This is not always true, for the regime of control depends on the value of m. Thus η can have a value as high as about 0.16 for $m = 3$ in regime 3, while for values of m less than 3 it will be lower than 0.16 in regimes 2-3.

3. The various points listed previously bring out the fact that in gas-liquid reactions what is involved is the region bounded by the effectiveness factor and modulus axes on two sides and by the curve for $\beta = 0$ on the third. This region represents a number of regimes, and the value of η depends on the regime in which the reaction is occurring. As against this surface based effectiveness factor for gas-liquid reactions, that for a solid catalyzed reaction is determined by a line. The curve $\beta = 0$ indeed represents the effectiveness factor for a gas-solid catalytic reaction as can be verified from the fact that Equation (19) with $\beta = 0$ reduces to

$$\eta = \frac{\tanh m}{m} \tag{41}$$

This equation is clearly the effectiveness factor equation for a slab. Thus the concept of the effectiveness factor as applied to gas-liquid reactions is considerably more complicated and is expressed in terms of a region instead of a line.

NOTATION

a = interfacial area
C_i = concentration of species i
D_A = diffusivity of species A
k = rate constant for the reaction
k_L = physical mass transfer coefficient
M^* = the ratio of rates of reaction, $\dfrac{k_2 C_A{}^{*q+1}}{k_1 C_A{}^{*p+1}}$
M = the ratio of rates of reaction in bulk, $\dfrac{k_2 C_{A0}{}^{q+1}}{k_1 C_{A0}{}^{p+1}}$
m = modulus defined as $\delta \sqrt{\dfrac{k_1 C_A{}^{*p-1}}{D_A}}$ for a pth order reaction
r_B = rate of reaction in bulk
w_A = dimensionless concentration
w_{A0} = dimensionless concentration in bulk
x = dimensionless distance, y/δ

Greek Letters

β = dimensionless number defined as $1/a\delta$
γ = selectivity ratio defined by Equation (34) and Equation (39) for consecutive and parallel reactions respectively
δ = film thickness
Δ = m_1/m_2

Superscript

$*$ = value at the interface

Subscripts

0 = value in the bulk of liquid
1, 2 = values for the first and second steps of consecutive and parallel reactions

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