Gas Absorption Accompanied by an Irreversible Reaction of General Order

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The use of idealized models of the fluid mechanics of the gas absorption process in order to calculate theoretical predictions of the effect of a simultaneous chemical reaction upon the rate of gas absorption dates back to the pioneering work of Hatta (*11*). The two models which have been most frequently used are the film-theory model (*23*) and the penetration-theory model (*12*). More recently, various surface-renewal models have also been used (*5, 7, 8*) which differ from the penetration theory in that they employ different surface age distribution functions. For a review of these theoretical models and their use in predicting the effect of a simultaneous chemical reaction upon the rate of gas absorption the reader is referred to references *1, 3, 4, 5, 7, 16, 20, 22*. Such theoretical solutions have had an important impact upon the understanding of mass transfer with simultaneous chemical reaction, guiding many experimental investigations (*2, 5, 6, 7, 9, 10, 13, 14, 15, 17, 18, 19, 21*). Indeed comparisons between experimental results and theoretical predictions have not only been used to check the applicability of the theory but they have also been used to infer the kinetics and the mechanisms of very fast gas-liquid reactions (*2, 5, 10, 18, 21*).

The type of chemical system which has received the most attention is that in which a gaseous species dissolves and then reacts irreversibly with a nonvolatile solute already present in the liquid phase. For the case of a second-order chemical reaction between the dissolving species and the nonvolatile solute, an approximate solution to the film theory was presented by Van Krevelen and Hoftijzer (*22*), and the accuracy of this approximate solution was demonstrated by Peaceman (*15*). The penetration-theory solution for this case was obtained numerically by Perry and Pigford (*16*) for a limited range of variables and later by Brian, Hurley, and Hasseltine (*1*) for a much wider range of variables. It is the purpose of this paper to generalize this penetration-theory solution with respect to the order of the chemical kinetic equation. This generalization will illustrate the effect of the form of the chemical reaction kinetic equation upon the gas absorption rate, and it should be especially useful as an aid to planning experiments for determining reaction kinetics from absorption rate measurements, as outlined in reference *10*.

THE THEORETICAL MODEL

The problem to be considered is that in which a gaseous species A dissolves into the liquid phase

$$A_{(G)} \leftrightharpoons A_{(L)} \tag{1}$$

and then reacts irreversibly with species B, a nonvolatile solute which is already present in the liquid phase:

$$A_{(L)} + \nu B_{(L)} \rightarrow \text{products, irreversibly} \tag{2}$$

It is assumed that the gas-phase resistance to absorption is negligible, and thus the concentration of species A at the gas-liquid interface corresponds to equilibrium with the partial pressure of species A in the bulk gas phase. The chemical reaction depicted by Equation (2) is assumed to proceed in accordance with the kinetic equation

$$R = k_F\,[A]^n[B]^m \tag{3}$$

in which k_F, n, and m are assumed to be constants. The penetration-theory model of the liquid flow pattern is used, and the assumptions of this model are presented in reference *1*.

The problem is described mathematically by two nonlinear partial differential equations

$$\left(\frac{\partial^2 a}{\partial z^2}\right) - \left(\frac{\partial a}{\partial \theta}\right) = a^n b^m \tag{4}$$

$$r\left(\frac{\partial^2 b}{\partial z^2}\right) - \left(\frac{\partial b}{\partial \theta}\right) = (1/q)\, a^n b^m \tag{5}$$

with the following boundary conditions:

$$\text{At } \theta = 0, \text{ any } z > 0 \quad \begin{cases} a = 0 \\ b = 1 \end{cases} \tag{6}$$

$$\text{At } z = 0, \text{ any } \theta > 0 \quad \begin{cases} a = 1 \\ \dfrac{\partial b}{\partial z} = 0 \end{cases} \tag{7}$$

$$\text{As } z \rightarrow \infty, \text{ any } \theta \quad \begin{cases} a = 0 \\ b = 1 \end{cases} \tag{8}$$

These equations, in dimensionless form, are the same as those presented in reference *1* except for the exponents n and m on the right-hand sides of Equations (4) and (5) and except for the definitions of the dimensionless time θ, the dimensionless distance z, and the concentration ratio, q.

The desired result is ϕ, the ratio of k_L to k_L°; thus ϕ is a measure of the amount by which the simultaneous chemical reaction increases the rate of absorption of species A. After the differential equations have been solved to yield a and b as functions of z and θ, ϕ can be obtained by any one of the following three equations:

$$\phi = \sqrt{\frac{\pi}{4\theta}} \int_0^\theta \left(\frac{-\partial a}{dz}\right)_{z=0} d\theta' \tag{9}$$

$$\phi = \sqrt{\frac{\pi}{4\theta}} \int_0^\infty [a + q(1-b)]\, dz' \tag{10}$$

$$\phi = \sqrt{\frac{\pi}{4\theta}} \left[\int_0^\infty a\, dz' + \int_0^\theta \int_0^\infty a^n b^m\, dz'\, d\theta' \right] \tag{11}$$

INFINITELY RAPID CHEMICAL REACTION

For given values of r and q the variable ϕ approaches an asymptotic value at large values of θ. This asymptote ϕ_a is the solution for an infinitely rapid chemical reaction. The relation between ϕ_a, r, and q has been obtained analytically by Danckwerts (*4*) and by Sherwood and Pigford (*20*). The result may be represented by the parametric equations

$$\left.\begin{aligned} \phi_a &= 1/\text{erf}\ (\sigma) \\ q\sqrt{r} &= \frac{1-\text{erf}\ (\sigma/\sqrt{r})}{\text{erf}\ (\sigma)\ \exp\ [\sigma^2(1-1/r)]} \end{aligned}\right\} \tag{12}$$

and a graphical presentation of this solution is given in reference *1*. When the rate of the chemical reaction is essentially infinite, relative to diffusion rates, the form of the reaction kinetic equation will have no effect upon the solution. Thus Equations (12) apply no matter what the values of n and m.

PSEUDO nth-ORDER REACTION

For a given value of θ, as the diffusivity ratio r or the concentration ratio q is increased, an asymptotic region will be approached in which the concentration of species B will vary negligibly throughout the liquid phase. Thus species A will undergo a pseudo nth -order reaction. In this region Equation (5) need not be considered, and Equation (4) can be simplified by setting b equal to unity:

$$\left(\frac{\partial^2 a}{\partial z^2}\right) - \left(\frac{\partial a}{\partial \theta}\right) = a^n \tag{13}$$

For the case of n equal to unity this problem has been solved by Danckwerts (*3*) and by Sherwood and Pigford (*20*), but the problem defies analytical solution for other values of n. However when the concentration profile of species A reaches its steady state profile, the problem is readily solved for any value of n. When one neglects the time derivative in Equation (13), the steady state concentration profile is found to be

$$a = \exp\left(-z\sqrt{\frac{2}{n+1}}\right) \quad (\text{for } n = 1) \tag{14a}$$

$$a^{[(1-n)/2]} = 1 - \sqrt{\frac{2}{n+1}}\left(\frac{1-n}{2}\right)z \quad (\text{for } n \neq 1) \tag{14b}$$

For values of n less than unity Equation (14*b*) applies only for values of z sufficiently small so that the right-hand side of Equation (14*b*) is positive. For larger values of z, a is simply equal to zero. When one differentiates Equations (14*a*) and (14*b*) and uses Equation (9), it is clear that, at large values of θ, ϕ will approach the value given by the following expression

$$\phi = \sqrt{\left(\frac{2}{n+1}\right)\left(\frac{\pi}{4}\right)\theta} \equiv \sqrt{M} \tag{15}$$

which applies for any positive value of n. The parameter M, defined in the second half of Equation (15), is a measure of the chemical kinetic rate relative to diffusion rates within the liquid phase. As in reference *1* it is convenient to use the penetration-theory equation for physical absorption

$$k_L{}^* = 2\sqrt{\frac{D_A}{\pi t}} \tag{16}$$

to eliminate the contact time from the definition of M and express it as

$$M \equiv \left(\frac{2}{n+1}\right) k_F D_A\ [B]_o{}^m\ [A]_i{}^{n-1}/(k_L{}^*)^2 \tag{17}$$

In this form M is expressed in terms not dependent upon the penetration-theory model.

Equation (15) presents a generalized definition of the reaction rate parameter M which will make the steady state portion of the pseudo nth-order curve insensitive to the value of n. This result had been given previously (*10*) without derivation or discussion for the film-theory solution (in the region of the straight-line portion of the pseudo nth-order curve the film and the penetration models converge to the same physical picture). In order to obtain the complete solution for a pseudo nth-order chemical reaction Equation (13) was solved numerically by a finite-difference method similar to that described in reference *1* on an IBM-7090 digital computer. The results are presented in Figure 1 as a plot of ϕ vs. $\sqrt{M}$ for three different values of n. The curve for $n = 1$ is the analytical solution (*3, 20*)

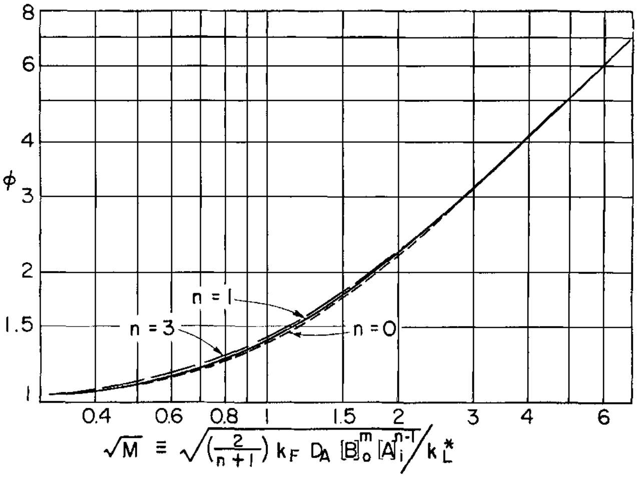

Fig. 1. Pseudo n^{th} order reaction.

$$\phi = \sqrt{\pi\theta/4}\left[1 + \frac{1}{2\theta}\right] \text{erf}\ (\sqrt{\theta}) + (1/2)\exp\ (-\theta) \tag{18}$$

The curves for $n = 0$ and $n = 3$ were computed numerically in this study. It can be seen in Figure 1 that the generalized definition of M which causes the various curves to converge at large values of M renders the complete solution quite insensitive to the value of n. Numerical solutions were also obtained for values of $n = 0.5$, 1.5, 2.0, and 2.5. These results were omitted from Figure 1 for clarity, but they all line up between the curve shown for $n = 0$ and the curve for $n = 3$, showing a monotonic variation with n. The maximum deviation between the upper and lower curves shown in Figure 1 is only 3%.

The curves for values of n less than unity deserve special mention. For values of n less than 1 the numerical solution to Equation (13) was found to be quite unstable. This is not at all surprising when one considers the physical significance of a reaction order less than unity, which implies that the rate of reaction divided by the concentration of species A approaches infinity as the concentration of species A approaches zero. It seems clear that it is physically unrealistic to assume that a reaction order could be less than unity and remain so right down to zero concentration. Such an assumption leads to the unrealistic branch of Equation (14*b*) at large values of z referred to earlier, and it would lead to a similarly unrealistic solution for the simple case of reaction in a well-mixed tank. Therefore in order to solve the problem for a value of n less than unity Equation (13) was replaced by

$$\left(\frac{\partial^2 a}{\partial z^2}\right) - \left(\frac{\partial a}{\partial \theta}\right) = \alpha \tag{19}$$

where

$$\left.\begin{aligned} \alpha &= a^n & &(\text{for } a_c \leq a \leq 1) \\ \alpha &= [(a_c)^{n-1}]a & &(\text{for } 0 \leq a \leq a_c) \end{aligned}\right\} \tag{20}$$

In Equation (20) a_c is a constant value of the concentration at which the reaction rate is changed from the nth-order expression to a linear expression. It was found that the curve of ϕ vs. $\sqrt{M}$, as shown in Figure 1, became in-

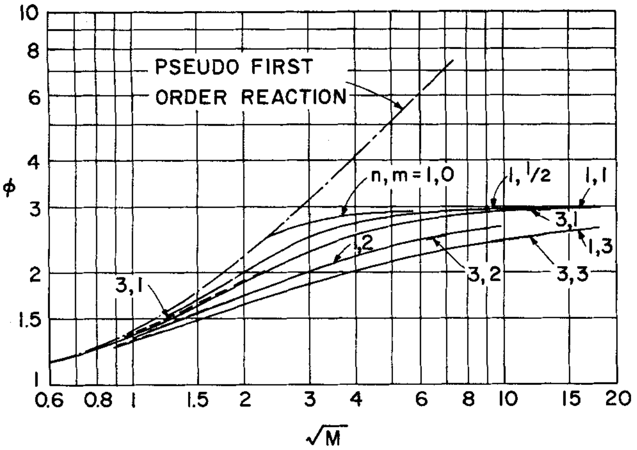

Fig. 2. Solution for $r = 1$, $q = 2$.

sensitive to the value chosen for a_c when this value was less than approximately 0.1. This asymptotic solution as the value of a_c was decreased is referred to here as "the solution for the nth-order reaction," but it is in reality the solution for a reaction order which changes from nth-order to first order at a very low value of the concentration of species A. The function given by Equation (20) should not however be thought of as simply a mathematical trick to render the numerical solution stable. Any chemical reaction which appears to have a reaction order less than unity must undoubtedly change over at very low concentrations to a reaction order greater than or equal to unity.

SOLUTION FOR REACTION OF ORDER $n + m$

Equations (4) and (5) were solved by a finite—difference method similar to that discussed in reference *1* for a number of different values of r and q at various combinations of n and m. As in the pseudo nth-order case the problem of a reaction order less than unity was handled by replacing the term $(a^n b^m)$ in Equations (4) and (5) by the term $(\alpha \beta)$, where α is defined by Equation (20) and β is defined by

$$\left.\begin{aligned} \beta &= b^m && (\text{for } b_c \leq b \leq 1) \\ \beta &= [(b_c)^{m-1}]b && (\text{for } 0 \leq b \leq b_c) \end{aligned}\right\} \qquad (21)$$

If n were greater than or equal to unity, a_c was chosen as zero. For values of n less than unity a_c was made successively smaller until the solution became insensitive to further decreases in a_c. Similarly b_c was set equal to zero if m was greater than or equal to unity, and for values of m less than unity b_c was made successively smaller until the solution became independent of b_c. In all cases convergence of the numerical integration was tested by varying the sizes of the increments in θ and z. These convergence tests, plus comparisons with known asymptotes, lead the author to conclude that the computed results represent the true solution to the parial differenial equations within 2%, the error being less than 1% over most of the range of variables. The computed results agree with those of reference *1* when n and m are both equal to unity.

Solution for Equal Diffusivities

When the diffusivity ratio r is equal to unity Equations (12) reduce to

$$\phi_a = 1 + q \qquad (22)$$

Figure 2 shows the computed results for $r = 1$ and $q = 2$; thus ϕ_a is equal to 3. The results are plotted as ϕ vs. $\sqrt{M}$ for various combinations of the reaction orders n and m. The same definition of M which resulted in the pseudo nth-order curve being so insensitive to the value of n has been maintained, and it can be seen in Figure 2 that this results in a remarkable insensitivity of the solution to the value of n for a given value of m. For example at high values of $\sqrt{M}$ the curve for $n,m = 3,1$ lies within ½% of the curve for $n,m = 1,1$. These two curves show a maximum departure from each other of less than 3% at low values of $\sqrt{M}$, where the former curve approaches the pseudo third-order reaction curve and the latter approaches the pseudo first-order reaction curve. Figure 2 reveals a similar behavior for the curves with $n,m = 1,3$ and 3,3 and for the curves with $n,m = 1,2$ and 3,2. In addition to the results shown in Figure 2 solutions were also obtained for $n,m = 3,0$; 0,1; 0.5,1; 2,1; 0,3; 0.5,3; and 2,3. These curves were omitted from Figure 2 for clarity, but they confirm the insensitivity of the solution to the value of n as convincingly as do the curves shown in Figure 2.

Figure 3 presents similar results for $r = 1$ and $q = 5$. As in Figure 2 the curves in Figure 3 can be seen to be quite insensitive to the value of n at a given value of m.

Figure 4 presents the results obtained for $r = 1$ and $q = 10$. In this graph the curve for $n,m = 3,1$ agrees with the curve for $n,m = 1,1$ within less than ½% at high values of $\sqrt{M}$. The same behavior is found for the curves for $n,m = 3,3$ and 1,3. Thus Figures 2, 3, and 4 show that the insensitivity of the solution to the value of n is maintained over a wide range of variation in q for a diffusivity ratio of unity.

Although the generalized definition of the relative rate parameter M has rendered the solution quite insensitive to the value of n, Figures 2, 3, and 4 show that the solu-

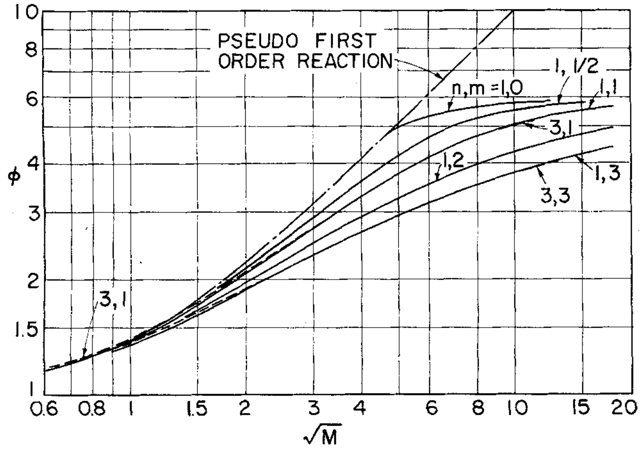

Fig. 3. Solution for $r = 1$, $q = 5$.

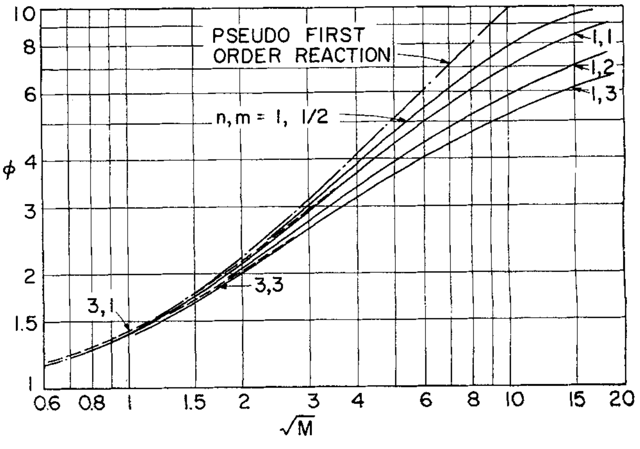

Fig. 4. Solution for $r = 1$, $q = 10$.

tion varies considerably with the value of m. As $\sqrt{M}$ is increased, ϕ approaches its asymptote rapidly as low values of m and more gradually at higher values of m. This behavior can be understood most readily by comparing the curves for $n,m = 1,0$ and $1,1$ (in Figure 3 for example). Both of these curves are for a reaction which is first order in the concentration of species A, but the former curve is for a reaction which is zero order in the concentration of species B while the latter is for a reaction which is first order in the concentration of species B. Consider first the reaction which is first order in species A and zero order in species B. At $\theta = 0$, b is equal to unity throughout the liquid phase. Then as the liquid is exposed to the gas b dips below unity at $z = 0$ because species B is consumed by the chemical reaction near the gas—liquid interface. As θ increases, b_i decreases more and more until finally it reaches zero. However since the reaction order is zero with respect to the concentration of species B, the rate of the chemical reaction is not affected by variations in b until b_i reaches zero. Thus species A reacts and diffuses just as it does in the pseudo first-order region up until the value of θ at which b_i reaches zero. This behavior can be seen in Figure 3 where the curve for $n,m = 1,0$ can be seen to agree exactly with the pseudo first-order curve up to a value of $\sqrt{M} = 4.7$; this corresponds to the value of θ at which b reaches zero at the gas-liquid interface. When one turns to the curve for $n,m = 1,1$, since the reaction rate is first order with respect to the concentration of species B, it is clear that the reaction rate near the gas-liquid interface must fall below the value for a pseudo first-order chemical reaction as soon as the value of b_i dips below unity. Thus the curve for $n,m = 1,1$ lies below the pseudo first-order curve for all positive values of θ. This comparison makes the behavior shown in Figures 2, 3, and 4 quite understandable; the greater the value of m the more rapidly the curve falls beneath the pseudo first-order curve as θ increases and b falls below unity in the region near the gas-liquid interface.

As mentioned in the preceding paragraph when $n,m = 1,0$ the rate of reaction and the rate of absorption of species A are the same as for a pseudo first-order reaction until the time at which b_i falls to zero. In this region the problem can be solved analytically, and the resulting expression relating b_i to θ (for r = unity) is

$$q(1 - b_i) = \exp(-\theta/2)[\theta I_1(\theta/2) + (1 + \theta)I_0(\theta/2)] - 1 \quad (23)$$

For the curves for $n,m = 1,0$ shown in Figures 2 and 3 the numerically computed values of b_i vs. θ were found to agree very well with Equation (23) except after b_i had fallen below the value of b_c for the particular computation. Figure 5 shows a graphical representation of Equation (23) in which the left-hand side of Equation (23) has been plotted vs. $\sqrt{M}$ instead of θ. For any value of q the value of $\sqrt{M}$ at which b_i falls to zero can be readily found from Figure 5.

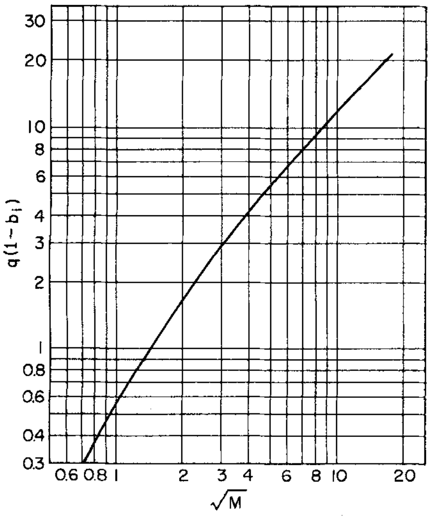

Fig. 5. Solute interface concentration for $n = 1$, $m = 0$, $r = 1$ (until b_i reaches zero).

Empirical Correlation for Equal Diffusivities

The utility of computer solutions to almost any problem can be enhanced considerably if the results can be simply correlated, even if the correlation is completely empirical. Thus the following correlation of the results in Figures 2, 3, and 4 is offered as an aid to interpolation and for minor extrapolations:

$$\left[\frac{(\sqrt{M})_{n,m,q}}{(\sqrt{M})_{\text{Pseudo nth order}}}\right]_{\text{Same } \phi} = \left(\frac{\phi_a - 1}{\phi_a - \phi}\right)^{\gamma} \quad (24)$$

where $\gamma = 0.4\, m$ for $1 \leq m \leq 3$
$\gamma = 0.23$ for $m = 0.5$

The correlation is most readily used by solving for the value of $\sqrt{M}$ at a given value of ϕ. For example consider the curve for $n,m = 1,2$ in Figure 3. The value of q for this figure is equal to 5, and thus ϕ_a is equal to 6. At a value of $\phi = 3$ the right-hand side of Equation (24) becomes

$$\left[\frac{6-1}{6-3}\right]^{0.8} = 1.506$$

The value of $\sqrt{M}$ at which the pseudo first-order curve reaches a ϕ value of 3 can be found from Figure 1 to be 2.85. Thus when $\phi = 3$, the empirical correlation predicts that $\sqrt{M}$ for the curve for $n,m = 1,2$ in Figure 3 will be

$$(1.506)(2.85) = 4.29$$

The curve for $n,m = 1,2$ in Figure 3 shows a value of $\sqrt{M}$ approximately 1% smaller than 4.29 when the value of ϕ is 3. The correlation expressed by Equation (24) correlates all of the results shown in Figures 2, 3, and 4 with a maximum deviation of 3% in the ϕ values except for the results for $m = 0$. The correlation is not recommended for values of m less than 0.5, but interpolation of a graph of γ vs. m for values of m between 0.5 and 3 would be expected to give satisfactory results. It should be emphasized that this correlation is for r equal to unity.

Effect of the Diffusivity Ratio

In comparing curves with different values of r the method of reference *1* will be followed in which the curves will be compared not at the same value of q but at values of q such that the value of ϕ_a is the same for each of the curves being compared. For example the upper three curves in Figure 6 are for $n,m = 1,1$, and they show curves for three different combinations of r and q, each of which yields a value of $\phi_a = 6$ according to Equations (12). These three curves must of course approach the pseudo first-order curve at low values of $\sqrt{M}$, and they approach an asymptotic value of ϕ equal to 6 at high values of $\sqrt{M}$. The curves for $r = 0.1$ and $r = 10$ show a maximum deviation of approximately 7% at $\sqrt{M}$ equal to approximately 5. The lower three curves in Figure 6 present analogous information for $n,m = 1,3$. Here the curves for the different values of r can be seen to deviate from each other by a greater amount, the maximum deviation being approximately 12%. It should be noted in Figure 6 that the curve for $r = 1$ does not lie midway between the curves for $r = 0.1$ and $r = 10$; it is generally closer to the curve for $r = 10$. Figure 7 presents a similar picture for runs with $n,m = 3,1$ and $3,3$. Here the curves for different values of r show much smaller devia-

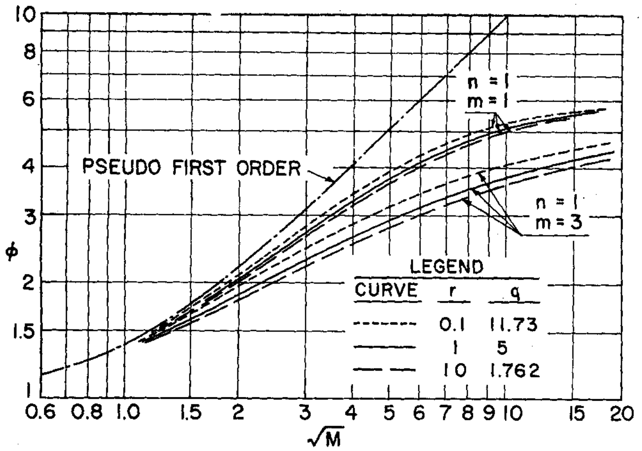

Fig. 6. Effect of the diffusivity ratio, $\phi_a = 6$.

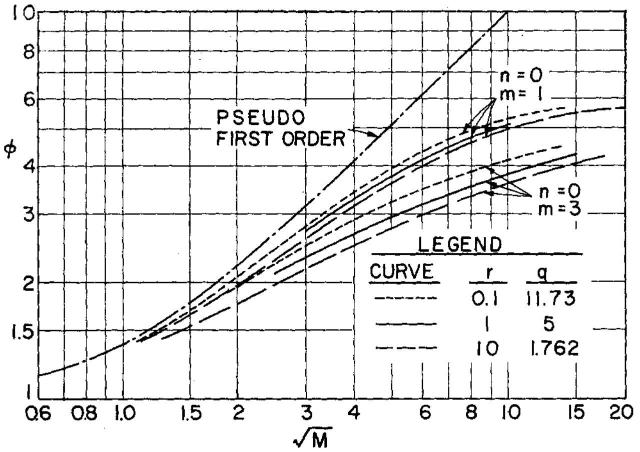

Fig. 8. Effect of the diffusivity ratio, $\phi_a = 6$.

tions from each other, and indeed for $n,m = 3,1$ the curves for $r = 0.1$ and 10 can be seen to cross each other. This is the only example observed of such curves crossing. In all other cases studied the curve for $r = 0.1$ was found to lie above the curve for $r = 10$ as in reference *1*. Figure 8 shows the comparisons for $n,m = 0,1$ and 0,3. A number of other cases were studied, but these complete curves will be omitted for brevity. They show the curve for $r = 0.1$ above the curve for $r = 10$, the curves exhibiting a maximum deviation at $\sqrt{M}$ equal to approximately 5. Figure 9 shows how this maximum deviation between the curves for $r = 0.1$ and $r = 10$ varies with n and m, and this figure, together with the solution for r equal to unity, should permit a fairly close estimation of the curve for any value of r between 0.1 and 10.

COMPLEX REACTION MECHANISM

The results of this study apply when Equation (2) represents the stoichiometry of the local chemical reaction and Equation (3) represents its kinetics. Of course, except for some very simple cases such as $\nu = n = m = 1$, most chemical reactions will proceed by multistep reaction mechanisms involving intermediate species, although it may appear that they are well described by equations such as (2) and (3). Even in such complex cases it is believed that the results of this study are applicable except when transient intermediate species are relatively long-lived and build up to an appreciable concentration level so that they can diffuse an appreciable distance between their formation and their consumption. Some simple examples will make this idea clearer.

Suppose a chemical reaction proceeds according to the following mechanism, in which each step is second order:

$$A + B \rightarrow C, \text{ irreversibly} \qquad (25a)$$

$$C + B \rightarrow \text{products, irreversibly} \qquad (25b)$$

If the rate of the second step is very fast relative to the rate of the first step and to diffusion rates, the system will behave as if it were described by Equations (2) and (3) with $\nu = 2$, $n = 1$, and $m = 1$. On the other hand if the rate of the second step is somewhat slow relative to that of the first step and to diffusion rates, then the intermediate species C will build up and diffuse an appreciable distance before it is consumed by the second reaction step. In this case Equation (2) will not describe the stoichiometry of the chemical reaction at a point, and the gas absorption rate will generally not correspond to the present results with any choice of ν, n, and m, as was discussed in reference *10*. Indeed in this case ϕ will go through a maximum as the contact time increases and will approach its asymptote from above.

As a second example suppose that the solute B polymerizes (or dissociates) according to the reversible reaction

$$\eta B \leftrightharpoons C \quad \text{(Very Fast)} \qquad (26a)$$

and that species A reacts only with species C according to the second-order reaction

$$A + C \rightarrow \text{products, irreversibly} \qquad (26b,$$

If the equilibrium of the first reaction is such that the equilibrium ratio of [C] to [B] is very small at the concentrations of interest, then the system will behave as if it were described by Equations (2) and (3) with $\nu = \eta$, $n = 1$, and $m = \eta$, and the results of this study will be applicable as such. On the other hand if the equilibrium of the first step is such that the equilibrium ratio of $[C]$ to $[B]$ is near unity, this equilibrium will generally shift

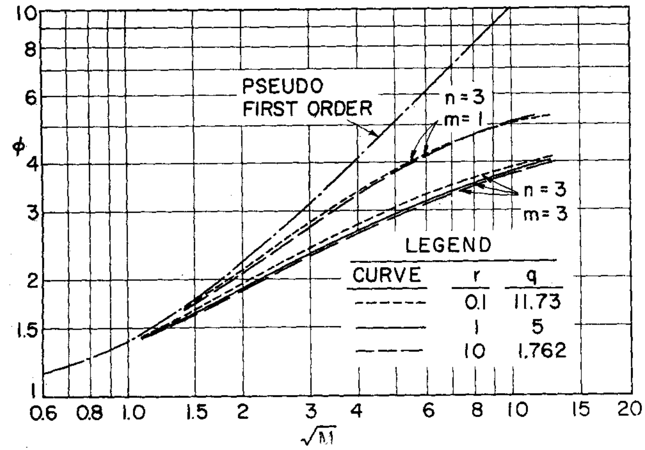

Fig. 7. Effect of the diffusivity ratio, $\phi_a = 6$.

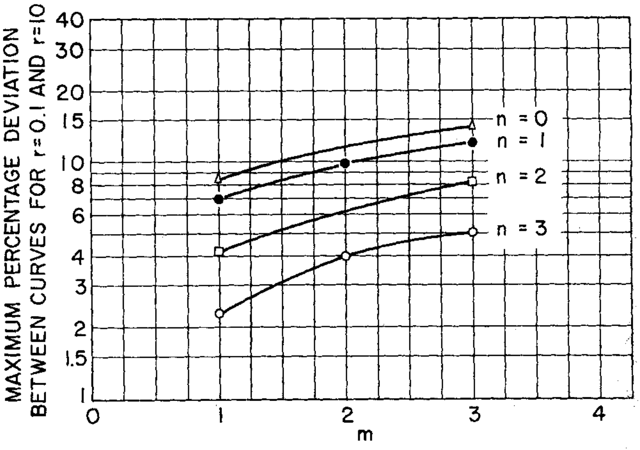

Fig. 9. Effect of diffusivity ratio correlated with reaction order, $\phi_a = 6$.

with concentration level, and Equation (2) will not describe the stoichiometry of the chemical reaction at a point. Of course if the equilibrium of the first reaction were shifted completely to the right at all concentrations of interest, the reaction would appear to be first order in the apparent concentration of species B.

CONCLUSION

The penetration-theory equations have been solved for gas absorption accompanied by an irreversible chemical reaction of general order. A generalized definition of the relative rate parameter M has been proposed which gives very simple expression to the straight-line portion of the curve for a pseudo nth-order reaction. This generalized definition of M has also been found to render the pseudo nth-order solution and indeed the general solution for equal diffusivities quite insensitive to the value of n, the order of the chemical reaction with respect to the concentration of the absorbing species. The effect of m, the order of the chemical reaction with respect to the solute component, has been shown in a number of example computations, and an empirical correlation is presented for the case of equal diffusivities. The curves are not very sensitive to the value of the diffusivity ratio r when compared at a contant value of the asymptotic solution for an infinitely rapid chemical reaction, and a graphical correlation is presented as a means of estimating the effect of r over the 100 fold range from $r = 0.1$ to $r = 10$.

ACKNOWLEDGMENT

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NOTATION

$[A]$ = concentration of species A, the gas being absorbed, moles/cc.
a = $[A]/[A]_i$
$[B]$ = concentration of species B, the nonvolatile solute, moles/cc.
b = $[B]/[B]_o$
$[C]$ = concentration of species C, the intermediate species in Equations (25*a*) to (26*b*)
D = liquid-phase diffusivity, sq. cm./sec.
e = 2.71828 . . .
$\text{erf}(\sigma) = (2/\sqrt{\pi}) \int_o^\sigma e^{-y^2} dy$
$\exp(\sigma) = e^\sigma$
$I_p(\theta/2)$ = modified Bessel function of the first kind of order p
k_F = reaction rate constant, (cc./mole)$^{[n+m-1]}$/sec.
k_L = liquid-phase absorption coefficient, cm./sec., based on average absorption rate for penetration theory
$M = \left(\dfrac{2}{n+1}\right)\left(\dfrac{\pi}{4}\right)\theta$ for penetration theory
$\quad = \left(\dfrac{2}{n+1}\right) k_F D_A [B]_o^m [A]_i^{n-1}/(k_L^*)^2$ in general
m = order of the chemical reaction with respect to the concentration of species B
n = order of the chemical reaction with respect to the concentration of species A
q = $[B]_o/\nu[A]_i$
R = chemical reaction rate, (moles of species A reacting) /(sec.) (cc.)
r = D_B/D_A
t = time, sec.
x = distance into the liquid phase, cm.
$z = x\sqrt{\dfrac{k_F[B]_o^m[A]_i^{n-1}}{D_A}}$, dimensionless distance

Greek Letters

α = function of a given by Equations (20)
β = function of b given by Equations (21)
γ = empirically determined exponent in Equation (24)
η = stoichiometric factor in Equation (26*a*)
θ = $k_F\, [B]_o^m\, [A]_i^{n-1}\, t$, dimensionless time
ν = stoichiometric coefficient in chemical reaction Equation (2)
π = 3.14159 . . .
σ = parameter in parametric equations
ϕ = k_L/k_L^*
ϕ_a = asymptotic value of ϕ at large values of θ (or $\sqrt{M}$)

Subscripts

A = species A
B = species B
c = value at which reaction order changes to first order, Equations (20) and (21)
(G) = gas phase
i = gas-liquid interface
(L) = liquid phase
o = in penetration theory the liquid at the start of a contact time interval

Superscripts

$*$ = physical absorption in which no chemical reaction occurs
$'$ = dummy variable in definite integral

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