The friction factor and velocity profile data are internally consistent, as evidenced by treatment with an extension of the von Kármán correlating equation.

NOTATION

c = empirical correction term, Equation (2)
D = pipe diameter, ft.
f = $\dfrac{\tau_w}{\rho V^2/2g_c}$, friction factor
n = parameter in the power law model, $\tau_{rz} = K\left(-\dfrac{du}{dr}\right)^n$
N_{Re} = $\dfrac{DV\rho}{u_w}$, Reynolds number
r = radial position, ft.
R = pipe radius, ft.
u = mean point velocity in pipe, ft./sec.
u^+ = u/u^*, dimensionless velocity
u^* = $\sqrt{\tau_w g_c/\rho}$, friction velocity, ft./sec.
$u_{\max}$ = center-line velocity, ft./sec.
V = mean velocity, ft./sec.
y = distance from wall, ft.
y^+ = $\dfrac{y\,u^*\,\rho}{\mu_w}$, dimensionless distance
ρ = density, lb.$_m$/cu. ft.
μ_w = apparent viscosity, Equation (4), lb.$_m$/(sec.)(ft.) (= μ, Newtonian fluids)
τ_w = shear stress at the wall, lb.$_f$/sq. ft.
τ_{rz} = shear stress in general, lb.$_f$/sq. ft.

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An Ionic Penetration Theory for Mass Transfer With Chemical Reaction

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Theoretical analyses based upon film theory and penetration theory models of the interphase mass transfer process have contributed greatly to the understanding of the effect of a simultaneous chemical reaction upon the rate of mass transfer. For a review of these and other models and their use in predicting the effect of a chemical reaction upon the mass transfer rate the reader is referred to references 2, 3, 4, 5, 6, 7, 19, and 22. An especially interesting aspect of these theoretical studies has been the surprising agreement of film theory predictions with penetration theory predictions except when diffusivity ratios depart greatly from unity (*3, 6*).

Most of the theoretical treatments of simultaneous mass transfer and chemical reaction have been based on the assumption that the various diffusing and reacting species were uncharged molecules, although in most commercially important examples of simultaneous mass transfer and chemical reaction ionic species are involved. Furthermore it has long been known (*14, 15, 17, 18*) that ions, since they are electrically charged, obey a different law of diffusion than that for molecular species. This lead Sherwood and Wei (*21*) and later Sherwood and Ryan (*20*) to a study of ion diffusion effects upon the film theory solution for mass transfer accompanied by an infinitely rapid irreversible chemical reaction. Sherwood and Wei showed that ion diffusion effects were large in the systems they studied and also that their diffusion cell data for these systems supported their ionic theory.

No studies have been reported on ionic diffusion effects in the penetration theory for simultaneous mass transfer and chemical reaction. In order to estimate this effect Brian (*1, 8*) used an effective diffusivity with molecular penetration theory equations. This effective diffusivity was obtained from a comparison of the molecular and ionic film theory results. This procedure will be demonstrated and discussed later in this paper and will be referred to as the *film theory approximation*. This method of approximation appears to have been used later independently by some other investigators (*11, 16*). The purpose of this work is to study the magnitude of ionic diffusion effects in the penetration model for simultaneous mass transfer and chemical reaction, to compare these effects with those found in the film theory model, and to evaluate the adequacy of the film theory approximation referred to above. For this purpose the ionic penetration theory equations have been formulated and solved for the case of acetic acid diffusing into an aqueous sodium hydroxide solution. This system was chosen because it is perhaps the simplest type of system which shows ionic effects and because it was one of the two examples contained in the film theory treatment of Sherwood and Wei.

THEORETICAL MODEL

The problem to be considered is the transfer of a molecular species S from a nonaqueous phase to an aqueous phase containing the solute CA. The solute is assumed to be completely ionized into C^+ ions and A^- ions in the aqueous phase and to be insoluble in the nonaqueous phase. The mass transfer process is accompanied by an irreversible chemical reaction between the transferring species and the solute anion:

$$S + A^- \rightarrow P^- \qquad (1)$$

The product of the chemical reaction is the anion P^-, which is assumed to be insoluble in the nonaqueous phase. The chemical reaction is assumed to proceed according to the second-order kinetic equation

$$\frac{(\text{moles of S reacting})}{(\text{time})\ (\text{volume})} = k_F\,[S]\,[A^-] \qquad (2)$$

A penetration theory model of mass transfer to the aqueous phase is adopted, in which a slug of aqueous phase is initially well mixed so that concentration gradients are absent and then brought into contact with the nonaqueous phase for a contact time interval. During the contact interval mass transfer occurs by molecular diffusion and accumulation within the aqueous phase. At the end of the contact interval the slug of aqueous phase is completely mixed before beginning another contacting interval of the same duration. For simplicity it is assumed that the mass transfer resistance of the nonaqueous phase is negligible, and thus the concentration of species S at the phase boundary is taken to be constant over the contact time interval. It is further assumed that the depth of the slug of aqueous phase is essentially infinite relative to the depth of penetration of the concentration boundary layer within the exposure time interval and that the aqueous phase contains no unreacted species S at the beginning of the contact interval (*3*).

If species S is identified with undissociated acetic acid, and if species C^+, A^-, and P^- are identified with sodium ions, hydroxyl ions, and acetate ions, respectively, the system treated in this study can be seen to be the same as the acetic acid-sodium hydroxide system treated by Sherwood and Wei (*21*). Of course Equation (1) does not contain a water molecule on the right-hand side as does the reaction between acetic acid and hydroxyl ion, but the presence of the water molecule would not affect the analysis. Thus the present study is analogous to the acetic acid-sodium hydroxide study of Sherwood and Wei except that it is based upon a penetration theory rather than on a film theory model of transfer within the aqueous phase. Since Sherwood and Wei treated only the case of an infinitely rapid chemical reaction, their analysis did not require a kinetic equation such as Equation (2).

The diffusion law for ions in dilute solution is given by the Nernst-Planck equation (*14, 15, 17, 18*):

$$N_I = -D_I \frac{\partial\,[I]}{\partial x} + \left(\frac{F}{RT}\right) E\, Z_I\, D_I\, [I] \qquad (3)$$

The second term on the right-hand side of Equation (3) represents the motion of the ionic species under the influence of the electric field E. In the present context this electric field is not imposed externally but results from the fact that the various diffusing ionic species, with their generally different ionic mobilities, will tend to diffuse at different velocities and thus will produce small local deviations from electrical neutrality which result in the establishment of this electric field. The quantity Z_I is the valence of the diffusing ionic species and is positive for cations and negative for anions. If Z_I is taken to be zero for an uncharged molecular species, then Equation (3) reduces to the usual Fick's law expression.

In accordance with the procedure of Vinograd and McBain (*23*) the electric field produced by the diffusion of the various ions can be computed as follows. Electrical neutrality requires that the net current flow must be zero:

$$N_C = N_A + N_P \qquad (4)$$

When the flux of each ionic species is formulated in terms of Equation (3) and substituted into Equation (4), the resulting equation can be solved for the electric field:

$$\left(\frac{F}{RT}\right) E = \frac{D_C \dfrac{\partial [C^+]}{\partial x} - D_A \dfrac{\partial [A^-]}{\partial x} - D_P \dfrac{\partial [P^-]}{\partial x}}{D_C[C^+] + D_A[A^-] + D_P[P^-]} \qquad (5)$$

The electrical neutrality condition can also be stated in terms of concentrations:

$$[C^+] = [A^-] + [P^-] \qquad (6)$$

Differentiating Equation (6) and using the result together with Equation (6) to eliminate the concentration and the concentration gradient of P^- ions from Equation (5) one obtains

$$\left(\frac{F}{RT}\right) E = \frac{(D_C - D_P)\dfrac{\partial [C^+]}{\partial x} - (D_A - D_P)\dfrac{\partial [A^-]}{\partial x}}{(D_C + D_P)\ [C^+] + (D_A - D_P)\ [A^-]} \qquad (7)$$

Equation (7) expresses the electric field in terms of the ionic self-diffusion coefficients, the concentrations, and the concentration gradients of the various diffusing ionic species. The substitution of Equation (7) into Equation (3) yields the flux equation for any ionic species in terms of these same quantities. It can be seen from Equation (7) that if the three ions have equal self-diffusion coefficients, the electric field is zero, and thus each ion obeys Fick's law. This is true in general, that is for an arbitrary number of ions, as can be shown by means of a development similar to the one which lead to Equation (7).

It was stated earlier that the electric field results from a local departure from electrical neutrality due to the fact that the more mobile ions diffuse ahead of the less mobile ions. The electric field so produced then acts as a restoring force to speed up the less mobile ions and to slow down the more mobile ions. Since the electric field results from a departure from electrical neutrality, the use of Equations (4) and (6) might at first appear to be a contradiction. The justification for their use is that the departure from electrical neutrality required to produce the electric field is a very small percentage of the ion concentrations involved. Thus while the ion imbalance produces an electric field sufficiently large to affect appreciably diffusion velocities, the effect upon stoichiometric relationships such as Equations (4) and (6) can be neglected. The adequacy of this analytical procedure has been well established (*9, 21, 23*). A similar justification of the assumption of electrical neutrality has been given by Helfferich (*10*), who used that assumption in the treatment of rates of ion exchange. On the other hand the present work involved a concern regarding the time required for the establishment of the electric field which the previous investigators did not face. The penetration theory model considered here is a model of transient diffusion, and the exposure time of usual interest is in the range of 1 to 100 msec. If Equation (7) is to be used to relate the instantaneous electric field to the instantaneous concentration profiles, it is clearly necessary that the time constant for establishing the departure from electrical neutrality which produces the field must be considerably shorter than a millisecond. Calculations have been made which indicate that the time constant for establishing the departure from electrical neutrality required to produce the electric field is of the order of 10^{-10} sec. Thus Equation (7) should be an excellent approximation to the relationship between the instantaneous electric field and the instantaneous concentration profiles during transient exposure periods of the order of 1 msec. or longer.

When C^+ ions and A^- ions are the only ionic species present in the aqueous phase, electrical neutrality requires that they diffuse together. In this case an analysis similar to the derivation of Equation (7) yields the result that the species CA diffuses as if it obeyed Fick's law with an apparent diffusivity equal to

$$D_{CA} = \frac{2\, D_C\, D_A}{D_C + D_A} \tag{8}$$

This apparent diffusivity of species CA when it diffuses in the absence of other ionic species is often called the *salt diffusivity* of the ionized substance CA. Equation (8) was first obtained by Nernst (*13, 14*).

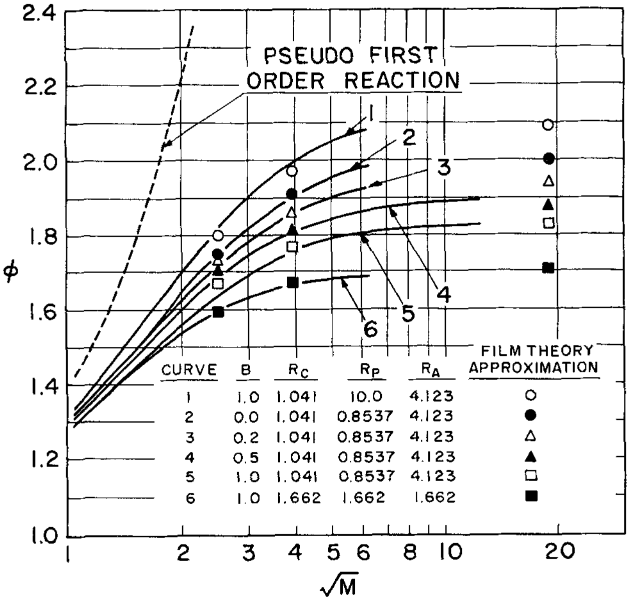

Fig. 1. Results for $Q = 0.614$, $R_{CA} = 1.662$.

Using Equation (2) to describe the reaction rate and using Equation (3) with Equation (7) to describe the ionic flux rates, one can derive the penetration theory partial differential equations in the usual manner. In dimensionless form these equations become

$$\frac{\partial^2 s}{\partial z^2} - \frac{\partial s}{\partial \theta} = sa \tag{9}$$

$$R_A\left(\frac{\partial^2 a}{\partial z^2}\right) - R_A \frac{\partial}{\partial z}\left[\frac{\alpha\left(\frac{\partial c}{\partial z}\right) - \beta\left(\frac{\partial a}{\partial z}\right)}{\frac{c}{a} + \beta}\right] - \left(\frac{\partial a}{\partial \theta}\right) = \left(\frac{1}{Q}\right) sa \tag{10}$$

$$R_C\left(\frac{\partial^2 c}{\partial z^2}\right) - R_C \frac{\partial}{\partial z}\left[\frac{\alpha\left(\frac{\partial c}{\partial z}\right) - \beta\left(\frac{\partial a}{\partial z}\right)}{1 + \beta\left(\frac{a}{c}\right)}\right] - \frac{\partial c}{\partial \theta} = 0 \tag{11}$$

Equations (9), (10), and (11) do not contain the concentration of the product anion because this has been eliminated by use of Equation (6). The boundary conditions to be imposed upon the simultaneous solution of these three partial differential equations are

$$\text{At } \theta = 0, \text{ any } z > 0 \;:\; s = 0, c = 1, a = 1 \tag{12}$$

$$\text{At } z = 0, \text{ any } \theta > 0 \;:\; s = 1, \frac{\partial c}{\partial z} = 0, \frac{\partial a}{\partial z} = 0 \tag{13}$$

$$\text{At } z \to \infty, \text{ any } \theta \;:\; s = 0, c = 1, a = 1 \tag{14}$$

The two zero slope conditions in Equations (13) require that none of the ionic species can flux across the phase boundary, as is evident by inspection of Equations (3), (4), and (7).

The problem simplifies considerably when the parameter β is equal to zero. This parameter would be equal to zero if the ionic self-diffusion coefficients of species A^- and P^- were equal or if the bulk concentration of species P^- were very large compared with that of species A^- (in which case B would be near zero). When β is zero, $c = 1$ at all θ and z, and Equation (10) degenerates to

$$R_A\left(\frac{\partial^2 a}{\partial z^2}\right) - \left(\frac{\partial a}{\partial \theta}\right) = \left(\frac{1}{Q}\right) sa \tag{15}$$

Equations (9) and (15), together with the boundary conditions imposed upon s and a, can be seen to agree exactly with the differential equations describing the molecular penetration theory in reference *3*. Thus when β is equal to zero, species A^- diffuses in accordance with Fick's law with a diffusivity equal to the ionic self-diffusion coefficient D_A, and the ionic penetration theory solution coincides with the molecular penetration theory solution.

Equations (9), (10), and (11), together with the conditions of Equations (12), (13), and (14), were solved by a linearized, time-centered finite difference method on an IBM-7090 digital computer. The method of solution was similar to that described in reference *3*, and the results were expressed as ϕ vs. $\sqrt{M}$, as discussed in that reference. The method of solution is described in detail in reference *12*. Convergence tests, in which the time and distance increments were reduced, and comparison of the computed results with known asymptotes and with molecular penetration theory results in special cases lead the authors to conclude that the computed results represent the solution to the partial differential equations within 3%.

RESULTS AND DISCUSSION

The curves in Figure 1 present the numerically computed results for $Q = 0.614$. The various curves represent different values of the various diffusivity ratios and of the parameter B, which is a measure of the concentration of P^- ions in the bulk liquid. While the various diffusivity ratios vary considerably from one curve to another, the group $2R_CR_A/(R_C + R_A) \equiv R_{CA}$ is constant at 1.662 for all curves in Figure 1. This group will be recognized as the ratio of the salt diffusivity of substance CA, as given by Equation (8), to the diffusivity of species S. Thus if one were to ignore ionic diffusion effects and thus to assume that A^- ions would diffuse with the salt diffusivity of species CA, one would conclude that all six curves in Figure 1 should coincide with the molecular penetration theory curve (*3*) for $r = 1.662$ and $q = 0.614$. Thus the deviations among the six curves shown in Figure 1 represent the error which would be made by neglecting ionic diffusion effects in the example problems chosen.

Curve 6 in Figure 1 does correspond to molecular penetration theory (*3*) with $r = 1.662$ and $q = 0.614$. This is because the ionic self-diffusion coefficients of all three ionic species are equal, and in this case β is equal to zero and the ionic penetration theory coincides with molecular penetration theory as explained previously. Curves 2, 3, 4, and 5 in Figure 1 were computed for values of the various diffusivity ratios which correspond to the acetic acid-sodium hydroxide system as reported by Sherwood and Wei (*21*). Curve 5 is for a bulk liquid which is free of acetate ion, while curve 2 is for a bulk concentration of acetate ion which is very large compared with the bulk concentration of hydroxyl ion. When one compares curves 2 through 5 with curve 6, it can be seen that the rate of mass transfer in the acetic acid-sodium hydroxide system is greater than would be the case if the hydroxyl ion diffused as a molecular species with the salt diffusivity of sodium hydroxide. Furthermore the error which would result from neglecting ionic diffusion effects increases with increasing conversion of the bulk liquid to the acetate form (that is with decreasing B). These effects are similar to those obtained by Sherwood and Wei in their film theory analysis, but the deviations between the ionic and molecular theories shown in Figure 1, even at large values of $\sqrt{M}$, are smaller in magnitude than those found by Sherwood and Wei.

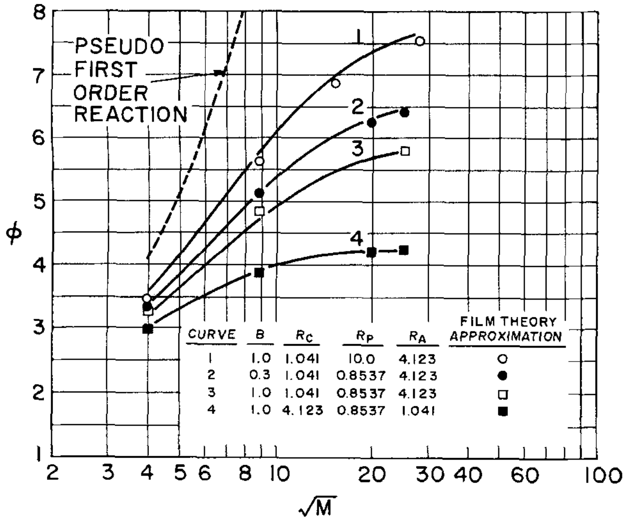

Fig. 2. Results for $Q = 3.30$, $R_{CA} = 1.662$.

The fact that curve 5 in Figure 1 lies above curve 6 shows that the effective diffusivity of the hydroxyl ion in this multi-ion system is greater than the salt diffusivity of sodium hydroxide. This is understandable because the hydroxyl ion is considerably more mobile than is the sodium ion, and when sodium hydroxide diffuses in the absence of other ionic species, the hydroxyl ion is slowed down by the necessity of dragging the sodium ion with it. On the other hand another degree of freedom is present in this multi-ion system; hydroxyl ion diffusion can take place either by the hydroxyl ions dragging sodium ions with them or by hydroxyl ions counterdiffusing with acetate ions.

The effect of B, as shown in curves 2 through 5, is best understood by considering $B = 0$, which corresponds to a very large concentration of sodium acetate relative to the concentration of sodium hydroxide throughout the liquid phase. In this case the hydroxyl ion can diffuse with its ionic self-diffusion coefficient, and thus curve 2 corresponds to molecular penetration theory (*3*) with $r = 4.123$ and $q = 0.614$.

Curve 1 in Figure 1 differs from curve 5 in that a very large ionic self-diffusion coefficient has been assigned to the P^- ion. The choice $R_P = 10$ corresponds to a value of D_P of almost twelve times the ionic self-diffusion coefficient of the acetate ion. It can be seen that this very high mobility of the P^- ion increases the net rate of transfer of species S to the aqueous phase to a value which is even greater than that shown in curve 2. Thus the rate of diffusion of A^- ions out to react with species S is even greater than that corresponding to the ionic self-diffusion coefficient of the A^- ion. In this case the very mobile P^- ion, as it diffuses from the reaction zone where it is produced into the bulk liquid, actually drags the less mobile A^- ion counter to it and thus speeds up the rate of transfer of the A^- ion out to react with species S. Of course lowering B would decrease this effect, and for $B = 0$ the result would coincide with curve 2. The pseudo first-order reaction curve (*4, 19*) is also shown in Figure 1. This curve corresponds to $Q \to \infty$ and is an upper bound on ϕ.

The curves in Figure 2 present the computed results for $Q = 3.30$. As in Figure 1 all curves in Figure 2 correspond to R_{CA} equal to 1.662. Curve 3 corresponds to the acetic acid-sodium hydroxide system with no sodium acetate in the bulk liquid. Curve 4 shows what would happen if the sodium ion and the hydroxyl ion were to swap ionic self-diffusion coefficients. This would not affect the salt diffusivity of sodium hydroxide, but the rate of transfer of acetic acid into aqueous sodium hydroxide would be slowed down considerably, as can be seen by comparing curves 3 and 4 in Figure 2. Thus the rate of mass transfer is larger when the more mobile ion is the one which takes part in the chemical reaction. The molecular penetration theory curve for $r = 1.662$ and $q = 3.30$ is not shown, but it would lie between curves 3 and 4 in Figure 2. Curve 2 in Figure 2 shows the effect of a large concentration of sodium acetate in the bulk liquid, and curve 1 shows the effect of a very mobile acetate ion. These effects are similar to those shown in Figure 1.

The curves in Figure 3 present computed results similar to those shown in Figures 1 and 2 except that the value of Q is 12.674. At this higher value of Q the ϕ values are relatively near the pseudo first-order curve and are quite far from the asymptotes for an infinitely rapid chemical reaction in the range of values of $\sqrt{M}$ covered. Thus the various curves in Figure 3 do not deviate from each other as much as they undoubtedly would at higher values of $\sqrt{M}$.

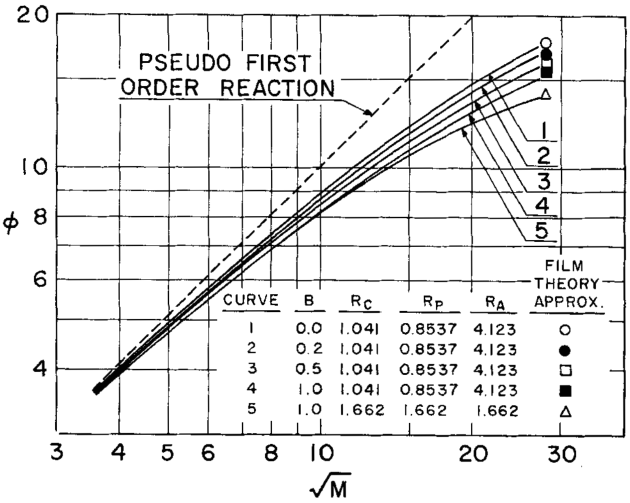

Fig. 3. Results for $Q = 12.674$, $R_{CA} = 1.662$.

The Film Theory Approximation

The result of molecular film theory (*19*) analysis for an infinitely rapid chemical reaction can be expressed as

$$\phi_a = 1 + r\,q \tag{16}$$

The analogous ionic film theory solution for the acetic acid-sodium hydroxide system was presented by Sherwood and Wei (*21*) and later in closed form by Sherwood and Ryan (*20*). The solution of Sherwood and Ryan can be expressed in the nomenclature of the present paper as

$$\phi = 1 + \frac{2\,R_A\,Q}{1 + \sqrt{B\left(\frac{R_A}{R_P} - 1\right) + 1}} \tag{17}$$

Since Q in the ionic problem is identified with q in the molecular problem, it is clear from Equations (16) and (17) that the ionic film theory for an infinitely rapid chemical reaction can be made to coincide with molecular film theory if an effective diffusivity ratio is employed in the latter:

$$r_{\text{EFF}} \equiv \frac{2\,R_A}{1 + \sqrt{B\left(\frac{R_A}{R_P} - 1\right) + 1}} \tag{18}$$

Equation (18) is of course simply the proper definition of the effective diffusivity ratio which reduces the ionic film theory solution for an infinitely rapid chemical reaction to the form

$$\phi_a = 1 + r_{\text{EFF}}\;Q \tag{19}$$

The hypothesis to be tested here is that the molecular penetration theory solution obtained by identifying q with Q and r with r_{EFF} as given by Equation (18) would be a good approximation to the ionic penetration theory solution at all values of $\sqrt{M}$ (not just for an infinitely rapid chemical reaction). If this hypothesis should prove to be true, it would be a great convenience because the molecular penetration theory solution can be estimated reasonably accurately from correlations in references *2* and *3* without the necessity of using a digital computer.

In order to test this film theory approximation values of r_{EFF} were computed from Equation (18) for each of the conditions represented in Figures 1, 2, and 3. The molecular penetration theory results were then obtained for these various diffusivity ratios and for values of q equal to the values of Q in question. These results are shown as the points plotted in Figures 1, 2, and 3. The points shown at the extreme right-hand side of Figure 1 correspond to molecular penetration theory for an infinitely rapid chemical reaction, and these results were computed from the analytical solution (*3, 5, 19*). A comparison of the film theory approximation points with the corresponding ionic penetration theory curves in Figures 1, 2, and 3 reveals that the film theory approximation is a very good approximation indeed. The maximum deviation between the ionic penetration theory and the film theory approximation shown in Figures 1 through 3 is less than 3%. The film theory approximation is exact when β is equal to zero, as in curves 2 and 6 in Figure 1, because in this case ionic penetration theory corresponds with molecular penetration theory. When β is not equal to zero, the film theory approximation is not exact, but it is a surprisingly good approximation to the ionic penetration theory results and to the effects of the various diffusivity ratios and of B upon the value of ϕ, at least for the cases treated in Figures 1, 2, and 3.

Effect of the Cation Diffusivity

The film theory approximation was so very successful in approximating the ionic diffusion effects shown in Figures 1, 2, and 3 that one is forced to inquire whether or not the approximation would be much less satisfactory if the various diffusivity ratios were to take on values somewhat different from the values used in Figures 1, 2, and 3. In this regard it is very enlightening to consider the effect of the cation diffusivity. Equation (18) reveals that r_{EFF} does not depend upon the value of R_C. This is because the cation does not enter into the chemical reaction, and thus in the steady state film theory model the cation flux is zero throughout the aqueous phase. The cation concentration profile will generally not be flat because the electric field produced by the anion diffusion fluxes will induce a gradient in the cation concentration. However since the cation flux is zero, the cation concentration profile produced by a given electric field will be independent of the ionic self-diffusion coefficient of the cations, as is apparent from Equation (3). Thus the cation diffusivity does not affect the ionic film theory solution and cannot therefore enter into the film theory approximation to the ionic penetration theory solution. Similarly, in the ionic penetration theory model, the electric field produced by the anion diffusion fluxes will produce a diffusive force upon the cations. In this case however, since the penetration theory model is a transient one, the cation flux will generally not be zero even though the cation is not entering into the chemical reaction. It is clear in this case that the ionic self-diffusion coefficient of the C^+ ions will affect the rate at which the cation concentration profile responds to the electric fields produced and thus will affect the ionic penetration theory solution. Here then is a flaw in the film theory approximation. The film theory approximation is independent of R_C, while the true ionic penetration theory solution obviously depends upon the value of R_C.

Curve 5 in Figure 1 has been replotted as the middle curve in Figure 4. The upper and lower curves in Figure 4 are for the same conditions except that the upper curve is for a cation considerably more mobile than the sodium ion, while the lower curve is for a considerably less mobile cation. The upper and lower curves show a maximum deviation from each other of 7%, although the R_C values for these curves differ by a factor of 25. Thus the ionic penetration theory is quite insensitive to the cation diffusivity, although not completely so. The film theory approximation points shown on Figure 4 are independent of R_C, and they can be seen to represent all three curves within 4 per cent.

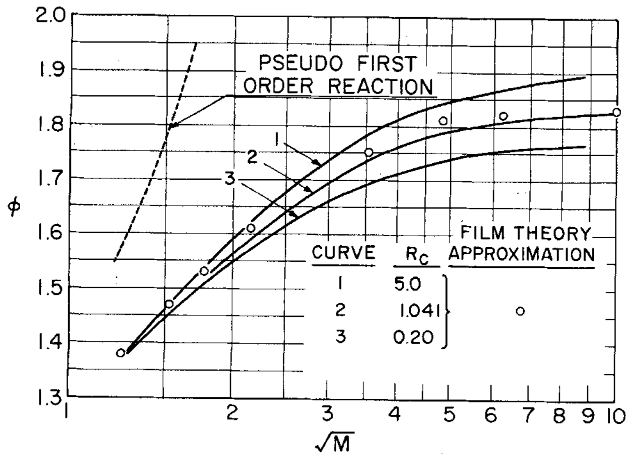

Fig. 4. Effect of cation diffusivity. $Q = 0.614$, $B = 1.0$, $R_P = 0.8537$, $R_A = 4.123$.

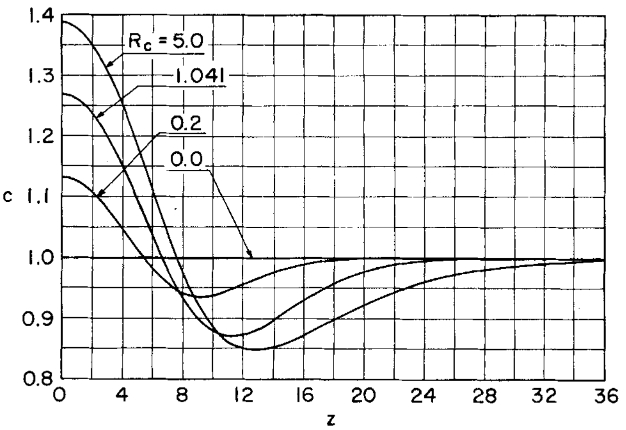

Fig. 5. Cation concentration profiles. $Q = 0.614$, $B = 1.0$, $R_P = 0.8537$, $R_A = 4.123$, $\sqrt{M} = 3.96$.

Figure 4 shows that ϕ increases as R_C increases. This can be understood by considering how A^- ions can diffuse out toward the interface to react with species S as it diffuses in. If electrical neutrality is to be preserved, the A^- ions must either counterdiffuse with P^- ions or carry some C^+ ions with them. If the second mechanism were important, one would expect that increasing R_C would increase ϕ because A^- ions would diffuse more readily when the cation diffusivity was greater. This can be seen to be true in Figure 5, where the cation concentration profiles corresponding to the results in Figure 4 at $\sqrt{M} = 3.96$ are plotted. Figure 5 reveals that the cation concentration at $z = 0$ has been increased considerably above its initial value. This is the result of the cations being dragged out toward the interface by the very mobile A^- ions diffusing out to react with species S, and the effect can be seen to be considerably greater at the higher cation diffusivities.

It should not be inferred from the previous discussion that ϕ will always increase when R_C increases. If the P^- ions are more mobile than the A^- ions, then the P^- ions will tend to diffuse in from the interface faster than the A^- ions tend to diffuse out toward the interface. In this case the electric field will be established in a direction such as to drag the cations in from the interface toward the bulk aqueous phase. This behavior can be seen in the numerically computed concentration profiles plotted in Figure 6. When R_P is greater than R_A, the mobile P^- ions will diffuse so rapidly that they will establish an electric field which drags cations toward the bulk aqueous phase and which accelerates the diffusion of A^- ions out toward the interface. The more mobile the cations are, the more readily the cations can be dragged toward the bulk liquid and thus the less the accelerating influence of the P^- ions upon the A^- ions will be. Thus when R_P is greater than R_A, ϕ will decrease when R_C is increased. When $R_P = R_A$, the cation concentration profile will remain flat, and ϕ will be independent of R_C.

These very interesting effects of the cation diffusivity do not occur in the film theory model and consequently are not taken into account in the film theory approximation as it has been presented. Nevertheless the results in Figure 4 suggest that the film theory approximation is still quite useful because of the very low sensitivity of ϕ to the value of R_C.

Other Systems

If species A^- and P^- were univalent cations instead of anions, and if species C^+ were a univalent anion instead of a cation, the ionic penetration theory result would remain unchanged. The electric field in this case would be of opposite sign to that in the system of Equations (1) and (2), but the diffusion fluxes and the mass transfer rate would remain unchanged. However, except for this invariance with respect to the signs of the ionic charges, the ionic penetration theory results presented in this paper are applicable only to a system described by Equations (1) and (2). Systems involving chemical reaction between two ionized substances, such as the hydrochloric acid-sodium hydroxide system treated by Sherwood and Wei, and systems involving multivalent ions are not included in the system of Equations (1) and (2). Nevertheless it seems reasonable to expect that the film theory approximation will be quite useful for such systems because of its great success in closely approximating the ionic penetration theory results of this study. Since the film theory for an infinitely rapid chemical reaction is a much simpler model to formulate and to solve than is the penetration theory model, the use of the film theory approximation in approaching more complicated systems is a great simplification indeed.

CONCLUSION

The ionic penetration theory equations have been formulated and solved for mass transfer accompanied by a second-order chemical reaction in a system which is a generalization of the acetic acid-sodium hydroxide system. Ion diffusion effects were found to be quite important for this system, the mass transfer rates departing significantly from those which would be obtained if the sodium hydroxide diffused as a molecular species with its salt diffusivity. The ion diffusion effects were found to be qualitatively similar to those reported by Sherwood and

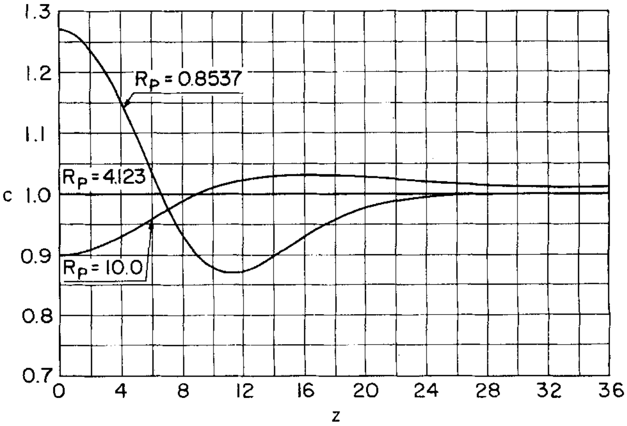

Fig. 6. Cation concentration profiles. $Q = 0.614$, $B = 1.0$, $R_C = 1.041$, $R_A = 4.123$. $\sqrt{M} = 3.96$.

Wei for their film theory analysis for an infinitely rapid chemical reaction, but the ionic diffusion effects were smaller in magnitude in the penetration theory results.

The film theory approximation, in which molecular penetration theory results are used with an effective diffusivity ratio obtained by comparing ionic and molecular film theory results, has been compared with all of the ionic penetration theory results of this study. The film theory approximation represented all of the computed results with a maximum deviation of 4%. Although this comparison has been made for only one type of chemical system, the success of the film theory approximation here leads the authors to expect that this should be a close and useful approximation for ionic penetration theory results in general. This conclusion is significant because film theory approximation solutions can be obtained much more simply than can ionic penetration theory results.

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NOTATION

$[A^-]$ = concentration of the anion reactant in the aqueous phase, g.-ions/cc.
a = $[A^-]/[A^-]_o$
B = $[A^-]_o/[C^+]_o = 1 - [P^-]_o/[C^+]_o$
$[C^+]$ = concentration of the cation in the aqueous phase, g.-ions/cc.
c = $[C^+]/[C^+]_o$
D_A = ionic self-diffusion coefficient of A^- in the aqueous phase, sq.cm./sec.
D_{CA} = salt diffusivity of C^+ and A^- in absence of other ions, sq.cm./sec. [Equation (8)]
D_C = ionic self-diffusion coefficient of C^+ in the aqueous phase, sq.cm./sec.
D_I = diffusion or ionic self-diffusion coefficiet of species I in the aqueous phase, sq.cm./sec.
D_P = ionic self-diffusion coefficient of P^- in the aqueous phase, sq.cm./sec.
D_S = diffusion coefficient of S in the aqueous phase, sq.cm./sec.
E = electric field, v./cm.
F = Faraday constant = 96,500 coulombs/g.-equivalent
$[I]$ = concentration of species I in the aqueous phase, g.-moles/cc. or g.-ions/cc.
k_F = chemical reaction rate constant, cc./(g.-ion)(sec.)
k_L = aqueous phase mass transfer coefficient in the presence of chemical reaction, cm./sec. For penetration theory it is based on time-average flux and driving force at start of exposure interval
k_L^* = aqueous phase mass transfer coefficient in absence of chemical reaction, cm./sec. = $2\sqrt{D_S/\pi t}$ in penetration theory
M = $k_F\,[A^-]_o\,D_S/(k_L^*)^2$ in general
$(\pi/4)\ \theta$ in penetration theory
N_I = flux of species I, (g.-moles or g.-ions)/(sq.cm.)(sec.). Positive if directed into aqueous phase
$[P^-]$ = concentration of the product anion in the aqueous phase, g.-ions/cc.
Q = $[A^-]_o/[S]_i$
q = solute bulk concentration divided by interfacial concentration of transferring species in molecular penetration theory, nomenclature of reference 3
$\mathfrak{R}$ = ideal gas law constant = 8.314 Joules/(g.-mole)(°K.)
R_A = D_A/D_S
R_C = D_C/D_S
R_{CA} = $D_{CA}/D_S \equiv 2R_CR_A/(R_C + R_A)$
R_P = D_P/D_S
r = diffusion coefficient of solute divided by diffusion coefficient of transferring species in molecular penetration theory, nomenclature of reference 3
r_{EFF} = effective value of r [Equation (21)]
$[S]$ = concentration of the transferring species in the aqueous phase, g.-moles/cc.
s = $[S]/[S]_i$
T = absolute temperature, °K.
t = exposure time, sec.
x = distance into the aqueous phase, cm.
Z_I = valence of species I, positive for cations, negative for anions, zero for uncharged molecular species
z = $x\sqrt{k_F[A^-]_o/D_S}$

Greek Letters

α = $(R_C - R_P)/(R_C + R_P)$
β = $B(R_A - R_P)/(R_C + R_P)$
θ = $k_F[A^-]_o t$
π = 3.14159 . . .
ϕ = k_L/k_L^*
ϕ_a = asymptotic value of ϕ at large values of $\sqrt{M}$

Subscripts

i = interface between aqueous and nonaqueous phases
o = bulk aqueous phase. In penetration theory the mixed aqueous phase before the start of the exposure interval

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