

Simultaneous Mass Transfer and Equilibrium Chemical Reaction

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Equations predicting the effect of various types of equilibrium chemical reactions on the liquid-phase mass transfer coefficient have been derived. In each case the reacting species were assumed to be present in equilibrium concentrations at all points along the diffusion path. Equations were derived for both the film and surface-renewal theories of simple mass transfer in conjunction with these equilibrium reactions.

The well-known Hatta equation for the rapid second-order irreversible reaction was shown to be a limiting case of the general equilibrium reaction $A + B \rightleftharpoons E$.

The calculated mass transfer coefficients were found to be functions of the concentration driving force and the average concentration level over the diffusion path as well as of the magnitude of the equilibrium constant and the diffusivities of the reacting species.

Ever since Hatta (5) modified the film concept of mass transfer to include simple simultaneous chemical reaction, there has been considerable theoretical work extending this analytical treatment to more complex reaction types. Each reaction is characterized by its kinetic order, degree of reversibility, and the relative rates of the diffusional and chemical-conversion steps. Thus Hatta's early investigation of the absorption of carbon dioxide by caustic solution pertained to a reaction the kinetics of which was second order, irreversible, and infinitely rapid compared with the diffusional rates involved. Subsequent studies have considered the slow (diffusion and chemical-conversion rates of comparable magnitudes), first order, reversible (2) or irreversible (8) reaction; the slow, irreversible reaction of n^{th} order in the transferring species (1); and the slow, second-order, irreversible reaction (10).

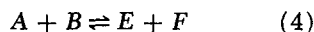
With the advent of the surface-renewal theories of Danckwerts and Kishinevsky, the diffusional step was no longer restricted to the oversimplified concept of the film theory, and a flurry of papers combining the same reaction types with these more realistic mass transfer models appeared (6, 2, 3).

However none of the previous studies have systematically examined the case of the infinitely rapid reversible reaction. It is the object of this paper to add the equilibrium reaction to the rogues' gallery of chemical interactions which can occur in conjunction with the mass transfer process.

The maintenance of chemical equi-

librium implies that throughout the diffusion path the reacting species are present in concentrations satisfying the mass action law. Consequently only the ratio of the forward and reverse chemical-rate constants appears as the equilibrium constant in the over-all transfer rate expression.

The reactions which will be considered are



Reactions (1) through (4) will be applied to the film theory and (1) through (3) to Danckwerts' surface-renewal theory.

Species A is assumed to transfer between an inert phase, in which no chemical reaction occurs, and a reacting liquid phase, in which any one of reactions (1) through (4) takes place. The inert phase can be a gas, another liquid immiscible with the reacting phase, or a solid. The restrictions on this phase are that it contain only A (and perhaps an inert diluent) and that it generate a known equilibrium concentration of A on the reacting-phase side of the interface.

Since for all cases the system includes more than two species (reactants, products, and inert solvent), a completely rigorous treatment of the problem would require the use of liquid multicomponent diffusion coefficients to characterize the transport rates. However in the following derivations it will be assumed that the re-

actants and products are sufficiently dilute such that Fick's Law is applicable; that is, the diffusion coefficients may be considered those of the binary system consisting of the particular species and the solvent.

Unlike the reactions previously studied, the method of approach to the equilibrium system is independent of the particular reaction under consideration; the differences in reaction type are reflected only in the boundary conditions and equilibrium restrictions. The development of the pertinent differential equations can be most easily illustrated by considering a particular reaction, for example the type exemplified by Equation (3).

If this reaction were not infinitely rapid, material balances for species A and E over a slice of fluid of thickness dx within the diffusion path would yield

$$D_A \frac{\partial^2 A}{\partial x^2} = kAB - k'E + \frac{\partial A}{\partial t} \quad (5)$$

$$D_E \frac{\partial^2 E}{\partial x^2} = -kAB + k'E + \frac{\partial E}{\partial t} \quad (6)$$

If the mass-action constant for the reaction is K , then

$$K = \frac{E}{AB} = \frac{k}{k'} \quad (7)$$

Equations (5) and (6) can be rewritten to yield

$$D_A \frac{\partial^2 A}{\partial x^2} = k(AB - E/K) + \frac{\partial A}{\partial t} \quad (5a)$$

$$D_E \frac{\partial^2 E}{\partial x^2} = -k(AB - E/K) + \frac{\partial E}{\partial t} \quad (6a)$$

If the reaction-rate constant is increased so that equilibrium conditions are approached at all points along the

diffusional path, the right-hand members of Equations (5a) and (6a) become indeterminate, since $(AB - E/K)$ approaches zero as k approaches infinity. This difficulty can be avoided by the addition of the two equations, which results in

$$D_A \frac{\partial^2 A}{\partial x^2} + D_B \frac{\partial^2 E}{\partial x^2} = \frac{\partial}{\partial t} (A + E) \quad (8)$$

Equation (8) can be viewed as the differential material balance of component A in all forms over a slab of thickness dx within the reacting phase. The first term on the left represents the contribution of unreacted A and the second term that of combined A. (In this case E represents the addition product of A and B.) Hereafter relations of the type represented by Equation (8) will be called *total-component* material balances; the total A component in this case denotes the sum of the concentrations of A + E. Equation (8) is directly applicable to the unsteady state processes of the penetration theory; in the film theory the time derivative is zero, since only steady state transfer is considered. In this example there would be an additional partial-differential equation representing the total B component material balance:

$$D_B \frac{\partial^2 B}{\partial x^2} + D_E \frac{\partial^2 E}{\partial x^2} = \frac{\partial}{\partial t} (B + E) \quad (9)$$

where the total B component = $B + E$.

Equations (8) and (9), in conjunction with the equilibrium restriction of Equation (7) and the appropriate boundary conditions, completely determine the concentration profiles of A, B, and E and the rate of transfer of species A between the inert phase and the reacting phase.

Following the total-component material-balance approach, one can derive the rate expressions for simultaneous mass transfer and each of the four types of equilibrium chemical reactions.

Mass transfer coefficients can be based on either the total driving force, $(C_i - C_L)$, or the driving force of unreacted solute $(A_i - A_L)$:

$$k_c = \frac{J}{C_i - C_L}$$

$$k_A = \frac{J}{A_i - A_L}$$

The most appropriate form depends on the particular reaction system and on the analytical techniques available. For many systems only the total A component can be determined, e.g., base titration of a partially ionized acid, and k_c is the only experimentally measurable coefficient possible. However for the last two cases [reactions (3) and

(4)] k_c is not a useful quantity, since C_i is a function of both the mass transfer and equilibrium characteristics of the system.

If the unreacted solute (species A) can be analytically differentiated from the reaction product (species E), then k_A is experimentally measurable. A_i is determined (and presumably known) by the physical distribution of A between the inert and reacting phases.

Case (1) Film-Theory Mass Transfer and the Reaction $A \rightleftharpoons E$

The total A component material balance is

$$D_A \frac{d^2 A}{dx^2} + D_E \frac{d^2 E}{dx^2} = 0 \quad (10)$$

The general solution of Equation (10) is

$$D_A A + D_E E = a_1 x + a_2 \quad (11)$$

With A and E subject to the equilibrium restriction

$$K = \frac{E}{A} \text{ for all } x \quad (12)$$

The boundary conditions are

$$\text{at } x = 0, A = A_i \quad (13a)$$

$$\text{at } x = x_L, A = A_L \quad (13b)$$

The transfer rate of species A from the inert phase is equal to the flux of the total A component within the reacting-phase film:

$$J = -D_A \frac{dA}{dx} - D_E \frac{dE}{dx} = -a_1 \quad (14)$$

Substituting Equations (12), (13), and (14) into Equation (11), one gets

$$J = \left(\frac{D_A}{x_L} \right) (A_i - A_L) \left(1 + \frac{D_E}{D_A} K \right) \quad (15)$$

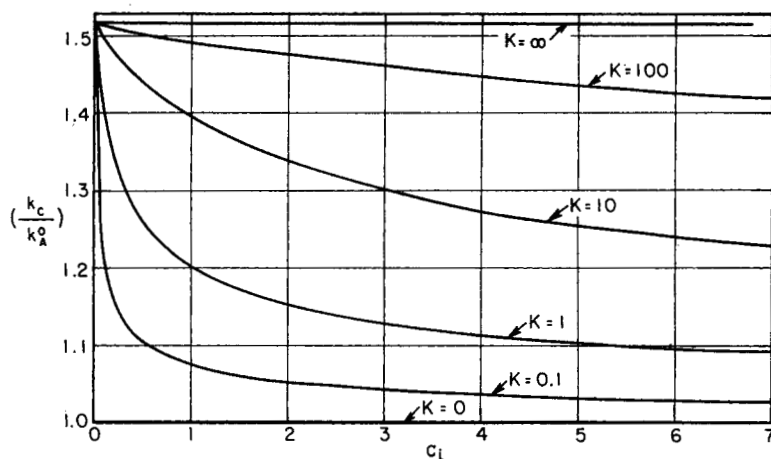


Fig. 1. Effect of interfacial concentration on the mass transfer coefficient for diffusion and the simultaneous equilibrium reaction $A \rightleftharpoons 2E$ as calculated from Equations (27) and (28): $0 \leq K \leq \infty$, $C_L = 0$, $D_E/D_A = 1.51$.

Or, with k_A defined as the flux divided by the driving force $(A_i - A_L)$ and k_A^0 as the mass transfer coefficient in the absence of chemical reaction (D_A/x_L)

$$k_A = k_A^0 \left(1 + \frac{D_E}{D_A} K \right) \quad (16)$$

If the concentrations at the film boundaries are specified in terms of the total A component, $C = A + E$:

$$\text{at } x = 0, C = C_i = (1 + K)A_i \quad (17a)$$

$$\text{at } x = x_L, C = C_L = (1 + K)A_L \quad (17b)$$

Then

$$J = \left(\frac{D_A}{x_L} \right) (C_i - C_L) \left[1 + \left(\frac{D_E}{D_A} - 1 \right) \theta \right] \quad (18)$$

where

$$\theta = \frac{K}{1 + K} \quad (19)$$

Again defining the mass transfer coefficient as the flux divided by the total A component driving force $(C_i - C_L)$, one obtains

$$k_c = k_A^0 \left[1 + \left(\frac{D_E}{D_A} - 1 \right) \theta \right] \quad (20)$$

Equation (15) has been derived by Peaceman (7) as a limiting case of the slow, first-order, reversible reaction. The concentration profiles are linear throughout the film for all values of K only for this case.

Case (2) Film-Theory Mass Transfer and the Reaction $A \rightleftharpoons 2E$

In this case A represents the dimer E_2 . A material balance on the total A component, $C = A + \frac{1}{2}E$, gives

$$D_A \frac{d^2 A}{dx^2} + \frac{1}{2} D_E \frac{d^2 E}{dx^2} = 0 \quad (21)$$

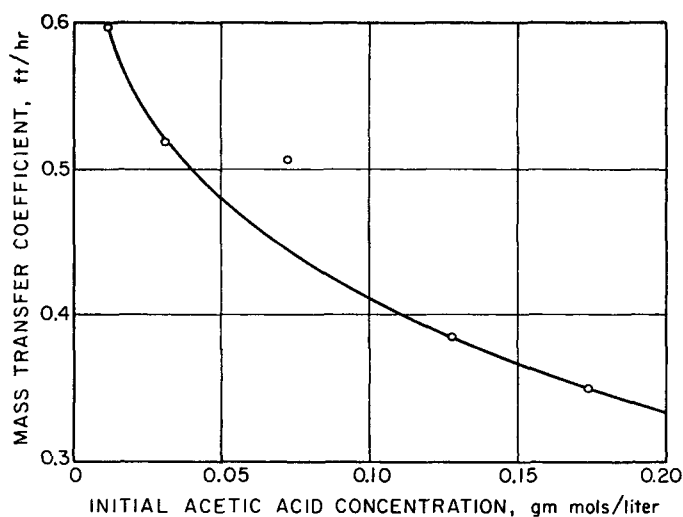


Fig. 2. Variation of the mass transfer coefficient with initial organic-phase solute concentration for the extraction of acetic acid from carbon tetrachloride into water (4).

the general solution of which is

$$D_A A + \frac{1}{2} D_B E = a_1 x + a_2 \quad (22)$$

The equilibrium condition is

$$K = \frac{E^2}{A} \quad (23)$$

and the boundary conditions are given by Equation (13). The flux of A is written as

$$J = -D_A \frac{dA}{dx} - \frac{1}{2} D_B \frac{dE}{dx} \quad (24)$$

The relation between the mass transfer coefficients with and without chemical reaction becomes*

$$k_A = k_A^0 \left[1 + \frac{D_B}{D_A} \frac{\sqrt{K/4}}{\sqrt{A_i} + \sqrt{A_L}} \right] \quad (25)$$

If the boundary conditions are specified in terms of the total A component, then

$$\text{at } x = 0, C = C_i = A_i + \frac{1}{2} \sqrt{KA_i} \quad (26a)$$

$$\text{at } x = x_L, C = C_L = A_L + \frac{1}{2} \sqrt{KA_L} \quad (26b)$$

and

$$k_c = k_A^0 \left[1 + \left(\frac{D_B}{D_A} - 1 \right) \theta' \right] \quad (27)$$

where

* For the general polymerization reaction, $A \rightleftharpoons nE$, the relation between the mass transfer coefficients with and without chemical reaction can be determined by a simple extension of this method:

$$k_A = k_A^0 \left[1 + \frac{K^{1/n} D_B}{n D_A} \left(\frac{A_i^{1/n} - A_L^{1/n}}{A_i - A_L} \right) \right]$$

However an analytical expression for the mass transfer coefficient based on the total component C is not obtainable, since the solution of a polynomial of order greater than 2 would be required.

$$\theta' = \frac{\sqrt{K^2/16 + KC_i} - \sqrt{K^2/16 + KC_L}}{2(C_i - C_L)} \quad (28)$$

A plot of k_c/k_A^0 as a function of C_i is shown in Figure 1 for $C_L = 0$ and for various values of K. The ratio D_B/D_A was estimated by the assumption that the molecular volume of A is twice that of E and by the use of the Wilke correlation (11). Thus

$$\frac{D_B}{D_A} = \left(\frac{V_A}{V_E} \right)^{0.6} = (2)^{0.6} = 1.51$$

Figure 1 indicates that there is a maximum increase of 51% in k_c as the equilibrium constant increases from zero (no dissociation) to infinity (complete dissociation). Moreover k_c decreases markedly with increasing concentration owing to the increased amount of undissociated A present at higher concentrations. At $C_i = 0$ all the diffusing material is present as the dissociation products, for all nonzero values of K.

Acetic acid is one of the few solutes known to dimerize appreciably in non-polar solvents. Farmer (4) has investigated the effect of initial solute concentration on the mass transfer coefficient for the extraction of acetic acid from single drops of carbon tetrachloride into a dispersed water phase. These results, shown in Figure 2, show the same general behavior as the predicted curves of Figure 1.

Since the solute was stripped from the reacting phase (carbon tetrachloride) into an essentially solute-free inert phase (water), Equations (27) and (28), with $C_i = 0$, are applicable. The variation of the mass transfer coefficient with the acetic acid concentration of the carbon tetrachloride phase should be described by the curve of Figure 1 with C_i replaced by C_L in the

abscissa. However Farmer's data are not amenable to a direct analysis by this theory, since the solute concentration decreased by 30 to 40% during an experiment, and neither the dissociation constant nor the diffusivity ratio is known. The rapid decrease in k_c with concentration suggests an equilibrium constant in the range of 0.01 to 0.1 for this system. Since the mass transfer coefficient decreases by 70% between $C_L = 0.011$ and $C_L = 0.174$, the diffusivity ratio D_B/D_A must be larger than the value of 1.51 predicted by Wilke's correlation if these data are to be explained on the basis of simultaneous mass transfer and equilibrium dissociation. Farmer also attributed this behavior to partial dimerization of the acetic acid in the organic solvent.

The measured distribution coefficients (organic to aqueous) were less than 0.05 for all experiments, and so the observed mass transfer coefficients were essentially equal to the organic film coefficients. Thus the decrease in k_c cannot reasonably be attributed to the effect of increasing distribution coefficient on the sum of the individual resistances.

Although the curves of Figure 1 have been extended to a concentration of 7 molar, other effects probably become more important at high concentrations. Wilke (12) has cited the photographic studies of the carbon tetrachloride-acetic acid-water system reported by Sigwart and Nassenstein (9). They offer strong evidence of interfacial turbulence at concentrations beyond about 0.2 molar, although the water-carbon tetrachloride interface appeared to be quite stable during acetic acid transfer for the low-concentration region to which Farmer's investigation was restricted.

Equations (27) and (28) apply in principle to the transfer of a partially dissociated electrolyte, such as nitric acid, through an aqueous film. Despite their difference in sizes, the two ions will exhibit the same effective diffusivity, since by electrical neutrality the two must diffuse at the same rate. However the restriction that the solution be ideal is not true for aqueous electrolytes, even at very low concentrations. Consequently the theory is not applicable to this class of dissociating systems.

Equations (20) and (27) indicate that for cases (1) and (2) the mass transfer coefficient is given by an expression of the general type:

$$k_c = \frac{J}{C_i - C_L} = \left(\frac{D_A}{x_L} \right) \left[1 + \left(\frac{D_B}{D_A} - 1 \right) \theta \right] \quad (29)$$

Only the θ term depends upon the particular reaction type under consideration; the physical meaning of θ can be described as follows. The mass transfer rate of the total component is based on the driving force $(\bar{C}_i - C_L)$. However for case (2) the nature of the equilibrium expression requires that the relative amount of unreacted solute (A) and reaction product (E) be an increasing function of the total concentration level (C) at any point along the diffusion path. Species A, because of its greater bulk, has lower diffusivity than the dissociated material. Hence the total flux, which is the sum of the transfer rates of A and one half that of E, depends upon the fraction of the total component in each form (which is in turn a function of the total concentration C) and of the diffusivity of each species. θ is a complex averaging parameter which accounts for the varying A to E ratio throughout the film, and $D_A \{1 + (D_B/D_A - 1)\theta\}$ is an average diffusivity for the transfer process.

Equation (29) shows that if $D_A = D_B$, then there is no effect of an equilibrium chemical reaction on the mass transfer coefficient if the reaction is of types (1) or (2). However it will be shown for cases (3) and (4) that C_i , and hence the driving force, depends on K. For these two cases equilibrium reaction will affect the transfer rate, even though $D_A = D_B$.

Case (3) Film Theory Mass Transfer and the Reaction $A + B \rightleftharpoons E$

Species E denotes the addition product of A and B. The total A component material balance gives

$$D_A \frac{d^2 A}{dx^2} + D_B \frac{d^2 E}{dx^2} = 0 \quad (30)$$

The total B component material balance gives

$$D_B \frac{d^2 B}{dx^2} + D_B \frac{d^2 E}{dx^2} = 0 \quad (31)$$

The general solutions to Equations (30) and (31) are

$$D_A A + D_B E = a_1 x + a_2 \quad (32)$$

$$D_B B + D_B E = a_3 x + a_4 \quad (33)$$

The equilibrium restriction, which applies throughout the film, is

$$K = \frac{E}{AB} \quad (34)$$

The four boundary conditions are

$$\text{at } x = 0, A = A_i \quad (35)$$

$$x = x_L, A = A_L \quad (36)$$

$$B = B_L \quad (37)$$

The final boundary condition reflects the inability of B or E to penetrate the interface:

$$D_B \frac{dB}{dx} + D_B \frac{dE}{dx} = 0 \quad (38)$$

With J given by Equation (14), Equations (32) and (33) can be solved for the mass transfer coefficient to give

$$k_A = k^{\circ}_A \left[1 + \left(\frac{D_B}{D_A} \right) \frac{B_L}{A_i + \frac{D_B/D_E}{K}} \right] \quad (39)$$

Even though a solution utilizing total component boundary conditions could also be obtained, this would not represent a useful description of the process. Although A_i is determined from the condition of physical equilibrium of species A between the inert and reacting phases at the interface, the total A component cannot be similarly specified. C_i is not a unique function of A_i , as it was for the two previous cases, [Equations (17) and (26)], but is given by

$$C_i = A_i + E_i = A_i (1 + KB_i) \quad (40)$$

C_i depends upon the concentration of reactant B at the interface as well as A_i . Owing to the chemical reaction occurring within the film, B_L is in general greater than B_i , the actual value of which is given by

$$B_i = B_L \left[\frac{\frac{D_B/D_E}{K} + A_L}{\frac{D_B/D_E}{K} + A_i} \right] \quad (41)$$

Thus

$$C_i = A_i \left[1 + KB_L \frac{\frac{D_B/D_E}{K} + A_L}{\frac{D_B/D_E}{K} + A_i} \right] \quad (42)$$

Since C_i is not a quantity which can be determined solely from equilibrium conditions but depends on both the mass transfer properties of the system and the bulk concentrations, it is not a useful boundary condition for this case. However A_i is fixed solely by the distribution coefficient of species A between the inert and reacting phases and is therefore an appropriate boundary condition.

If K becomes large, the system approaches that of the rapid, irreversible, second-order reaction, which has received considerable attention in the literature (5, 8). As K approaches in-

finiteness, the group $(D_B/D_A)/K$ in Equation (39) approaches zero, and the mass transfer coefficient is given by

$$k_A = k^{\circ}_A \left(1 + \frac{D_B B_L}{D_A A_i} \right) \quad (43)$$

which is the Hatta equation for this reaction type.

The concentration profiles of the three species can be determined from Equations (32), (33), and (34) and the known values of the constants a_1 , a_2 , a_3 , and a_4 . The variation of the concentration of A through the film is given by

$$A = \frac{1}{2} \{ [R - P(x)]^2 + 4\beta P(x) \}^{1/2} - \frac{1}{2} [R - P(x)] \quad (44)$$

where

$$R = \beta + \alpha \left(1 + \frac{A_L}{\beta} \right) \quad (45)$$

$$P(x) = A_i \left[1 + \frac{\alpha(1 + A_L/\beta)}{A_i + \beta} \right] - (A_i - A_L) \left[1 + \frac{\alpha}{A_i + \beta} \right] \left(\frac{x}{x_L} \right) \quad (46)$$

$$\alpha = \frac{D_B B_L}{D_A} \quad (47)$$

$$\beta = \frac{D_B/D_E}{K} \quad (48)$$

The concentration profiles of B and E are given by

$$B = B_L \left(\frac{\beta + A_L}{\beta + A} \right) \quad (49)$$

$$E = KAB \quad (50)$$

The behavior of the concentration profiles as K ranges from 10^{-3} to 10^{-4} is shown for a hypothetical system in Figure 3. The appearance of the characteristic reaction zone, at which $A = B = 0$, becomes evident at large values of K. As K approaches infinity, Equation (44) reduces to

$$A = A_i - (A_i + \alpha) \left(\frac{x}{x_L} \right) \quad (51)$$

which is identical to the result obtained from the Hatta model.

Similarly, as K approaches zero, the system reduces to the simple mass transfer of species A and Equation (44) becomes

$$A = A_i - (A_i - A_L) \left(\frac{x}{x_L} \right) \quad (52)$$

which is the film-theory expression for mass transfer in the absence of chemical reaction.

Another interesting limiting case is that in which K is large and A_i is small. This behavior is characteristic of the extraction of metallic salts by organic complexing or chelating agents. The metal salts are quite insoluble in

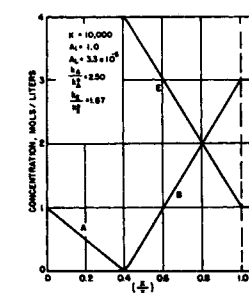
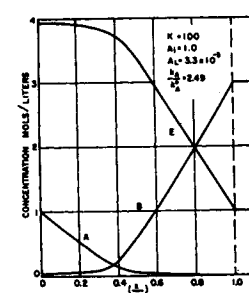
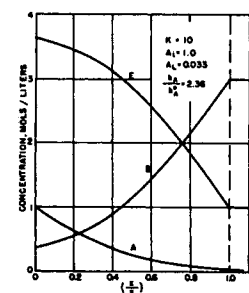
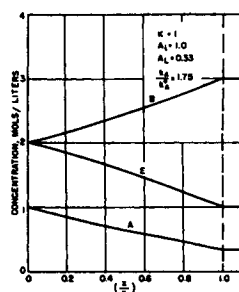
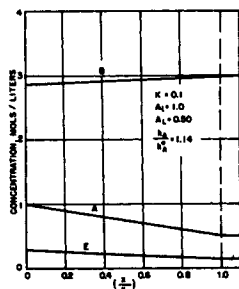
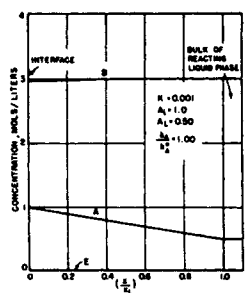
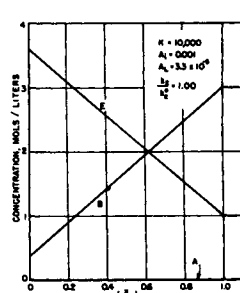
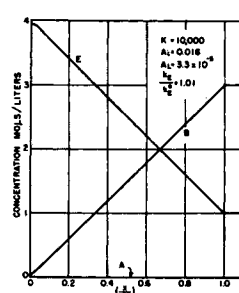
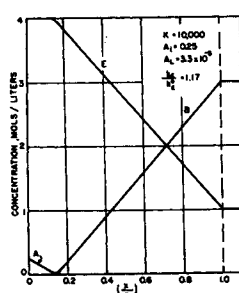
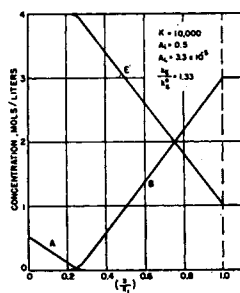


Fig. 3. Effect of the equilibrium constant on the concentration profiles for simultaneous mass transfer and the equilibrium chemical reaction $A + B \rightleftharpoons E$: $D_B/D_A = 0.5$, $D_B/D_E = 1.0$, $B_L = 3.0$, $A_i = 1.0$. A_L is adjusted to keep $T = E_L + B_L$ between 3 and 4, and $A_L \leq 0.5A_i$. k_A/k_A° is determined from Equation (39).

Fig. 4. Effect of decreasing A_i on the concentration profiles for simultaneous mass transfer and equilibrium chemical reaction $A + B \rightleftharpoons E$: $D_B/D_A = 0.5$, $D_B/D_E = 1.0$, $B_L = 3.0$, $K = 10,000$. A_L is adjusted to keep $T = E_L + B_L$ between 3 and 4, and $A_L \leq 0.5A_i$. k_B/k_B° is determined from Equation (58).



the inert solvent of the organic phase and are extractable only by virtue of the complexes or chelates formed with an active agent added to the diluent. For example uranyl nitrate is practically insoluble in kerosene but is quite extractable in a solvent composed of kerosene and the complexing agent tributyl phosphate. In these reactions K is large but not infinite, since generally all of the complexing agent is not consumed at equilibrium. The reduction of Equation (39) to Equation (43) does not apply to this case, since both $(D_B/D_E)/K$ and A_i approach zero. However Equation (39) can be rewritten as

$$J = \left(\frac{D_A}{x_L} \right) (KA_i - KA_L) \left[\frac{1}{K} + \frac{D_B}{D_A} \frac{B_L}{KA_i + D_B/D_E} \right] \quad (53)$$

By the equilibrium restrictions

$$KA_i = \frac{E_i}{B_i} \quad (54)$$

$$KA_L = \frac{E_L}{B_L} \quad (55)$$

If K is sufficiently large, $1/K \approx 0$, Equation (53) becomes

$$J = \left(\frac{D_B}{x_L} \right) \left[\frac{E_i}{B_i} - \frac{E_L}{B_L} \right] \left[\frac{B_L}{\frac{E_i}{B_i} + \frac{D_B}{D_E}} \right] \quad (56)$$

Upon elimination of B_i by Equations (41), (54), and (55), Equation (56) reduces to

$$J = \left(\frac{D_B}{x_L} \right) (E_i - E_L) \quad (57)$$

Furthermore since at all points along the diffusion path A is small, $C = E + A \approx E$, and

$$J = k_B^\circ (C_i - C_L) \quad (57a)$$

The change in the profiles of A , B , and E for $K = 10^4$ as A_i is decreased is shown in Figure 4. k_B/k_B° has been computed by the relationship

$$\frac{k_B}{k_B^\circ} = \frac{(D_B/D_A)}{(D_B/D_A)} \left(\frac{A_i - A_L}{E_i - E_L} \right) \left(\frac{k_A}{k_A^\circ} \right) \quad (58)$$

and presented along with the concentration profiles. E_i and E_L are the calculated values of E at the film boundaries, and k_A/k_A° is obtained from Equation (39). At $K = 10^4$ and $A_i = 10^{-8}$, the concentration of E is nearly linear across the film and $k_B/k_B^\circ = 1.00$, as would be expected from Equation (57).

Thus for the case of large K and small A_i , the system is equivalent to the simple mass transfer of reaction product E between the interface and the bulk. However the limitations on C_i previously discussed apply to this special case as well. It can be shown that only if $D_B = D_E$, is C_i a function of the equilibrium conditions at the interface (KA_i) and the total B component concentration, $T = B_L + E_L = \text{constant}$.

For the general case of $D_B \neq D_E$ the problem of determining either C_i or A_i may be the major obstacle in analyzing the mass transfer data. For the complexing of uranyl nitrate by tri-butyl phosphate, for example, no analytical technique has been devised for differentiating between the small amount of uncomplexed material and the complex in the organic phase; only their sum is experimentally available. In addition, the organic phase equilibrium constants are generally unknown, since only over-all aqueous to organic equilibrium constants (which include the distribution constant of species A) are measurable. Thus neither C_i nor A_i is known, and the rate equations are inapplicable for lack of sufficient equilibrium information.

Another variation of this case should also be noted. If in addition to large K and small A_i , B_L is also small, the $1/K$ term in Equation (53) is not negligible and the mass transfer coefficient is again given by Equation (43).

Case (4) Film-Theory Mass Transfer and the Reaction $A + B \rightleftharpoons E + F$

In order to determine clearly the requisite material balance reactions, it

$$\phi = \frac{1}{2} \left\{ \left[\left(\frac{D_F}{D_B} - 1 \right) \sqrt{KB_L A_L} + \frac{D_F}{D_B} A_i K \right]^2 + 4 \left[\frac{D_B}{D_F} B_L + \sqrt{KA_L B_L} \right] \left(\frac{D_F}{D_B} A_i K \right) \right\}^{1/2} - \frac{1}{2} \left[\frac{D_F}{D_B} \sqrt{KA_L B_L} + \frac{D_F}{D_B} KA_i \right] \quad (72)$$

is convenient to rewrite this exchange reaction in terms of the subspecies which constitute the reactants and products: $ab + cd \rightleftharpoons ad + cb$, where $A = ab$, $B = cd$, $E = ad$, $F = cb$. The material balances on each of the subspecies, a, b, c , and d are

Subspecies a :

$$D_A \frac{d^2 A}{dx^2} + D_B \frac{d^2 E}{dx^2} = 0 \quad (59)$$

Subspecies b :

$$D_A \frac{d^2 A}{dx^2} + D_F \frac{d^2 F}{dx^2} = 0 \quad (60)$$

Subspecies c :

$$D_B \frac{d^2 B}{dx^2} + D_F \frac{d^2 F}{dx^2} = 0 \quad (61)$$

Subspecies d :

$$D_B \frac{d^2 B}{dx^2} + D_E \frac{d^2 E}{dx^2} = 0 \quad (62)$$

However only three of these equations are independent; Equations (59), (61), and (62) have arbitrarily been chosen, although any other combination would have been equally valid. The general solutions of these three differential equations are

$$D_A A + D_E E = a_1 x + a_2 \quad (63)$$

$$D_B B + D_F F = a_3 x + a_4 \quad (64)$$

$$D_B B + D_E E = a_5 x + a_6 \quad (65)$$

By the restriction that B , E , and F must remain in the reacting phase, a_3 and a_6 are zero. Furthermore by Equation (14) $a_1 = -J$. The remaining boundary conditions are

$$\text{at } x = 0, A = A_i \quad (66)$$

$$\text{at } x = x_L, A = A_L \quad (67)$$

$$B = B_L \quad (68)$$

and, by the stoichiometry of the reaction

$$E_L = F_L \quad (69)$$

with

$$K = \frac{EF}{AB} \quad (70)$$

The effect of the reaction on the mass transfer coefficient is then given by

$$k_A = k^\circ_A \left[1 + \frac{D_B}{D_A} \frac{\phi}{A_i - A_L} \right] \quad (71)$$

where ϕ is

In all four cases considered, except the first, the mass transfer coefficients k_e or k_A are functions not only of the various diffusivities and equilibrium constants but of the concentrations at the interface and in the bulk of the reacting phase. Generally, the larger the driving force, the more pronounced is the effect of the chemical reaction, but even for small driving forces the mass transfer coefficient will depend on the concentration level. The effect of the concentration level for zero driving force can be obtained by calculating the limiting values of k_e and k_A as $C_i \rightarrow C_L$ and $A_i \rightarrow A_L$ respectively.

The equations are probably not valid at high concentrations where the effects of solution nonideality on the

$$J(t) = \left(\frac{D_A}{\pi t} \right)^{1/2} \left[\left(1 + K \frac{D_B}{D_A} \right) (1 + K) \right]^{1/2} (A_i - A_L) \quad (78)$$

diffusion coefficients become more pronounced. Moreover the reacting phase must contain an inert solvent which sufficiently dilutes the reacting species so that Fick's law is applicable to each. Otherwise each diffusivity must be estimated from untested and complex equations for multicomponent diffusion (1).

$$J = \sqrt{D_A s} (A_i - A_L) \sqrt{\left(1 + \frac{D_B}{D_A} K \right) (1 + K)} \quad (80)$$

Another limitation to these derivations is their complete dependence on the somewhat antiquated concepts of the film theory, namely the assumption of a stagnant film in which molecular diffusion is the sole transport process. This assumption is implicit in the application of Fick's law to each species and in the assumption that (D_A/x_L) is equal to the mass transfer coefficient k°_A . However since only diffusivity ratios appear in the correction factors, it might be more realistic to replace them by ratios of the mass transfer coefficients of the particular species; e.g., k°_B/k°_B would be substituted for

D_B/D_B . If from available correlations the mass transfer coefficient were known to vary as some fractional power of the diffusivity, then the ratio $(D_B/D_B)^n$ would be appropriate. These devices are tantamount to replacing Fick's law for each species by rate expressions of the type $J = k^\circ x_L \left(\frac{dC}{dx} \right)$.

Case (1a) Surface Renewal Mass Transfer and the Reaction $A \rightleftharpoons E$

The unsteady state material balance of the total A component is

$$D_A \frac{\partial^2 A}{\partial x^2} + D_E \frac{\partial^2 E}{\partial x^2} = \frac{\partial}{\partial t} (A + E) \quad (73)$$

E and A are related by Equation (12), and the appropriate boundary conditions are

$$\text{at } t = 0, A = A_L \quad (74)$$

$$\text{at } x = \infty, A = A_L \quad (75)$$

$$\text{at } x = 0, A = A_i \quad (76)$$

Equation (73), subject to these boundary conditions, can be solved for the instantaneous absorption rate, defined by

$$J(t) = -D_A \left(\frac{\partial A}{\partial x} \right)_{x=0} - D_E \left(\frac{\partial E}{\partial x} \right)_{x=0} \quad (77)$$

to yield

In accordance with Danckwerts' surface renewal theory (3), the steady state absorption rate is related to $J(t)$ by

$$J = \int_0^\infty J(t) s e^{-st} dt \quad (79)$$

Combining Equations (78) and (79) one obtains

with $k^\circ_A = \sqrt{D_A s}$

$$k_A = k^\circ_A \sqrt{\left(1 + \frac{D_B}{D_A} K \right) (1 + K)} \quad (81)$$

If the boundary conditions are expressed in terms of the total A components, then

$$k_e = k^\circ_A \sqrt{1 + \left(\frac{D_B}{D_A} - 1 \right) \theta} \quad (82)$$

where

$$\theta = \frac{K}{1 + K}$$

A comparison of Equations (20) and (82) indicates that the film theory predicts the effect of this type of equilibrium reaction on the mass transfer coefficient to be directly proportional to $\{1 + [(D_B/D_A) - 1]\theta\}$, while the surface-renewal theory predicts only a one-half power dependence of k_A on this group.

Case (2a) Surface Renewal Mass Transfer and the Reaction $A \rightleftharpoons 2E$

The appropriate material-balance equation is

$$D_A \frac{\partial^2 A}{\partial x^2} + \frac{1}{2} D_B \frac{\partial^2 E}{\partial x^2} = \frac{\partial}{\partial t} (A + \frac{1}{2} E) \quad (83)$$

E can be eliminated from the equilibrium relations of Equation (23) and Equation (83) rewritten as

$$D_A \frac{\partial^2}{\partial x^2} \left[A + \frac{\sqrt{K}}{2} \frac{D_B}{D_A} \sqrt{A} \right] = \frac{\partial}{\partial t} \left[A + \frac{\sqrt{K}}{2} \sqrt{A} \right] \quad (84)$$

where boundary conditions are given by Equations (74), (75), and (76). With $J(t)$ given by the relations

$$J(t) = -D_A \left(\frac{\partial A}{\partial x} \right)_{x=0} - \frac{1}{2} D_B \left(\frac{\partial E}{\partial x} \right)_{x=0} \quad (85)$$

and the steady state transfer rate by Equation (79), an approximate solution can be written as

$$J = \sqrt{D_A s} (A_i - A_L) \left[\frac{\sqrt{A_i} + \frac{\sqrt{K}}{4} \frac{D_B}{D_A}}{\left(\frac{A_i}{b} \right)^{1/2} e^{a^2/b} \operatorname{erfc} \left(\frac{a}{\sqrt{b}} \right)} \right] \quad (86)$$

where a and b are given by

$$a = \frac{\frac{\sqrt{K}}{4} \frac{D_B}{D_A} (A_i - A_L)}{A_i \left(2\sqrt{A_i} + \frac{\sqrt{K}}{2} \frac{D_B}{D_A} \right) e^{a^2/b} \left(\frac{\pi}{b} \right)^{1/2} \operatorname{erfc} \left(\frac{a}{\sqrt{b}} \right)} \quad (87)$$

and

$$b = \frac{1}{2} \left[\frac{\sqrt{A_i} + \sqrt{K}/4}{\sqrt{A_i} + \frac{\sqrt{K}}{4} \frac{D_B}{D_A}} \right] + a^2 \left(\frac{12\sqrt{A_i}}{\sqrt{K}} \frac{D_A}{D_B} + 1 \right) \quad (88)$$

The bracketed term in Equation (86) is a measure of the effect of the equilibrium chemical reaction $A \rightleftharpoons 2E$ on the surface-renewal mass transfer coefficient.

Case (3a) Surface Renewal Mass Transfer and the Reaction $A + B \rightleftharpoons E$

The total component material balances for surface renewal mass transfer

and the reaction $A + B \rightleftharpoons E$ have no analytical solutions except for the special case of $D_A = D_B = D_B$. With this simplification the flux can be described by

$$J = \sqrt{D_A s} (A_i - A_L) \left[1 + \frac{B_L}{A_i + 1/K} \right] \quad (89)$$

or

$$k_A = k^\circ_A \left(1 + \frac{B_L}{A_i + 1/K} \right) \quad (90)$$

Equation (90) is identical to the film-theory expression for equal diffusivities, Equation (39). Similarly the surface-renewal and film theories lead to identical rate expressions (except for the k°_A term) for the equal-diffusivity cases of reactions (1) and (2) as well. This phenomenon appears to be true for all surface-renewal expressions with unsteady state material-balance equations that can be solved by a similarity transformation, that is reduction of the partial differential equation to an ordinary differential equation by the substitution $\eta = x/\sqrt{t}$.

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NOTATION

- a_1, a_2, \dots, a_n = integration constants in Equations (11), (22), (32), (33), (63), (64, and (65)
 a, b, c, d = subspecies in the exchange reaction of case (4)
 a, b = constants defined by Equations (87) and (88)
 A, B, E, F = molar concentrations of the reacting species
 C = molar concentration of total A component, equal to $A + E$ or $A + \frac{1}{2}E$ (reaction 2)
 D = Fick's law diffusivity

the absence of chemical reaction

- k_A = mass transfer coefficient based on the driving force $(A_i - A_L)$
 k_C = mass transfer coefficient based on the driving force $(C_i - C_L)$
 k_E = mass transfer coefficient based on the driving force $(E_i - E_L)$
 $P(x)$ = defined by Equation (46)
 R = defined by Equation (45)
 s = hydrodynamic parameter in Danckwerts' surface-renewal theory
 t = time
 T = molar concentration of total B component in bulk of reacting phase, equal to $E_L + B_L$
 V = molar volume
 x = distance along diffusion path away from interface
 x_L = film thickness

Greek Letters

- α = defined by Equation (47)
 β = defined by Equation (48)
 θ, θ' = functions defined by Equations (19) or (28)
 ϕ = defined by Equation (72)

Subscripts

- A, B, E, F = one of the transferring species
 i = interfacial value
 L = bulk liquid-phase value

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