Diffusion-controlled Chemical Reactions

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Transformations are obtained which reduce the system of differential equations for certain types of diffusion-controlled reactions to the equation for pure diffusion.

Simple relationships between the diffusion rate with and without reactions are presented for reversible unimolecular reactions, certain types of reversible bimolecular reactions, and irreversible reactions between species with equal diffusivities. It is shown that these relationships are independent of geometry, hydrodynamics, or boundary conditions, and so the mass transfer coefficient in the presence of reactions can be obtained from the coefficient in the absence of reactions without an explicit knowledge of the mass transfer mechanism.

The reaction factor for irreversible reactions with equal diffusivities, obtained by others for specific mass transfer mechanisms, is found to be quite general and essentially independent of the mechanism.

Some data on the absorption of sulfur dioxide in a laminar water jet is considered.

The theory of simultaneous diffusion and chemical reaction is basic to the study of mass transfer in reacting systems. Although many systems are difficult to handle analytically, even when the reactions are rapid relative to the diffusion, a number can be considerably simplified by reducing them to pure diffusion problems. It will be shown that this reduction is possible for certain classes of reactions and that in these cases the effect of the chemical reaction on the transfer rate may be obtained even though the pure diffusion problem is too complicated to handle analytically.

A combination of a differential material balance with Fick's law gives the equation for pure diffusion in an isothermal system (*2*):

$$\frac{DC_1^0}{D\theta} = D_1^0 \nabla^2 C_1^0 \qquad (1)$$

The diffusion coefficient is assumed constant, and the substantial derivative is used in this and subsequent equations to account for any bulk motion superimposed on the system. If bulk motion is present, the term *diffusion-controlled reactions* is used in a somewhat general sense to include diffusion-convection controlled reactions as well. The system is taken to be dilute enough so that the hydrodynamic velocities are independent of the diffusion, and it is assumed that there is no convection across the boundaries. Solutions of Equation (1) with the appropriate boundary conditions give the concentration profile of the diffusing species, which, upon application of Fick's first law at the system boundary

$$N_{1B}^0 = -D_1^0 (\nabla C_1^0)_B \qquad (2)$$

yields the rate of transfer across the boundary.

If the flow is turbulent, the equations can be considered to apply at every instant of time, and the solutions give the instantaneous concentration and flux. Although many of the conclusions given below are valid for turbulent flow, this paper is concerned specifically with a stagnant fluid or laminar flow.

Equations (1) and (2) with the boundary conditions fix the diffusion rate and also yield the mass transfer coefficient. The two simplest solutions, which are used as models for mass transfer in systems such as packed towers (*7*), are the semi infinite slab solution (pentration model)

$$N_{1B}^0 = \sqrt{\frac{D_1^0}{\pi\theta}} (C_{1I}^0 - C_{10}^0) \qquad (3)$$

and the steady state solution (film model)

$$N_{1B}^0 = \frac{D_1^0}{L} (C_{1I}^0 - C_{1II}^0) \qquad (4)$$

When a chemical reaction takes place, Equation (1), with a source or sink term to account for the reaction, applies to each molecular species in turn,

$$\frac{DC_i}{D\theta} = D_i \nabla^2 C_i + r_i, \qquad i = 1, 2, \cdots n. \qquad (5)$$

and there are n equations for n species. The diffusion flux for each species is given by Fick's law, since the system is dilute enough so that there are no diffusional interactions:

$$N_i = -D_i \nabla C_i \qquad (6)$$

In the presence of convection this is the flux with respect to the local bulk-fluid velocity.

REVERSIBLE REACTIONS

To determine the relationship among the concentrations of reversibly reacting species in a diffusion controlled system, it is necessary to examine the rate equation for reversible reactions. This can be written for species 1 as

$$-r_1 = k_f \, \Delta_1 \qquad (7)$$

where Δ_1 depends upon the mechanism of the reaction. For first-order reactions in both directions, for example,

$$\Delta_1 = \left(C_1 - \frac{C_2}{K}\right) \qquad (8)$$

It will be seen later that the form of Δ_1 is not important here, but the important characteristic is that when Δ_1 is zero, local chemical equilibrium exists whatever the order of the reactions.

Now if a number of diffusion-reaction systems which differ only in their values of k_f are examined, it is seen that at low values of k_f, Δ_1 will not generally be zero. However if k_f is allowed to increase without limit by the consideration of systems with larger and larger values of k_f, Equation (7) shows that the reaction rate will also increase without limit unless Δ_1 approaches zero. But the reaction rate cannot increase without limit, since it will be limited at any point by the finite rate of supply and removal of reacting species to the region of the point. Consequently as k_f gets large, Δ_1 must approach zero as the reactions become diffusion controlled, and local chemical equilibrium is approached at all points in the system. Equation (7) is then indeterminate, and the reaction rate must be obtained from the diffusion equations. [See Equation (20) for example.]

Thus in general a diffusion-controlled reversible reaction system can be defined as one in which local chemical equilibrium exists at all points. Strictly this demands infinite reaction velocity constants, but for any system there is some finite value of k_f which is large enough to render negligible the error caused by the assumption of local equilibrium. Reactions in which k_f is equal to or greater than this value are considered to be rapid reactions. As long as the reactions are rapid, it is not necessary to restrict k_f, but it is assumed in the subsequent work that the equilibrium constants are true constants.

For rapid irreversible reactions the analogue of the above result is the well-known fact that the reaction must take place at a surface (*15*).

REVERSIBLE UNIMOLECULAR REACTIONS

An isothermal system with a dilute solute will be considered. Species 1 is diffusing in the solvent which is stagnant or in laminar flow, and it reacts rapidly and reversibly to form species 2. Species 2 is not immobilized and is free to diffuse. The reactions are unimolecular or psuedo-unimolecular

$$1 \rightleftarrows 2$$

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so the equilibrium constant K is given by

$$K = \frac{C_2}{C_1} \tag{9}$$

Since the reaction is rapid, local chemical equilibrium exists at all points; therefore C_1 and C_2 are always in a constant ratio, and the diffusion and reaction rates are both controlled by the diffusion. If it it assumed that any intermediate reactions are much more rapid than the first and last steps and that the amount of the intermediate species present at any time is negligible, $r_1 + r_2 = 0$. (It is shown that these qualifications are unnecessary if the intermediate reactions are unimolecular). If the first two equations of (5) are added together, since $r_1 + r_2 = 0$, the reaction terms are eliminated and

$$\frac{D(C_1 + C_2)}{D\theta} = D_1\nabla^2 C_1 + D_2\nabla^2 C_2 \tag{10}$$

This simplifies with the aid of Equation (9) to

$$\frac{DC_1}{D\theta} = \left(\frac{D_1 + KD_2}{1 + K}\right)\nabla^2 C_1 = D_e\nabla^2 C_1 \tag{11}$$

Comparison of Equation (11) with Equation (1) shows that species 1 diffuses as if there were no chemical reaction, but its effective diffusivity is given by

$$D_e = \frac{D_1 + KD_2}{1 + K} = \frac{C_1D_1 + C_2D_2}{C_1 + C_2} \tag{12}$$

and the effective diffusivity is the concentration weighted, mean diffusivity. Since D_1, D_2, and K were assumed to be constants, D_e is also a constant, independent of concentration, and is a true diffusivity for the system. [If species 2 is immobilized, D_2 is zero and the result given by Crank (*5*) is obtained. If the reaction is irreversible, $K = \infty$ and $D_e = D_2$; only species 2 exists inside the system.]

Although it is tempting to visualize the complex $1 \rightleftarrows 2$ as diffusing as a unit, this is not generally the case, for a comparison of Equations (11) and (5) shows that

$$r_1 = -r_2 = -\frac{K}{1 + K}(D_1 - D_2)\nabla^2 C_1 \tag{13}$$

Thus if the diffusivities are not equal, the reaction continues throughout the system and varies from point to point (unless $\nabla^2 C_1 = 0$). This is a direct consequence of the diffusivity difference which tends to eliminate local equilibrium and which must be balanced by the reaction which restores the equilibrium. The direction of the reaction depends upon the relative magnitude of the diffusion coefficients (it will shortly be shown that the sign of $\nabla^2 C_1$ is unaffected by the reaction) so with $\nabla^2 C_1$ positive species 1 is removed by the reaction when $D_1 > D_2$, but when $D_2 > D_1$, species 1 is formed by the reaction.

When $D_1 = D_2$, the rate of reaction is zero. After local chemical equilibrium is reached at the boundaries of the system, the complex $1 \rightleftarrows 2$ does diffuse as a unit, since as far as diffusion is concerned 1 and 2 are the same species if their diffusivities in the solvent are equal.

Equation (11) can be written in another form by noting that the concentration of species 1 is linearly related to the total concentration of diffusing species:

$$C_t = C_1 + C_2 = (K + 1)C_1 \tag{14}$$

Therefore

$$\frac{DC_t}{D\theta} = D_e\nabla^2 C_t \tag{15}$$

If there are a series of reactions of the form

$$1 \rightleftarrows 2 \rightleftarrows 3$$

or any combination of reactions of this type, then $\sum_{i=1}^{n} r_i = 0$, and by the same procedure as before it can be shown that Equations (11) and (15) hold if the effective diffusivity is defined as

$$D_e = \sum_{i=1}^{n} K_iD_i \Big/ \sum_{i=1}^{n} K_i \tag{16}$$

where the equilibrium constants K_i are defined by

$$K_i = \frac{C_i}{C_1} \tag{17}$$

and C_t is

$$C_t = \sum_{i=1}^{n} C_i = C_1\sum_{i=1}^{n} K_i \tag{18}$$

Equations (17) and (18) show that the C_i are linearly related to C_t by

$$C_i = \frac{K_i}{\sum_{j=1}^{n} K_j} C_t \tag{19}$$

The equilibrium constants defined by Equation (17) are not necessarily the normal chemical equilibrium constants but are combinations of them which depend upon the reaction scheme.

The rate of reaction of species i is given by

$$r_i = -\frac{\sum_{j=1}^{n} K_j(D_i - D_j)}{\sum_{j=1}^{n} K_j}\nabla^2 C_i \tag{20}$$

or alternately

$$r_i = -\frac{K_i\sum_{j=1}^{n} K_j(D_i - D_j)}{\left(\sum_{j=1}^{n} K_j\right)^2}\nabla^2 C_t \tag{21}$$

Again the reaction rate in the system is zero only when all the diffusivities are equal, and the direction of the reaction depends upon the relative magnitudes of the diffusivities and the equilibrium constants. The total diffusion flux of solute is obtained by the summing of Equation (6) over all species;

$$N_t = \sum_{i=1}^{n} N_i = -\sum_{i=1}^{n} D_i\nabla C_i \tag{22}$$

which from Equation (16) and (19) becomes

$$N_t = -D_e\nabla C_t \tag{23}$$

If this equation is applied on the inner side of the system boundary, it gives the rate at which species 1 crosses the boundary, while inside the system it gives the rate of diffusion of species 1 in all forms with respect to the local bulk velocity. At the boundary then with no ambiguity

$$N_{1B} = -D_e(\nabla C_t)_B \tag{24}$$

Equations (15) and (24) are mathematically identical to the pure diffusion Equations (1) and (2), since D_e is constant, and if the boundary conditions have the same form, the two solutions will be identical when the following transformations are carried out:

$$\begin{aligned} D_1^0 &\rightarrow D_e \\ C_1^0 &\rightarrow C_t \\ N_{1B}^0 &\rightarrow N_{1B} \end{aligned} \tag{25}$$

These transformations are only of immediate use if the boundary conditions on C_t can be obtained without the necessity of an explicit knowledge of the behavior of each species. When the reacting phase is contacted by another phase containing species 1, and there is no interfacial resistance, the interfacial concentration of species 1 is fixed by the physical equilibrium relationship between 1 in the external phase and the reacting phase. But C_1 and C_t are related by the reaction equilibria [Equation (18)], and so C_{tI} is also fixed by the equilibria. Since the phase equilibrium relationship is usually reported in terms of the total amount of species 1 present in the reacting phase at complete equilibrium, C_{tI} is the normal equilibrium value.

Generally the concentration of only one species can be fixed at a boundary; the others are then set by the chemical equilibrium relationships. If the reaction products are volatile, the external composition adjacent to the interface must adjust to satisfy the solubility relationship for each species.

For example if a pure gas is absorbed

in a layer of stagnant liquid in which it reacts by one or more rapid unimolecular reactions, the instantaneous absorption rate is obtained by applying Equation (25) to (3):

$$N_{1B} = \sqrt{\frac{D_e}{\pi\theta}}\,(C_{tI} - C_{t0}) \qquad (26)$$

and the transformation of Equation (4) gives the steady state solution

$$N_{1B} = \frac{D_e}{L}\,(C_{tI} - C_{tII}) \qquad (27)$$

Since equations of the above type are used to measure diffusivities, what is measured is D_e as defined by Equation (16), and since D_e is a constant (within the limitations of the previous assumptions), it may be used in all the solutions to Fick's law for pure physical absorption. Consequently diffusion with rapid reversible (or irreversible) unimolecular reactions may be treated as a pure diffusion problem by ignoring the reaction altogether, since the diffusivity and solubility data will already contain the effects of the reaction.

However if the diffusivity has not been experimentally determined and must be estimated from one of the correlations, Equation (16) should be used to determine the effect of the reaction on the diffusivity.

Although the above analysis has focused on diffusion rate, it can be seen that the reduced concentration profiles of total solute are identical to the profiles which would be obtained in a nonreacting system. The concentration profile for each species is then obtained from Equation (19), and the local rate of reaction then follows from Equation (20) or (21). Since the functional form of $\nabla^2 C_i$ and $\nabla^2 C_t$ are fixed by the boundary conditions and hydrodynamics, the rate and direction of the reactions are set by the relationships among the diffusion coefficients and equilibrium constants.

Finally since the transformations given by Equation (25) do not depend upon hydrodynamics, geometry, or boundary conditions, the mass transfer rate in the presence of rapid unimolecular reactions can be obtained from the rate in the absence of reactions by means of Equation (25), even in such complex systems as packed columns. [Equation (25) applies directly to the various types of mixing models considered by Danckwerts (*7*) for packed columns, but if the reactions are first order, it is easy to show that the result is valid even if the flow is turbulent.]

The simplifications which occur with unimolecular reactions arise because of the simple relationship among concentrations and cannot be expected to be general. However certain types of bimolecular reactions can be reduced to simple forms by an approach similar to the one above.

REVERSIBLE BIMOLECULAR REACTIONS

Diffusion with the bimolecular reactions

$$1 + 2 \rightleftarrows 3 + 4$$

is described by Equation (5) with

$$r_1 = r_2 = -r_3 = -r_4 \qquad (28)$$

When the reactions are rapid enough so that local chemical equilibrium exists at all points, the concentrations are related by

$$K = \frac{C_3 C_4}{C_1 C_2} \qquad (29)$$

It is convenient in this case to add the first and third equations of (5), and with Equation (28)

$$\frac{D(C_1 + C_3)}{D\theta} = D_1\nabla^2 C_1 + D_3\nabla^2 C_3 \qquad (30)$$

$$C_t = C_1 + C_3 \qquad (31)$$

is defined. At this point it should be noticed that the effective diffusivity for the total solute as defined by Equation (23) is given by

$$D_e = \frac{\nabla(D_1 C_1 + D_3 C_3)}{\nabla(C_1 + C_3)} \qquad (32)$$

so even if C_t were fixed at the system boundaries, the transfer of total solute could not be treated as a purely diffusional problem, since the effective diffusivity would be a function of the concentration gradients. Only when the diffusivities of species 1 and 3 are equal does Equation (30) reduce to the simple form of Equation (15). It still does not follow that the problem can be treated as pure diffusion, for if the concentration of species 1 is held constant at the system boundaries, Equation (29) shows that C_t is not fixed.

To fix C_t one must assume that species 3 and 4 are initially at zero concentration or present in equal amounts and that $D_3 = D_4$, so $C_3 = C_4$ at all points during the process. This also gives C_t a clear physical meaning, for it can now be interpreted as the total concentration of species 1 in all forms at any point. Further it is necessary to reduce the forward reaction to psuedo first order by the assumption that species 2 is present in large excess. Then Equation (29) becomes

$$C_3 = \sqrt{KC_2C_1} = \sqrt{K'C_1} \qquad (33)$$

and

$$C_t = C_1 + \sqrt{K'C_1} \qquad (34)$$

Under these conditions C_t is a function only of C_1, so the relationship between C_t at the system boundary and the concentration of species 1 in an external phase is the normal equilibrium relationship for total solute. Finally it is seen that the rate of transfer of total solute is given by Equation (23).

Thus this reaction problem is reduced to the equivalent pure-diffusion problem, and the mathematical solutions for the two cases are related by the transformations (25) with $D_e = D_1 = D_3 = D_4$. The rate of diffusion of total solute, or species 1 at the boundary, then follows the equations for pure diffusion if the total solute concentration at the boundaries is used in the integrated rate equations. These results are only valid when species 3 and 4 are initially present in equal amounts, species 2 is in large excess, and $D_1 = D_3 = D_4$. Generally the effective diffusivity may vary from D_1 to D_3, and the interfacial concentration of total solute will vary with time and depend upon the conditions of the experiment as well as the relationship among the diffusivities.

IRREVERSIBLE REACTIONS

Diffusion with the rapid irreversible reaction

$$a1 + b2 \rightarrow \text{products}$$

is discussed by Sherwood and Pigford (*15*) in terms of the film and penetration models for the case $a = b$.

Previous methods of analysis have treated the diffusion-reaction equations for each species as a system of partial differential equations to be solved simultaneously. The mathematics are quite complex, and only a few special cases have been solved. It will be shown by a modification of the method used in the preceding sections that very general solutions may easily be obtained for the special case of equal diffusivities.

The defining equations are given by (5) but here

$$r_1 + \frac{a}{b}r_2 = 0 \qquad (35)$$

Multiplying the first equation of (5) by b and the second by a, letting $D_2 = D_1$, and substracting one from the other removes the reaction term and yields

$$\frac{DC_t'}{D\theta} = D_1\,\nabla^2 C_t' \qquad (36)$$

where

$$C_t' = bC_1 - aC_2 \qquad (37)$$

Although C_t' satisfies Equation (36), even for a slow reaction, generally the boundary conditions and the relationship between N_t' and N_1 cannot be obtained without a direct solution of the separate diffusion-reaction equations.

When the reaction is rapid and irreversible, at no point can there be both species 1 and 2 present, and so C_t' at some points equals bC_1 and at others equals $-aC_2$. As this is also true at the system boundaries, there is no difficulty in fixing the boundary concentrations.

For convenience one defines

$$N_t' = -D_1 \nabla C_t' \qquad (38)$$

which from Equations (37) and (6) reduces to

$$N_t' = bN_1 - aN_2 \qquad (39)$$

At a boundary where the concentration of species 1 is fixed, no species 2 can be present, so at this boundary

$$N_{tB}' = bN_{1B} = -D_1(\nabla C_t')_B \qquad (40)$$

By the comparison of Equations (36) and (40) with the pure diffusion equations it is seen that the transfer rate with the reaction is obtained from the rate without reaction by the following transformations:

$$\begin{aligned} C_1^0 &\to C_t' \\ N_{1B}^0 &\to bN_{1B} \qquad (41) \\ D_1^0 &\to D_1 \end{aligned}$$

These equations are quite useful; in addition to yielding explicit solutions when the pure diffusion problem can be solved, they also allow a quantitative determination of the effect of the reaction on the mass transfer coefficient for cases where the pure diffusion problem is intractable.

The penetration solution follows immediately by the application of the above transformations to Equation (3). For a slab which initially has a constant composition of species 2, $C_{t0}' = -aC_{20}$, and if the interface is saturated with species 1 at time zero, $C_{tB}' = bC_{1I}$. The rate of transfer of species 1 across the interface is then

$$N_{1B} = \sqrt{\frac{D_1}{\pi\theta}}\left(1 + \frac{a}{b}\frac{C_{20}}{C_{1I}}\right)C_{1I} \qquad (42)$$

which for $a = b$ is the solution obtained by Danckwerts (*6*) by a direct solution of the equations for each species.

If a plane at a distance L from the interface is held at the composition C_{2II}, then the steady state solution obtained by the application of the transformations (41) to Equation (4) gives

$$N_{1B} = \frac{D_1}{L}\left(1 + \frac{a}{b}\frac{C_{2II}}{C_{1I}}\right)C_{1I} \qquad (43)$$

and for $a = b$ this is Hatta's solution (*10*).

Since C_1 is zero at time zero and at plane II, the bracketed term in both of the equations above is a correction factor which accounts for the effect of the chemical reaction on the rate, the reaction factor. If $C_{2II} = C_{20}$, then for both the penetration and film mechanisms

$$k = k^0\left(1 + \frac{a}{b}\frac{C_{20}}{C_{1I}}\right) \qquad (44)$$

This equation is considerably more general than Equations (42) and (43). It holds for example if the transfer mechanism is neither a pure penetration type nor a pure film type but a combination of both such as film penetration (*16*), and it is valid even in the presence of externally imposed convection.

Friedlander and Litt (*8*) recently obtained Equation (44) by direct integration of the separate diffusion equations for a laminar boundary layer on a flat plate, and they suggested that the same reaction factor be used as a first approximation for geometries where the diffusion problem cannot be solved. The present approach allows a direct proof of the validity of this assumption, for it will be shown that the reaction factor does not depend upon geometry.

A laminar boundary layer with a geometry such that the following boundary conditions may be applied in the case of pure diffusion will be considered.

$$\begin{aligned} x &= 0, \quad C_1^0 = C_{1m}^0 \\ y &= 0, \quad C_1^0 = C_{1I}^0 \qquad (45) \\ y &= L, \quad C_1^0 = C_{1m}^0 \end{aligned}$$

where L may be infinite. By the use of dimensionless units the solution to the pure diffusion problem, Equations (1) and (2) with the above boundary conditions, may readily be shown to have the form

$$N_1 = k^0(C_{1I}^0 - C_{1m}^0) \qquad (46)$$

where k^0 depends upon the geometry and is a function of position.

If the concentration of species 1 at the wall is C_{1I} and species 1 reacts with species 2, which initially is evenly distributed theoughout the fluid, the transformations (41) as in the previous cases immediately yield Equation (44) as the solution to the problem under consideration. Thus the reaction factor $[1 + (a/b)\ (C_{20}/C_{1I})]$ applies to any laminar boundary layer (even if the normal boundary layer assumptions do not hold) when the boundary conditions (45) apply, and it can be used to correct empirical mass transfer coefficients for the effect of an irreversible reaction.

Friedlander and Litt also obtained the reaction factor for the flat plate when the diffusivities are not equal, and since the transformations (41) do not apply under these circumstances, it is likely that the reaction factor will have different forms for other geometries.

The first equation of (41) transforms the equation for the concentration profile in the absence of reaction to the profile for C_t' in the presence of the reaction. Generally it will be possible to obtain the separate concentration profiles for both species 1 and 2 from the C_t' profile in the following manner.

Since the two species will meet and react at surface moving in time, on one side of the surface only species 1 will exist and on the other side only species 2; at the surface itself C_1 and C_2 will be zero. Consequently on one side C_t' reduces to bC_1, and on the other side it reduces to $-aC_2$; the equation for the reaction surface can be determined by setting C_t' equal to zero in the equation for the C_t' profile. If so desired, the flux profile for each species can then be explicitly determined by the application of Equation (6) to each of the separate concentration profiles.

For example boundary conditions of the type considered earlier lead to solutions of the form

$$\frac{C_1^0 - C_{10}^0}{C_{1I}^0 - C_{10}^0} = f(\vec{r}, \theta) \qquad (47)$$

where $f(\vec{r}, \theta)$ depends upon geometry and hydrodynamics; in the boundary-layer problem f does not depend upon θ, and C_{10} is C_{1m}.

Equation (47) transforms by (41) to

$$\frac{C_t' - C_{t0}'}{C_{tI}' - C_{t0}'} = f(\vec{r}, \theta) \qquad (48)$$

when $D_1 = D_1^0$ is assumed for simplicity. The reaction takes place on the surface at which $C_t = 0$, and so from Equations (48) and (37)

$$\frac{1}{\dfrac{b}{a}\dfrac{C_{1I}}{C_{20}} + 1} = f(\vec{r}, \theta) \qquad (49)$$

and this equation can be solved for the reaction surface as a function of time. On the side of the surface where only species 1 exists, Equation (48) yields

$$\frac{C_1 + \dfrac{a}{b}C_{20}}{C_{1I} + \dfrac{a}{b}C_{20}} = f(\vec{r}, \theta) \qquad (50)$$

and on the other side where only species 2 exists

$$\frac{C_{20} - C_2}{C_{20} + \dfrac{b}{a}C_{1I}} = f(\vec{r}, \theta) \qquad (51)$$

The separate concentration profiles are now completely defined.

ABSORPTION OF SULFUR DIOXIDE BY WATER

Sulfur dioxide reacts with water as follows:

$$SO_2 + H_2O \rightleftarrows H_2SO_3 \rightleftarrows HSO_3^- + H^+$$

$$1 + 2 \rightleftarrows 3 \rightleftarrows 4 + 5$$

There is evidence that all these forms are present at equilibrium, and although the equilibrium amounts of ionized and total unionized species are known, the amounts of sulfur dioxide and sulfurous acid present are not known (*11*).

If the reactions are assumed to be rapid, then in the absorption of sulfur dioxide by water the following equilibria exist at all points during the diffusion process$_4$

$$K_\alpha = \frac{C_3}{C_1 C_2} \tag{52}$$

$$K_\beta = \frac{C_4 C_5}{C_3} \tag{53}$$

As discussed earlier, equilibria of these types generally will not reduce the diffusion equations to the form corresponding to pure diffusion. In fact if the above equilibria are not qualified, the effective diffusivity is a variable, and the interfacial concentration of total solute depends upon the concentration profiles of all species even when there is equilibrium between the sulfur dioxide gas and the liquid solution at the interface.

However if the sulfur dioxide concentration is not too large, then the water concentration may be taken as constant in Equation (52). Furthermore if the solution is not too dilute, the major part of the H^+ is produced by the dissociation reaction, and so HSO_3^- and H^+ are produced at the same rate. As ionic forces will keep the two species from separating in order to preserve local electrical neutrality, it can be assumed that $C_4 = C_5$ at all points. Equation (53) then reduces to

$$\frac{C_4^2}{C_3} = K_\beta \tag{54}$$

The total solute concentration is, from Equations (52) and (54),

$$C_t = C_1 + C_3 + C_4$$
$$= C_1\left(1 + C_2 K_\alpha + \sqrt{\frac{C_2 K_\alpha K_\beta}{C_1}}\right) \tag{55}$$

and Equation (55) shows that with C_2 constant C_t is a function only of C_1. Consequently the equilibrium relationship between sulfur dioxide gas and unreacted sulfur dioxide fixes the total solute concentration at the interface. However unless all the diffusivities are equal, which is unlikely, or the amount of HSO_3^- is negligible, the effective diffusion coefficient will be a variable.

Even if the ionized sulfurous acid is assumed to have the same diffusivity as the unionized form, the effective diffusivity should not be constant, for the ratio of total sulfurous acid in both forms to dissolved sulfur dioxide will vary with total concentration.

In solutions saturated at 1 atm. sulfur dioxide partial pressure at room temperature about 10% of the total sulfur dioxide in solution is ionized, and the percentage ionized increases as the total sulfur dioxide concentration decreases, so that at 10% of saturation about 30% is ionized (*13*).

Lynn *et al.* (*12*) have measured the rate of absorption of sulfur dioxide into water flowing down the outside of a rod. These data have been extended by the absorption of pure sulfur dioxide into a laminar water jet, which is in rodlike flow (*4*), by a technique described in an earlier paper (*14*). In Figure 1 the average rate of absorption over the jet is plotted against $1/\sqrt{\theta}$, and the range of Lynn's data is also shown. The absorption rate follows the reciprocal square-root time dependence over the full 300-fold range of contact time, and the data extrapolate to zero at infinite contact time.

Since the mean absorption rate is twice the point rate, Equation (26) indicates that the effective diffusivity is a constant and the interfacial resistance is negligible. This constant effective diffusivity would result if the ionization reaction were so slow that this reaction did not occur over the range of contact time studied, for the hydrolysis step is psuedo first order, and it was shown above that this leads to a constant effective diffusivity. However Lynn (*12*) showed independently that the entire sequence of reactions reaches completion in less than 0.1 sec. and concluded that all the reactions must rapidly reach equilibrium. If this is the case the present data indicate that the reactions must be completed in less than 0.003 sec.

Another possible explanation of the constant diffusivity is that the high ionization which takes place at the dilute end of the concentration profile has little effect on the diffusion rate, and since only 10% of the total sulfur dioxide is ionized near the saturated jet surface, this small effect may be negligible.

In any case the rate measurements allow determination of the effective diffusivity. The jet surface temperature is estimated to be 1°C. higher than the surrounding temperature of 22.2°C. (*4*), and at 23.2°C. the total solubility of sulfur dioxide in water is 1.42×10^{-3} *g.* moles/cc. (*13*). This solubility is considered to be reliable and is within ± 2% of two other independent measurements (*1, 3*).

By the use of the time average of Equation (26) it is found that the straight line through the data corresponds to an effective diffusivity of 1.54×10^{-5} sq. cm./sec. When corrected to 20°C. by the Stokes-Einstein equation the measured value is 1.41×10^{-5}, compared with Lynn's measurement (*12*) of 1.46×10^{-5} and Groothuis and Kramers' (*9*) value of 1.40×10^{-5}.

As mentioned earlier, in the estimation of the diffusivity of a solute in a solvent with which it reacts the various molecular species present should be taken into account. If the ionized sulfurous acid is assumed to have the same diffusivity as the unionized portion, then only sulfur dioxide and sulfurous acid need be considered. Table 1 gives the values calculated from Wilke's correlation (17) at 20°C.

TABLE 1. DIFFUSIVITIES AT 20°C. IN WATER

	SO_2	H_2SO_3	Experimental
$D \times 10^5$, sq. cm./sec.	1.46	1.17	1.41

Since the average deviation of Wilke's correlation is 6% and there are other uncertainties as well, no definite conclusions can be drawn from these figures; if they are accepted at their face value they indicate that most of the unionized material is in the form of sulfur dioxide rather than sulfurous acid.

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NOTATION

a, b = stoichiometric coefficients
C_i = concentration of species i
C_t = total solute concentration
C_t' = concentration of total solute defined by Equation (37)

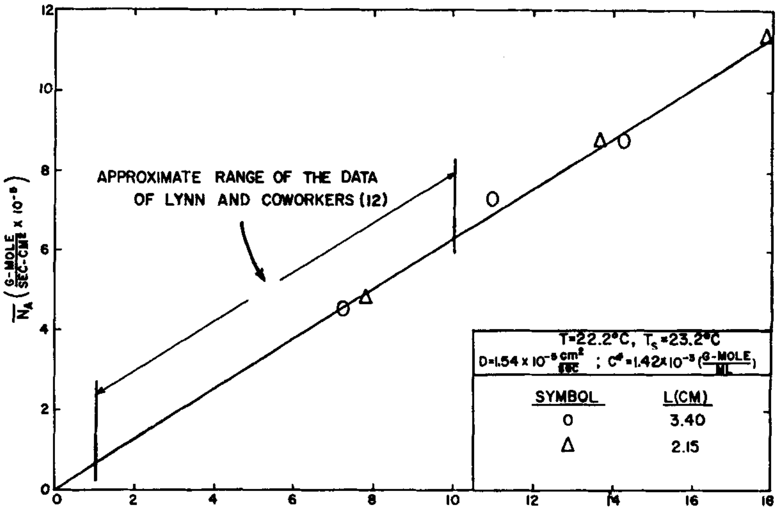

Fig. 1. Rate of sulfur dioxide adsorption into water.

D_e = effective diffusivity
D_i = diffusivity of species i
f = functional symbol
k = local mass transfer coefficient
k_f = forward reaction-velocity constant
K, K_α, K_β = equilibrium constants
K_i = modified equilibrium constants defined by Equation (17)
K' = effective equilibrium constant defined by Equation (33)
L = film thickness, jet length in Figure (1)
n = number of species
N_i = flux of species i
N_t = flux of total solute
N_t' = flux defined by Equation (38)
r_i = volumetric rate of production of species i by reaction
$\vec{r}$ = position vector
x, y = generalized position coordinates
Δ = displacement from chemical equilibrium
θ = time
∇ = gradient
∇^2 = Laplacian operator
$D/D\theta$ = substantial derivative

Subscripts

B = boundary
i, j = indices taking on values $1, 2, \ldots n$.
m = main stream
0 = time zero
I = boundary I
II = boundary II

Superscript

^{0} = absence of reaction

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Mechanism of Drying Thick Porous Bodies During the Falling-Rate Period

II. A Hygroscopic Material

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A further analysis of the second falling-rate period in the drying of thick highly porous textile structures is made, this time in the case of drying wool, special attention being paid to the adsorbed water held by the wool in the air-dry region. As the solid-to-void ratio is low, the quantities of adsorbed water are small and have little effect on the general equilibrium. Values of thermal conductivity are calculated for wet wool.

In part 1 (*1*) experimental results were given for the heating and air drying of two thick highly porous textile structures. Extremes were chosen in a Terylene (British form of a polyester fiber) net fabric of open structure and a woolen flannel of close structure and the results compared for the two materials. It was found that despite the difference in structure a similar equilibrium between heat transfer inward and vapor diffusion outward was established at a constant pseudo-wet-bulb temperature during the second falling rate period.

A further important difference between the fabrics, which was neglected in the first treatment, is the hygroscopic nature of the wool, whereby some 30% of bound water is in equilibrium with the fibers when the surrounding atmosphere is saturated with water vapor. In this paper the data given previously for the wool are further analyzed with the adsorbed water taken into account. Values of the apparent thermal conductivity of the wet porous solid are also calculated.

WATER DISTRIBUTION IN WOOL BOBBIN

The woolen cloth, being wound on a spindle, formed an annular package just over 1 in. thick of about 3-in. O.D. and 6-in. long. The hot air flowed parallel to the outer surface, and thermocouples situated at each succeeding $\frac{1}{8}$ in. in depth and also just below the surface thickness of cloth provided a record of the temperature distribution during the drying cycle. Weighing gave the total weight of water held by the package as drying proceeded.

The General Distribution Deduced from the Temperature Record

In Figure 1 the curves showing the temperatures at the different depths are reproduced. In the case of Terylene it was shown that when the temperature registered by a thermocouple embedded in the cloth rises from the pseudo-wet-bulb temperature level, the material outside the position of the thermocouple is dry and the material within is wet. In other words, as the thermocouple is left

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