Analytical and Experimental Studies of Facilitated Transport

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Facilitated transport is a process in which permeation through a liquid film is chemically augmented. Because of the scientific and engineering interest in this phenomenon, the purpose of this work was to carry out a detailed mathematical and experimental investigation of facilitated transport. The differential equations describing facilitated transport are presented, and a generally applicable numerical solution recently developed by G. M. Roe for this type of boundary value problem is summarized. The experimental investigation consisted of measuring the steady state rate of transport of nitric oxide through thin films of ferrous chloride solution and of determining independently the values of the system parameters of which the nitric oxide flux was a function. The experimental results were accurately predicted by using the model developed by Roe. This is the first demonstration of a general quantitative understanding of facilitated transport.

Over the years there have been many attempts to develop semipermeable membranes for separation processes, and patents on potential processes date back more than a century. However, it is only in the past 10 yr. that membranes have been developed which make certain membrane separation processes within range of being economically and technically feasible. Although several polymers such as silicone rubber and cellulose acetate are useful membrane materials, in general polymeric materials are not desirable as semipermeable membranes, since most are relatively impermeable to all gases and liquids. Several years ago W. L. Robb (*1*) considered liquids as potential membrane materials, and based on this concept a highly effective immobilized liquid membrane for carbon dioxide removal from a life supporting environment was developed by Ward and Robb (*2*). During this work it was found that it was possible to augment chemically the transport of carbon dioxide across the liquid film. This phenomenon, known as *facilitated transport,* was first observed in 1959 by Scholander (*3*) and Wittenberg (*4*) in the steady state diffusion of oxygen across thin films of aqueous hemoglobin solutions.

There is a continuing interest in facilitated transport in the life sciences, and, as already demonstrated, facilitated transport can have important practical application in improving the performance of liquid membranes for separation processes. There are a number of experimental and analytical studies of facilitated transport in the literature (*2, 5*). However, these studies represent special cases in which simplifying assumptions could be made, making it possible to describe the performance of these systems analytically. Because it was not previously available, the present investigation was undertaken to develop a general quantitative understanding of facilitated transport.

Facilitated transport is a process whereby the permeation of a solute across a membrane is chemically augmented. The simplest type of facilitated transport system consists of a gas A and nonvolatile molecular or ionic species B and AB present in a liquid film. A reacts with B according to the reaction $A + B = AB$. If the equilibrium constant for this reaction is favorable, when a concentration difference in A is maintained across the film there is established a concentration difference in AB which is in the same direction as the A concentration difference. A concentration difference in B is also established which is in the opposite direction to the A concentration difference. As a result of the concentration differences, there is a net transport of A and AB in the same direction across the film and a net transport of B which at steady state is equal in magnitude and opposite in direction to the transport of AB. Since the total flux of A across the film is equal to the flux of A plus AB at any point in the film, the flux of A is facilitated or augmented as a result of the presence of the nonvolatile species B and AB.

The system selected for the present experimental investigation was nitric oxide in ferrous chloride solution. Nitric oxide reacts reversibly with ferrous ion according to the reaction (*6*)

$$NO + Fe^{2+} \rightleftarrows FeNO^{2+} \tag{1}$$

The solvent used was formamide which has a low vapor pressure and high dielectric constant. The latter property assured reasonably complete ion dissociation in dilute solutions. Water could not be used as the solvent because of its high vapor pressure. The object of the experimental investigation was to measure the steady state rate of transport of nitric oxide through thin films of ferrous chloride solutions and to measure independently the values of the system parameters of which the nitric oxide flux was a function. These parameters are the total ferrous ion concentration (present as Fe^{2+} and $Fe\,NO^{2+}$); the solubility of nitric oxide; the equilibrium constant and the forward and reverse reaction rates of reaction (1); the diffusion coefficients of nitric oxide, ferrous ion, and the ferrous nitric oxide complex; and the film thickness.

EXPERIMENTAL PROCEDURES

Measurements of the solubility of nitric oxide, the equilibrium constant of reaction (1), and forward and reverse reaction rates of reaction (1) were routine and are detailed elsewhere (*7*). The diffusion coefficients of ferrous ion and the ferrous nitric oxide complex are discussed below. The diffusion coefficient of nitric oxide in formamide and the steady state flux of nitric oxide through thin films of ferrous chloride were determined with the same equipment. A sketch of the apparatus for holding the liquid film is shown in Figure 1. The cell consisted of three stainless steel disks. The formamide solution was contained in the well shown in piece No. 2. The liquid film was bounded on both sides by 1-mil silicone rubber membranes. The silicone rubber films were stretched over washers which fit into the slots shown in pieces 1 and 3. In all runs there was 750 mm. nitric oxide and essentially a vacuum on the high and low pressure sides of the film, respectively. The liquid film was supported against this pressure difference by a

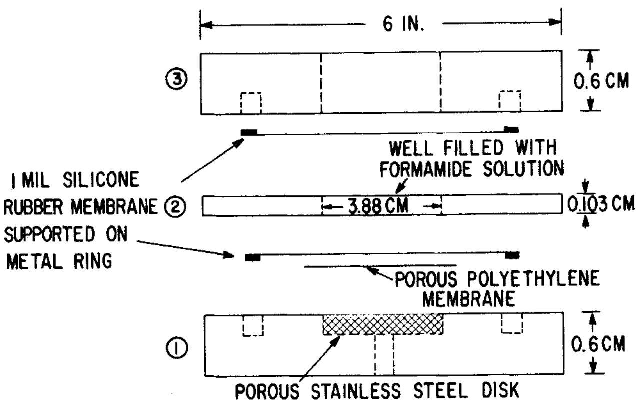

Fig. 1. Liquid film holder.

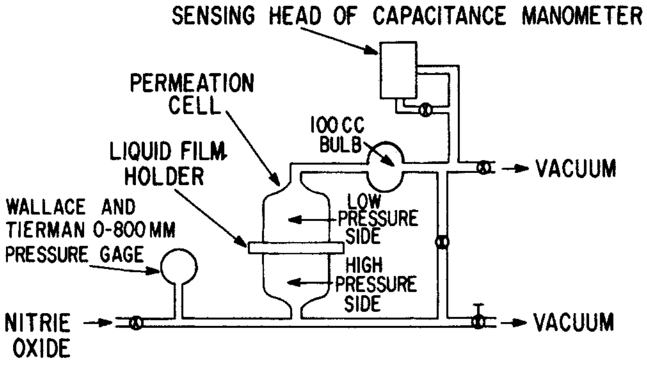

Fig. 2. Vacuum system for the diffusion experiment.

porous stainless steel disk which fit into piece No. 1. Silicone rubber was swelled by formamide, and the pressure difference across the liquid film was enough to force formamide through the silicone rubber and into the stainless steel disk. To prevent this a 3-mil film of porous polyethylene (which formamide does not wet) was inserted between the silicone rubber on the low pressure side and the porous stainless steel disk. Although the porous polyethylene film alone was probably a suitable support, the silicone rubber was also used on the low pressure side to insure that no liquid could enter the stainless steel disk. The resistance of the silicone rubber and polyethylene films to nitric oxide transport was neglected, since it was less than 1% of the resistance of formamide film.

The liquid film was installed in the system shown in Figure 2. The permeation cell consisted of two sections of 1-in. glass pipe. The film holder was securely clamped between the glass pipes, and vacuum seals were made with O rings. In making a run the low pressure side and then the high pressure side were evacuated. When the system was thoroughly degassed, nitric oxide was admitted to the high pressure side to a pressure of 750 mm. Hg. The buildup of pressure in the low pressure side was followed with a capacitance manometer, one side of which was maintained at a vacuum. At maximum sensitivity a full scale deflection of the capacitance manometer corresponded to a pressure buildup in the low pressure side of the system of 60 μ Hg. The pressure in the low pressure side never reached more than 1 mm. Hg. Steady state values of the mass flux through the film were calculated from the steady state rate of pressure buildup in the low pressure side. Two independent measurements of D_{NO} in pure formamide were obtained by running the system as outlined above.

When the flux of nitric oxide through films of ferrous chloride solution was measured, it was necessary that the high pressure side of the film be positioned below the low pressure side. This was because ferrous-nitric oxide complex solution (which was dark brown) was more dense than a ferrous solution containing no complex (which was colorless). Clearly visible Benard cells were established in the liquid film if the high pressure side was above the low pressure side.

MATHEMATICAL TREATMENTS OF FACILITATED TRANSPORT

In the following analyses, the reaction to be considered is

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} AB \tag{2}$$

The object of the following is to obtain an expression for the total flux of A across a film of thickness L which contains the nonvolatile species B and AB. The analysis through Equation (12) is similar to that of Olander (8) who studied analytically a system involving mass transfer and equilibrium chemical reaction. Differential mass balances on A, B, and AB at any point in the film are

$$D_A \frac{d^2C_A}{dx^2} = k_1\, C_A C_B - k_2\, C_{AB} \tag{3}$$

$$D_B \frac{d^2C_B}{dx^2} = k_1\, C_A C_B - k_2\, C_{AB} \tag{4}$$

$$D_{AB} \frac{d^2C_{AB}}{dx^2} = -\, k_1\, C_A C_B + k_2\, C_{AB} \tag{5}$$

In writing these equations, it was assumed that Fick's law was applicable, and thus diffusion coefficients are considered to be those of the binary system consisting of the particular specie and the solvent. It was also assumed that the electrical migration term of the Nernst-Planck equation was negligible. This is discussed below. The boundary conditions which apply are

$$C_A(x = 0) = C_A{}^0$$

$$C_A(x = L) = C_A{}^L$$

$$\int_0^L (C_B + C_{AB})dx = M \tag{6}$$

$$\left.\frac{dC_{AB}}{dx}\right|_{x=0} = \left.\frac{dC_{AB}}{dx}\right|_{x=L} = 0$$

$C_A{}^0$, $C_A{}^L$, and M are known.

There is no general closed solution to Equations (3) to (5) from which $N_A{}^T$ could be calculated, but there are two sets of simplifying assumptions which do apply in certain cases which lead to expressions for $N_A{}^T$. In the first case, assume that reaction (2) is sufficiently fast that the reacting species are present in equilibrium concentrations. In this case, it is useful to proceed by adding Equations (3) and (5):

$$D_A \frac{d^2C_A}{dx^2} + D_{AB} \frac{d^2C_{AB}}{dx^2} = 0 \tag{7}$$

The solution of Equation (7) is

$$D_A C_A + D_{AB} C_{AB} = a_1 x + a_2 \tag{8}$$

where a_1 and a_2 are constants. The total flux of A is

$$N_A{}^T = -\, D_A \frac{dC_A}{dx} - D_{AB} \frac{dC_{AB}}{dx} \tag{9}$$

Equation (9) is valid at all points in the film, and it is seen from Equation (8) that

$$N_A{}^T = -\, a_1 \tag{10}$$

If D_B and D_{AB} are equal, then

$$C_{AB} + C_B = C_T \tag{11}$$

where C_T is a constant. Equation (11) plus the assumption of chemical equilibrium among all reacting species leads to the expression for the total flux of A:

$$N_A{}^T = \frac{D_A}{L}(C_A{}^0 - C_A{}^L) + \frac{D_{AB}\,K_{eq}\,C_T}{L(1 + K_{eq}\,C_A{}^0)(1 + K_{eq}\,C_A{}^L)}(C_A{}^0 - C_A{}^L) \quad (12)$$

It has been shown that Equation (12) applies to the diffusion of oxygen across thin films of aqueous hemoglobin solutions (5).

The other assumption which leads to an expression for $N_A{}^T$ is that reaction (2) is sufficiently slow that the concentrations of B and AB are essentially constant throughout the film. In this case, Equation (3) can be solved. The result is

$$C_A = \frac{B_1}{K_1}\sinh\sqrt{K}x + \frac{B_2}{K_1}\cosh\sqrt{K}x + \frac{K_2}{K_1} \quad (13)$$

where $K_1 = k_1\,\overline{C}_B$

$$\begin{aligned} K_2 &= k_2\,\overline{C}_{AB} \\ K &= \frac{K_1}{D_A} \\ B_2 &= K_1C_A{}^0 - K_2 \\ B_1 &= \frac{K_1C_A{}^L - K_2 - B_2\cosh\sqrt{KL}}{\sinh\sqrt{KL}} \end{aligned} \quad (14)$$

The obvious method to calculate $\overline{C}_B$ and $\overline{C}_{AB}$ is to use the fact that

$$D_A\frac{dC_A}{dx}\bigg|_{x=0} = D_A\frac{dC_A}{dx}\bigg|_{x=L} \quad (15)$$

However, it is not simple to extract $\overline{C}_B$ and $\overline{C}_{AB}$ from Equation (15), and a more useful relationship is to assume that

$$\frac{d^2C_A}{dx^2}\bigg|_{x=0} = -\frac{d^2C_A}{dx^2}\bigg|_{x=L} \quad (16)$$

Equation (16) leads directly to expressions for $\overline{C}_B$ and $\overline{C}_{AB}$. It can be shown that Equation (16) is valid if

$$\frac{1 + \cosh\sqrt{KL}}{\sinh\sqrt{KL}} = \frac{-\sinh\sqrt{KL}}{1 - \cosh\sqrt{KL}} \quad (17)$$

Equation (17) is an identity.

Since AB is nonvolatile and thus does not leave the film, Equation (9) gives

$$N_A{}^T = -D_A\frac{dC_A}{dx}\bigg|_{x=0} \quad (18)$$

Substituting Equation (13) into Equation (18), we get the very simple expression for the total flux of A:

$$N_A{}^T = -\frac{B_1}{\sqrt{K}} \quad (19)$$

It was shown by Ward and Robb (2) that an analogous expression to Equation (19) applied to the steady state transport of carbon dioxide across a thin film of a concentrated $HCO_3{}^-/CO_3{}^=$ solution. Clearly, when Equation (19) does apply, the total flux of A is reaction rate limited. In general, Equation (19) applies when the concentration of carrier is large compared with the concentration of gas and when the reactions involved are slow.

For the general case in which neither Equation (12) nor Equation (19) applies, Equations (3) to (5) must be solved numerically. G. M. Roe (9) has developed a numerical method of solving this type of boundary value problem. A summary of the method follows. First, it is convenient to transform x such that

$$z = \frac{2x - L}{L} \quad (20)$$

From Equations (3) to (5) it can be seen that C_B and C_{AB} differ from C_A by a linear function of z (or x). Combining these equations and integrating, we obtain

$$C_B = \frac{D_A}{D_B}[C_A(z) - R_1z] - R_0 + R_2 \quad (21)$$

$$C_{AB} = \frac{D_A}{D_{AB}}[-C_A(z) + R_1z] + R_0 \quad (22)$$

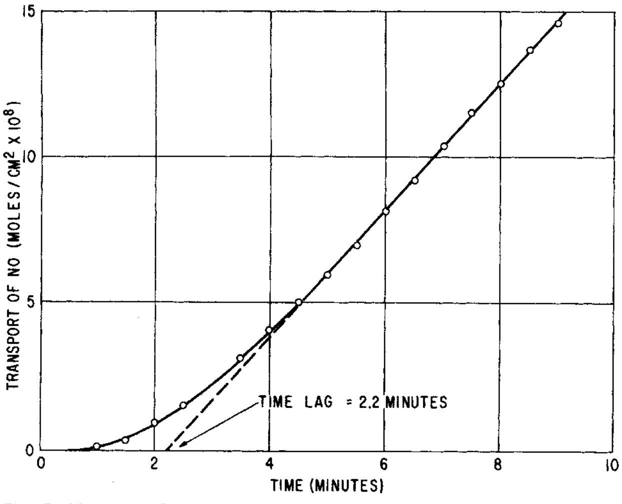

Fig. 3. Nitric oxide transport vs. time for nitric oxide diffusion across pure formamide film.

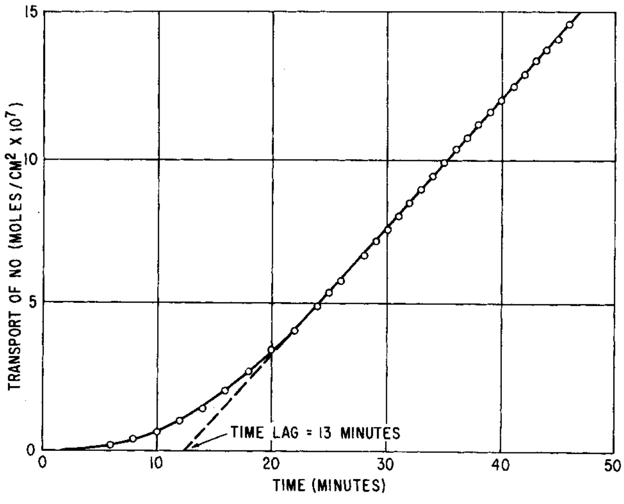

Fig. 4. Nitric oxide transport vs. time for nitric oxide diffusion across 0.05M ferrous chloride film.

where the R's are constants of integration. The boundary conditions then become

$$C_A(-1) = C_A^0$$

$$C_A(1) = C_A^L$$

$$2\,R_2 + \left[\frac{D_A}{D_B} - \frac{D_A}{D_{AB}}\right] \int_{-1}^{1} C_A(z)dz = \frac{2M}{L} \qquad (23)$$

$$\left.\frac{dC_A}{dz}\right|_{z=-1} = R_1$$

$$\left.\frac{dC_A}{dz}\right|_{z=1} = R_1$$

Substitution of Equations (21) and (22) into Equation (3) gives

$$\frac{d^2C_A}{dz^2} - G_1C_A(C_A - R_1x) - G_2(C_A - R_1x) + G_3(R_0 - R_2)C_A + G_4R_0 = 0 \qquad (24)$$

where

$$G_1 = \frac{k_1L^2}{4D_B} \qquad G_3 = \frac{k_1L^2}{4D_A}$$
$$G_2 = \frac{k_2L^2}{4D_{AB}} \qquad G_4 = \frac{k_2L^2}{4D_A} \qquad (25)$$

Thus, the original differential equations have been reduced to a second-order, nonlinear differential equation in a single function. Equation (24) can be solved by successive approximations. At each stage of the iteration, the correct values for C_A, R_0, R_1, and R_2 are assumed to differ from their previous approximate values by amounts $\hat{C}_A$ and $\hat{R}_i$. The corrected values for C_A and R_i are inserted into Equation (24) which is then linearized by ignoring powers and products of the hatted variables. The linear differential equation for $\hat{C}_A$ is solved by Galerkin's method (*10*). The unknown function $\hat{C}_A$ and the latest approximation to C_A are expressed as truncated series of Chebychev polynomials. The recurrence relations among the polynomials can be used to set up a set of linear algebraic equations involving R_0, R_1, and R_2 and the N unknown coefficients in the N term Chebychev polynomial for $\hat{C}_A$. A computer program was written to carry out the successive approximations automatically for any preselected degree of approximation. Each pass through a loop of the program found the corrections to the coefficients of the expansion by inverting a matrix of order $N + 3$. The process was repeated until the correction terms were satisfactorily small.

RESULTS AND DISCUSSION

The solubility of nitric oxide in formamide was found to be 2.62×10^{-3} moles/liter at 1 atm. nitric oxide over the solution at 23°C. The solubility of nitric oxide in solutions of ferrous chloride cannot be determined directly. However, the effect of increasing ferrous chloride concentration in formamide on the solubility of argon was determined. In going from pure formamide to 0.2M ferrous chloride (the range of concentration covered in this work), the solubility of argon decreased less than 5%. Thus, within this range it is reasonable to assume that the effect of increasing ferrous chloride concentration on the solubility of nitric oxide is negligible.

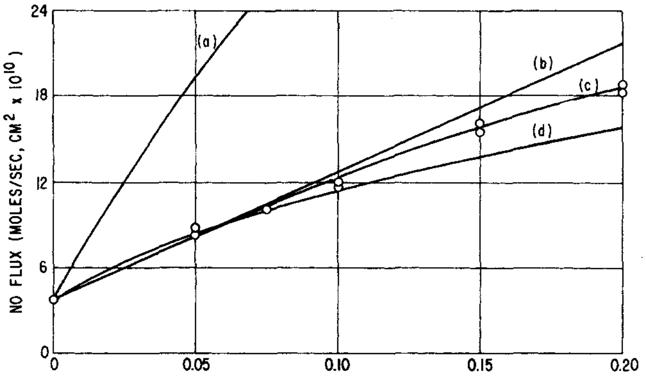

Fig. 5. Steady state nitric oxide flux vs. total ferrous ion concentration. Line (b) calculated from Equation (12). Lines (a) and (d) calculated from Equation (19). Line (c) calculated from analysis of Roe.

The equilibrium constant of reaction (1) was found to be 7.94×10^5 cc./mole at 23°C.

An accurate measurement of the forward and reverse reaction rates presented difficulty. If a reaction is sufficiently slow, diffusional resistance can be made negligible by rapid stirring, and reaction rates can be calculated by observing the rate of absorption (or desorption) of gas in the solution. In the present case, the rates were too large for this to be an accurate procedure. However, it was used because it gave values which were correct at least within a factor of 2, and, as seen below, a higher degree of accuracy was not required. The values of k_1 and k_2 were found to be approximately 7.2×10^3 cc./mole, sec. and 9×10^{-3} sec.$^{-1}$, respectively.

As a first approximation, the diffusion coefficient of an ion can be related to its equivalent conductivity by the relation

$$D_i = \frac{RT\Lambda_i}{Z_iF^2} \qquad (26)$$

From Equation (26) it was thought that the diffusion coefficients of Fe^{2+} and $FeNO^{2+}$ could be readily determined from conductivity measurements on solutions containing ferrous and ferrous-nitric oxide ions and from the data of Dawson et al. (*11, 12*) on conductivities and transport numbers of electrolytes in formamide. Following this procedure, the details of which are given elsewhere (*7*), it was found that the diffusivity of Fe^{2+} in 0.05M ferrous chloride solution was 0.5×10^{-6} sq.cm./sec. This is undoubtedly less than the true value. The most serious error was introduced in assuming complete ion dissociation, which resulted in an incorrect value for Λ_{Cl^-}, and a small error in Λ_{Cl^-} made a large error in $\Lambda_{Fe^{2+}}$. As discussed below, in order to interpret the data obtained for the transport of nitric oxide in ferrous solutions, it was assumed that $D_{Fe^{2+}}$ and $D_{FeNO^{2+}}$ were both equal to 2×10^{-6} sq.cm./sec.

Results from a typical run for nitric oxide diffusion through a film of pure formamide are shown in Figure 3, in which is plotted the moles per square centimeter of nitric oxide passed through the film as a function of time. At time zero, nitric oxide was introduced to the high pressure side of the film to a pressure of 750 mm. Hg. Admitting the nitric oxide required approximately 10 sec. Two values of the diffusivity of nitric oxide can be obtained from Figure 3. The time lag, which is the intercept on the time axis of the steady state portion of the plot of nitric oxide transport vs. time, and the diffusion coefficient are related by (13)

$$D = \frac{L^2}{6\tau} \tag{27}$$

From Equation (27) the average value of the diffusivity of nitric oxide was 1.37×10^{-5} sq.cm./sec., with a spread of 20%. A second value for the diffusivity of nitric oxide, calculated from the steady state rate of transport of nitric oxide through the film, is 1.51×10^{-5} sq.cm./sec. This is in good agreement with the previous value. The spread in this value was also 20%, but it is this value that was used below, since the steady state nitric oxide flux was more accurately known than the time lag.

Results from a typical run for the diffusion of nitric oxide through 0.05M ferrous chloride solution are shown in Figure 4. In all of these runs the pressure of nitric oxide on the high pressure and low pressure sides of the film was 750 mm. Hg. and essentially a vacuum, respectively. The film thickness was 0.103 cm. As expected, the time lag in this case was substantially larger than in the case of nitric oxide diffusion through pure formamide. The time lag is a function of C^0_{NO}, C^L_{NO}, k_1, k_2, L, $C^T_{Fe^{2+}}$, and the diffusion coefficients of nitric oxide, Fe^{2+}, and $FeNO^{2+}$. No attempt was made to determine analytically or experimentally the relation between the time lag and these variables.

The effect of the total ferrous ion concentration (present as ferrous ion and ferrous nitric oxide complex) from 0 to 0.2M on the steady state transport of nitric oxide was determined and is shown in Figure 5. The solid lines in Figure 5 were calculated from the various analyses of facilitated transport discussed previously. Line (b) was calculated by using Equation (12), for which it was assumed all species were present in equilibrium concentrations. The following parameters were used:

C^0_{NO} = 2.62×10^{-6} mole/cc.
C^L_{NO} = 0
L = 0.103 cm.
D_{NO} = 1.5×10^{-5} sq.cm./sec.
$D_{Fe^{2+}}$ = 0.21×10^{-5} sq.cm./sec.
K_{eq} = 7.94×10^{-5} cc./mole

The value of $D_{Fe^{2+}}$ was selected such that at $C^T_{Fe^{2+}}$ of 0.05M, the calculated and experimental values of N^T_{NO} would be equal. It is clear that Equation (12) does not accurately represent the present system.

Line (a)of Figure 5 was calculated by using Equation (19), for which it was assumed that reaction (1) was sufficiently slow that the concentrations of Fe^{2+} and $FeNO^{2+}$ were essentially constant throughout the fim. The following system parameters were used:

C^0_{NO} = 2.62×10^{-6} mole/cc.
C^L_{NO} = 0
L = 0.103
k_1 = 7.15×10^3 cc./mole, sec.
k_2 = 9×10^{-3} sec.$^{-1}$
D_{NO} = 1.5×10^{-5} sq.cm./sec.

Line (d) of Figure 5 was calculated by using these same parameters except with k_1 and k_2 equal to 1.09×10^3 cc./mole, sec. and 1.37×10^{-3} sec.$^{-1}$, respectively. With these values, the calculated and experimental fluxes were equal at $C^T_{Fe^{2+}}$ of 0.05M. Clearly, neither line (a) nor (d) fits the data, and there is no set of reasonable system parameters which could make Equation (19) accurately represent the present system.

Line (c) was calculated from the analysis of Roe, summarized above, by using the following parameters:

C^0_{NO} = 2.62×10^{-6} mole/cc.
C^L_{NO} = 0
L = 0.103 cm.
D_{NO} = 1.5×10^{-5} sq.cm./sec.
k_1 = 7.15×10^3 cc./mole, sec.
k_2 = 9×10^{-3} sec.$^{-1}$
$D_{Fe^{2+}}$ = 2×10^{-6} sq.cm./sec.
$D_{FeNO^{2+}}$ = 2×10^{-6} sq.cm./sec.

This is the only analysis that accurately represents all of the data. The first four parameters above were known accurately. As discussed, k_1 and k_2 were not known accurately, but raising their values an order of magnitude increased N^T_{NO} only 10%. Thus, while the values used were approximate, they were sufficiently accurate for the present purpose. It was assumed that $D_{Fe^{2+}}$ and $D_{FeNO^{2+}}$ were equal, and $D_{Fe^{2+}}$ was set at 2×10^{-6} in order to obtain a best fit for all the data. If the diffusivities of Fe^{2+} and $FeNO^{2+}$ were indeed equal, then the electrical migration term in the flux equations for these species was zero, as originally assumed. If the diffusivities differed as much as 15%, the migration term would still be small. The calculated flux was very sensitive to the values of $D_{FeNO^{2+}}$ and $D_{Fe^{2+}}$, which were used. For example, at $C^T_{Fe^{2+}}$ of 0.05M and $D_{Fe^{2+}}$ and $D_{FeNO^{2+}}$ at 1×10^{-6} sq.cm./sec., the predicted flux was 20% below the observed flux.

While accurate, independent measurements of the values of $D_{Fe^{2+}}$ and $D_{FeNO^{2+}}$ were not obtained in this investigation, the value of 2×10^{-6} sq.cm./sec. used above is reasonable. Thus, it is significant that this value, together with the other system parameters which were known, could be used in Roe's analysis to predict accurately the nitric oxide flux at all values of $C^T_{Fe^{2+}}$. Although there are other quantitative treatments of facilitated transport in the literature, this is the first case in which a general quantitative understanding of facilitated transport has been demonstrated.

ACKNOWLEDGMENT

The author is indebted to G. M. Roe for a general mathematical solution to the problem of facilitated transport in a liquid film. The author wishes to acknowledge many valuable discussions and suggestions of C. P. Bean prior to and during the course of this investigation.

NOTATION

a_1 = constant defined by Equation (8)
a_2 = constant defined by Equation (8)
B_1 = constant defined by Equation (14)
B_2 = constant defined by Equation (14)
C_i = concentration of species i, (moles/cc.)
D_i = diffusion coefficient of species i, (sq.cm./sec.)
F = Faraday constant, 23,062 cal./volt, equiv.
G_i = constants defined by Equation (25)
K_{eq} = equilibrium constant, cc./mole
k_1 = forward reaction rate, cc./mole, sec.
k_2 = reverse reaction rate, sec.$^{-1}$
K, K_1, K_2 = constants defined by Equation (14)
L = film thickness, cm.
M = constant defined by Equation (23)
N_i^T = total flux of species i, moles/sec., sq.cm.
R = gas constant, 1.987 cal./deg., mole
R_0, R_1, R_2 = integration constants, Equations (21) and (22)
t = time, sec.
T = temperature, °R.
x = coordinate axis
z = defined by Equation (20)

z_i = charge on ion i
Λ_i = equivalent conductivity of species i, sq.cm./equiv., ohm
τ = time lag, Equation (27)

Superscripts

0 = evaluated at $x = 0$
L = evaluated at $x = L$

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An Experimental Study of Steady State Multiplicity and Stability in an Adiabatic Stirred Reactor

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Steady state and transient characteristics of an adiabatic, continuous flow, stirred reactor were studied in experiments employing the exothermic reaction between sodium thiosulfate and hydrogen peroxide in aqueous solution. Results illustrate the multiplicity of steady states in this system over a range of residence times. Temperatures of unstable states were attained experimentally by observing the effect of perturbations from stable temperatures. The observed steady states of the reactor under various mixing conditions are shown to be in good agreement with the predictions of a mathematical model which is based on the assumptions that mixing is perfect and that a single independent chemical reaction occurs. Less exact quantitative agreement between theoretical and experimental unsteady performance is accounted for in terms of the sensitivity of the unsteady state to small errors in the system parameters and the existence of appreciable extraneous heat capacities of the experimental equipment.

Continuous flow chemical reactors involving exothermic reactions are often operated autothermally; that is, the operating temperature is sustained entirely by the heat generated by reaction. Van Heerden (*1*, *2*) studied the characteristics of such processes and showed that they may possess multiple steady states and that some steady states are unstable to small perturbations. A number of theoretical studies treating control and start-up problems as well as the general nature of steady and unsteady behavior in various reactor models followed Van Heerden's work. The majority of these were focused on the continuous flow, stirred tank reactor (CSTR) for reasons of mathematical tractability. We refer particularly to papers by Bilous and Amundson (*3*) and Aris and Amundson (*4*). Additional treatments and references may be found in some recent textbooks (*5* to *9*).

Multiple steady states are common in combustion processes as evidenced by the fact that a flowing combustible mixture may be either burning or almost completely nonreacting, depending on whether or not it has been ignited. Several experimental studies with continuous flow, mixed combustion chambers involving combustible gas mixtures have been reported. These date back to a publication by Longwell and Weiss (*10*) in 1955; further bibliography and discussion are available in reference *11*. Generally such studies have been concerned primarily with extinction phenomena and in effect utilized the notion of multiple steady states to interpret and correlate observations.

At the outset of the present study, there was not available in the literature, to our knowledge, any experimental or actual plant data showing the existence of multiple steady states in a CSTR that did not involve a combustion reaction, a surprising observation in view of the fact that numerous theoretical studies have been devoted to

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