Mass Transfer Across a Nonequilibrium Interface

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The problem of mass transfer with nonequilibrium at, and significant convection across, the interface has been studied by the method of matched asymptotic expansions. The inner solution for small values of t or z/U_m was found in terms of f_k functions which were obtained in closed analytical form. The outer solution for large values of t or z/U_m was found in terms of g_k functions which had to be determined numerically. With these solutions, calculation of concentration distributions or instantaneous rates of mass transfer is straightforward, but determination of the total amount of mass transfer as a function of time is complicated by the lack of an intersection wherein the inner and outer solutions overlap and converge. To avoid the need for graphical interpolation and integration of the interfacial concentration as a function of time to obtain the total mass transferred, the constant of integration M_1 is found to be $(-\kappa\gamma\sqrt{\pi}/2h)$ by assuming that the ratio of mass transferred with an equilibrium interface to that with a nonequilibrium interface is independent of whether or not V_y ccnvection is negligible in the system as $t \rightarrow \infty$.

The effect of a nonequilibrium interface is greatest for small t in unsteady systems and z/U_m in steady state systems. This occurs because the departure from their equilibrium values of the interfacial concentrations of the phases in contact is greatest when they are first brought into contact. The larger the interfacial mass transfer coefficient α, the smaller is the time required for the interfacial concentrations to achieve their equilibrium values.

Other things being equal, the rate of mass transfer is greatest when the driving force $x_A{}^* - x_{A0}$ is greatest. Since the departure from equilibrium at the interface is greatest for small values of time, it follows that nonequilibrium interfacial phenomena can be observed most easily in systems where the rate of mass transfer is high. This is also the case when one cannot neglect the effect of finite velocity at the interface which is shown in the present work to be a significant effect.

The method of analysis can be used to study a variety of problems in addition to the specific system considered here. In particular, both batch and flow reverse osmosis problems can be attacked by the present approach.

Investigations of the departure from equilibrium at an interface have been conducted for different processes. Evaporation was first studied in the nineteenth century, and such work is still continuing. The early work appeared almost exclusively in the German literature of which Schrage (*28*) has given an extensive review.

Heideger (*19*) measured the evaporation coefficient of pure glycerol in a vacuum system to be 0.05, which indicated a nonequilibrium interface. Recently, Bonacci (*4*) determined the condensation coefficient of water and carbon tetrachloride in two slightly different unsteady state experiments and concluded that the condensation coefficient of water is at least 0.7 and could easily be 1.0. This indicates no interfacial resistance at the interface. In a recent comprehensive review, Hickman concludes that the evaporation coefficient of water is greater than one-half and that observations to the contrary are plagued by inaccurate estimates of interfacial temperature (*20*). Maa (*22*), a colleague of Hickman, concludes that the evaporation coefficient is unity for isopropyl alcohol, carbon tetrachloride, water, and toluene.

The condensation problem was studied by Sparrow (*24*) who employed the model of the condensation process (*3, 32*) which stated that the saturation temperature of the vapor adjacent to the surface of the condensate is different from the temperature of the liquid at the surface. Since the presence of noncondensable gases also affects heat transfer, it is sometimes difficult to tell whether the reduction of heat transfer is due to the interfacial or noncondensable effect. Conflicts on this point have appeared in the literature (*2, 17, 18, 23*). McKelvey (*2*) showed that the resistance due to the condensation process at the vapor-liquid interface should be taken into account under conditions of low pressure and low heat flux. However, Harriott (*17*) disagrees with McKelvey and argues that bulk phase resistance better explains the interfacial effects.

Sukhatme and Rohsenow (*32*) investigated the film condensation of mercury on a vertical nickel surface at low pressures in the absence of noncondensable gases and found a significant thermal resistance existing at the liquid-vapor interface. They found the condensation coefficient was less than unity, which differs from Knudsen's experimental value (*28*).*

In 1935, Higbie (*21*) studied the absorption of gases by liquids during short periods of exposure. Because a diffusional theory proposed by him failed to correlate the data obtained, he concluded that the assumption of interfacial equilibrium was incorrect for the conditions of his experimental work. Danckwerts (*9*) used the concept of a condensation coefficient, taking it equal to 4×10^{-6}, to explain Higbie's absorption data.

After these two pioneering studies, further work was

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* Recently, Fedorovich and Rohsenow (*14*) took into account vapor subcooling effects near the liquid surface during film condensation of liquid metal vapors. Using this model, they were able to recalculate the value of the condensation coefficient that Sukhatme and Rohsenow obtained and found it to be close to unity.

done on absorption of slightly soluble gases. In the case of absorption of carbon dioxide in water (*8, 12, 16, 27, 29*), conflicting results were found by different investigators.

Generally, each investigator developed a mathematical model using the equilibrium interface as a boundary condition and compared the results obtained with their experimental data. If there is disagreement, they interpret it as indicating significant resistance. The results are summarized in Table 1. On the basis of this work, it is generally concluded that conditions existing at a freshly formed water-carbon dioxide interface are indiscernible from equilibrium for contact times greater than 1 msec. In contrast, Chiang and Toor (*5*) concluded interfacial resistance exists in the oxygen-water system.

For the case of liquid-liquid mass transfer, conflicting results also have been reported (*15, 26, 31, 33*). Early experiments were performed by Tung and Drickamer (*33*) and by Sinfelt and Drickamer (*31*). Both of these were conducted in a static diffusion cell by using a radioactive tracer technique.

There are some disadvantages in using a static system. First, long contact times are involved; second, interfacial resistances smaller than 10^3 sec./cm. are difficult to detect in the presence of large bulk phase resistance; third, interfacial turbulence complicates measurements of the system. Hence, a laminar liquid jet was used by Quinn and Jeannin (*26*) to investigate the liquid-liquid interface effect. They reported an interfacial resistance of approximately 80 sec./cm. for isobutanol diffusing into water at contact times of 0.05 to 0.5 sec. However, Ward and Quinn (*34*) remark that there is some question as to the acceleration of the laminar liquid jet in the work of Jeannin which may have been the cause of the observed resistance. They measured benzene-water and toluene-water systems in a liquid jet and concluded that the resistance is less than 11 sec./cm.

Fosberg and Heideger (*15*) developed a finite difference solution for mass transfer through a steady state laminar jet and performed experiments on cyclohexanol-water, isobutanol-water, and ethyl acetate-water systems. From their observations, interfacial equilibrium prevailed in their systems for contact times on the order of ½ sec.

Ward and Quinn (*35*) measured the interfacial resistance in three component systems. Solute species such as acetic acid, oleic acid, benzoic acid, and cholesterol were transferred between benzene and water at their liquid-liquid interface. It was found that any interfacial resistance in those systems was negligibly small.

For the case where convection is negligible, Duda and Vrentas (*11*) considered a system having a time dependent interface mass transfer coefficient $\alpha(t)$. Two special cases for $\alpha(t)$, a constant and a linear function of time, are assumed in their analysis. Their solution can be applied to mass transfer through an aging interface in the presence of a soluble surface active material.

Previous works dealing with the mathematical analysis of convective diffusion in one-dimensional, unsteady state, or rodlike jet systems have all assumed either that the departure from equilibrium at the interface is negligible (*1*) and/or that convection in the direction normal to the interface is negligible (*6*). These assumptions permit closed form solutions to be obtained. However, the departure from equilibrium is likely to be greatest when mass transfer rates are high, and this is precisely the case when convection normal to the interface is important. Therefore, in the present study we shall develop a method of analysis for the general case wherein both effects are considered simultaneously. This involves essentially matched asymptotic expansions, but the regions of convergence of the inner and outer solutions do not overlap to form an intersection. Once the solution is developed, the purposes of the calculations are to determine the effect of contact time on the departure from equilibrium and the effect of mass transfer rate on the departure from equilibrium.

ANALYSIS

Two of the simplest gas absorption systems are the rodlike liquid jet and one-dimensional unsteady state systems. Since the rodlike jet has constant axial velocity, the mathematical description of it is identical to that of one-dimensional unsteady convective diffusion. The fluid mechanical state of a jet depends on how it is created. In all cases, however, contact with the walls, due to viscosity effects, creates a nonuniform velocity across the jet as it issues from the nozzle, and these nonuniformities decay to a flat profile downstream. One can expose the entire jet to the gas to be absorbed and attempt to account for the effects of a nonuniform velocity field as Scriven and Pigford did (*30*), or one can shield the jet so that the active gas

TABLE 1. SUMMARY OF PREVIOUS INVESTIGATIONS ON THE ABSORPTION OF SLIGHTLY SOLUBLE GASES IN WATER

Investigators	Apparatus	Contact time, sec.	Solute gas	Departure of absorption rates from interfacial equilibrium model
Danckwerts and Kennedy (*8, 8a*)	Rotating drum	0.0075 to 0.25	CO_2	(*8*) yes, (*8a*) no
Cullen and Davidson (*7*)	Orifice jet	0.01 to 0.34	CO_2	No
Davidson and Cullen (*10*)	Wetted sphere	0.12 to 0.57	CO_2 O_2 H_2 H_2O	No
Govindan and Quinn (*16*)	Moving band	0.0008 to 0.063	CO_2	Not appreciable
Scriven and Pigford (*29*)	Jet	0.003 to 0.05	CO_2	No
Chiang and Toor (*5*)	Jet	0.0008 to 0.0118	O_2	Yes
Raimondi and Toor (*27*)	Jet	0.001 to 0.02	CO_2	Slightly

is in contact with only the rodlike portion of it as Maa has done (*22*). The latter case has the advantage of being the simplest to analyze mathematically, and therefore it may provide the sharpest physical insights.

For either unsteady one-dimensional systems or absorption on the surface of an ideal rodlike jet (Figure 1), the convective diffusion equation is

$$\frac{\partial C_A}{\partial t} + V_y \frac{\partial C_A}{\partial y} = D \frac{\partial^2 C_A}{\partial y^2} \tag{1}$$

where y is the distance perpendicular to the interface and t is real time for the former and axial distance divided by mean velocity, z/U_m for the latter. We refer to the jet as phase 1 and the surrounding environment as phase 2.

If the concentration of A in phase 1 is initially at a constant value C_{A0}, we can write the corresponding initial and boundary conditions as

$$\begin{aligned} C_A(y, 0) &= C_{A0} \\ C_A(\infty, t) &= C_{A0} \end{aligned} \tag{2}$$

For a nonequilibrium interface, there is a difference in concentration between the actual interfacial concentration and the concentration which would exist if the surface were in equilibrium. The flux across the interface is, therefore, represented by the concentration difference at the interface multiplied by an interface mass transfer coefficient $N_{A_i} = \alpha(C_A^* - C_{A_i})$. The total flux from the interface to the bulk results from bulk flow and molecular diffusion, where

$$N_{A_i} = -D \frac{\partial C_A}{\partial y}\bigg|_{y=0} + V_y C_{A_i} \tag{3}$$

Therefore, we can write a second boundary condition as

$$y = 0, \quad V_y C_{A_i} - D \frac{\partial C_A}{\partial y}\bigg|_{y=0} = \alpha(C_A^* - C_{A_i}) \tag{4}$$

where C_A^* is the equilibrium concentration of component A at the interface of phase 1 corresponding to the interfacial concentration of A in phase 2. Subscript i indicates concentration at the interface. If the total molar concentration C in phase 1 is constant, then N, the total molar flux, is independent of y, and since only component A passes through the interface while the other specie is rejected, we can equate the total molar flux to that across the interface

$$N = N_{A_i} = CV_y = x_{A_i} N - D \frac{\partial C_A}{\partial y}\bigg|_{y=0} \tag{5}$$

or

$$V_y = \frac{D \left.\dfrac{\partial C_A}{\partial y}\right|_{y=0}}{C_{A_i} - C} = \frac{D \dfrac{\partial C_A(t, 0)}{\partial y}}{C_A(t,0) - C} \tag{6}$$

It is obvious in this expression that V_y is only a function of time.

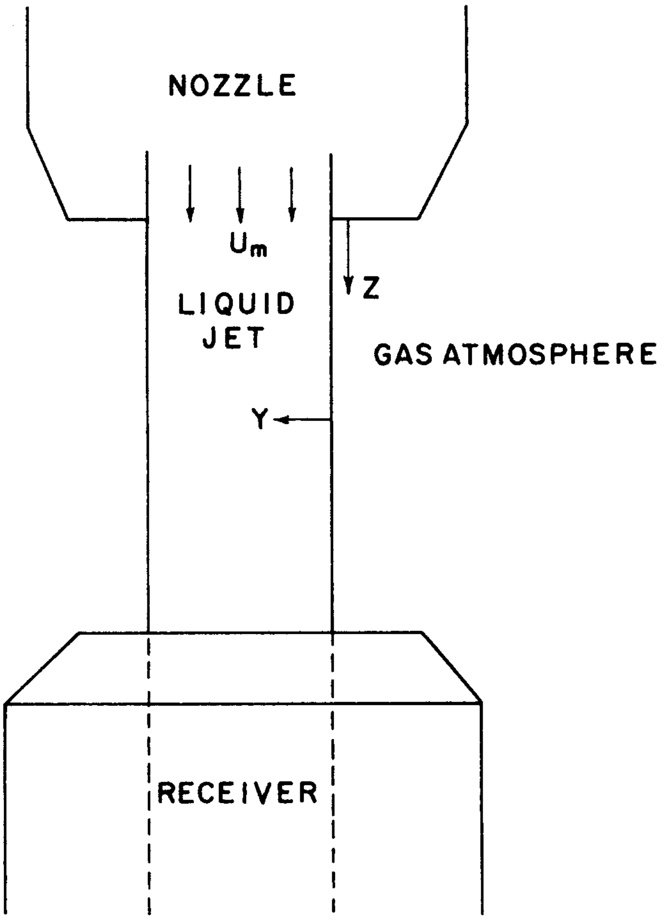

Fig. 1. Schematic diagram of an ideal laminar liquid jet.

Equations (1), (2), (4), and (6) constitute a complete description of the problem. This formulation is quite general and can reduce to more familiar expressions when additional assumptions are made. Thus, if one considers an equilibrium interface, as is often done, then the problem reduces to that solved by Arnold (*1*). In his article, some experiments on evaporation were also given. This analysis was later used by Fairbanks and Wilke (*13*) to determine the diffusion coefficients in gas mixtures. Another mathematically similar (but physically different) problem has been recently examined by Nakano, Tien, and Gill (*25*) who solved the diffusion problem for a batch reverse osmosis desalination system.

SOLUTION

The primary difficulty involved in the solution of Equation (1) is the presence of the nonlinear convective term as well as the nonlinear boundary condition, both arising from the form of transverse velocity given by Equation (6). Nonlinear systems usually arise in the analysis of transport processes, and no general method has been found to solve

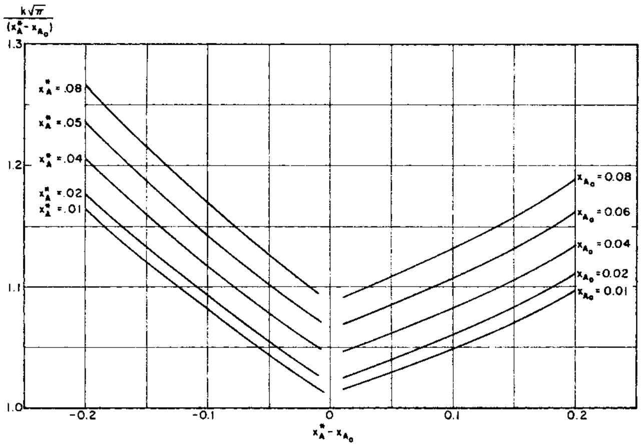

Fig. 2. Ratio of mass transfer with and without convective term, Equation (50), as a function of driving force x_A^*-x_{A_0}.

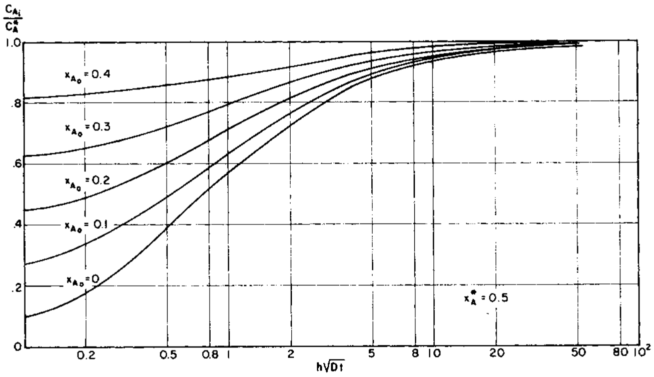

Fig. 3. Dimensionless interfacial concentration as a function of dimensionless time, $h\sqrt{Dt}$ for various x_{A_0} with $X_A{}^* = 0.5$.

them. Closed form solutions are rarely obtained, and usually one must resort to numerical techniques. To obtain a complete solution for all values of t, the principles of the method of matched asymptotic expansions were employed in the present work.

THE INNER SOLUTION

If one introduces the following dimensionless variables

$$\theta = \frac{C_A}{C_{A_0}},\ \xi = \frac{y}{2\sqrt{Dt}},\ \beta = 2\alpha\sqrt{\frac{t}{D}},$$

$$\gamma = \frac{C}{C_{A_0}},\ \theta^* = \frac{C^*{}_A}{C_{A_0}} \tag{7}$$

Equation (1) becomes

$$\frac{\partial^2\theta}{\partial\xi^2} + \left[\ 2\xi - \frac{1}{(\theta(0,\beta)\ -\gamma)}\ \frac{\partial\theta(0,\beta)}{\partial\xi}\ \right]\frac{\partial\theta}{\partial\xi} - 2\beta\frac{\partial\theta}{\partial\beta} = 0 \tag{8}$$

and the boundary conditions are

$$\theta(\infty, \beta) = 1 \tag{9}$$

$$\gamma\frac{\partial\theta(0,\beta)}{\partial\xi} = -\ \beta[\theta(0,\beta)\ -\theta^*]\ [\theta(0,\beta)\ -\gamma] \tag{10}$$

Equations (8), (9), and (10) thus constitute the set of transformed equations for the present problem. A direct closed form solution of this problem has not been found. However, one can employ a series solution of the form

$$\theta(\xi,\beta,\gamma,\theta^*) = \sum_{k=0}^{\infty} f_k\ (\xi,\gamma,\theta^*)\beta^k \tag{11}$$

where the parametric dependence on γ and θ^* is shown explicitly.

This form of solution is suggested because

$$V_y \to \frac{\alpha(C^*{}_A - C_{A0})}{C}$$

and

$$D\frac{\partial C_A}{\partial y}\bigg|_{y=0} \to \frac{\alpha(C_{A0} - C)\,(C^*{}_A - C_{A0})}{C}$$

as $\beta \to 0$. Consequently, one can show that the first two terms of Equation (11) are the exact solution as $\beta \to 0$ if one neglects convection in Equation (8).

If we insert Equation (11) into Equation (8), the result is

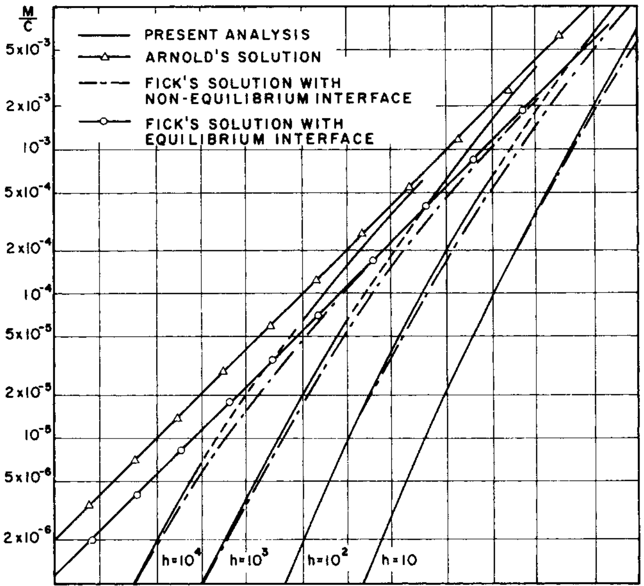

Fig. 4. Comparison of mass transferred, M/C, as a function of time, $\sqrt{Dt}$, for various values of the interface mass transfer coefficient, $h = \alpha/D$.

$$\begin{aligned}
&\left[\sum_{k=0}^{\infty} f_k(0)\beta^k - \gamma\right]\sum_{k=0}^{\infty} f_k''(\xi)\beta^k \\
&\quad + 2\xi\left[\sum_{k=0}^{\infty} f_k(0)\beta^k - \gamma\right]\sum_{k=0}^{\infty} f_k'(\xi)\beta^k \\
&\quad - \left(\sum_{k=0}^{\infty} f_k'(0)\beta^k\right)\left(\sum_{k=0}^{\infty} f_k'(\xi)\beta^k\right) \\
&\quad - 2\beta\left[\sum_{k=0}^{\infty} f_k(0)\beta^k - \gamma\right]\sum_{k=0}^{\infty} (k+1)f_{k+1}(\xi)\beta^k = 0
\end{aligned} \tag{12}$$

By collecting like power terms in β, we get a set of differential equations for the $f_k(\xi)$ functions. The general form for these $f_k(\xi)$ functions can be written as

$$\begin{aligned}
&\sum_{j=0}^{k} f_j(0)f''{}_{k-j}(\xi)\ -\gamma f_K''(\xi) \\
&\quad + 2\xi\left[\sum_{j=0}^{k} f_j(0)f'{}_{k-j}(\xi)\ -\gamma f_k'(\xi)\right] \\
&\quad - \sum_{j=0}^{k} f_j'(0)f'{}_{k-j}(\xi)\ - 2\left[\sum_{j=0}^{k-1}(k-j)f_j(0)f_{k-j}(\xi)\right. \\
&\quad \left. -\gamma k f_k(\xi)\right] = 0 \quad k = 0, 1, 2 \cdots
\end{aligned} \tag{13}$$

The solution for $f_0(\xi)$ can easily be shown to be

$$f_0(\xi) = 1 \tag{14}$$

By using Equations (13) and (14), it follows that

$$f_1''(\xi) + 2\xi f_1'(\xi) - 2f_1(\xi) = 0 \tag{15}$$

$$f_1(\infty) = 0 \tag{16}$$

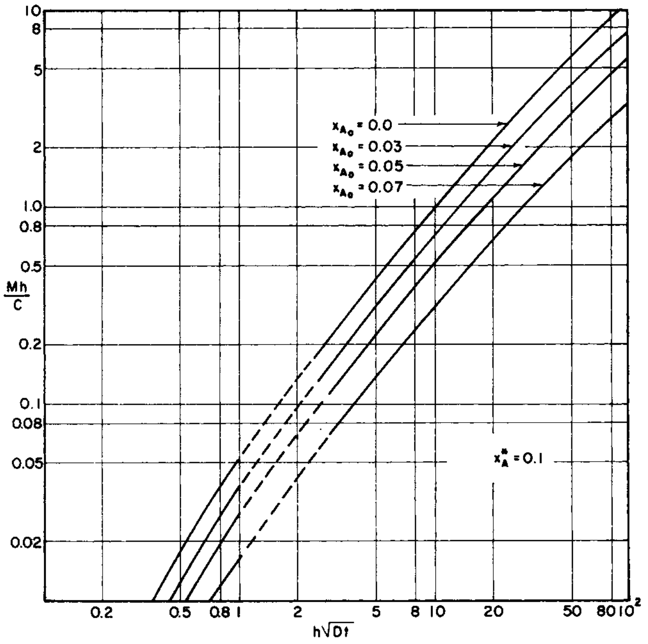

Fig. 5. Dimensionless total mass transfer as a function of dimensionless time, $h\sqrt{Dt}$.

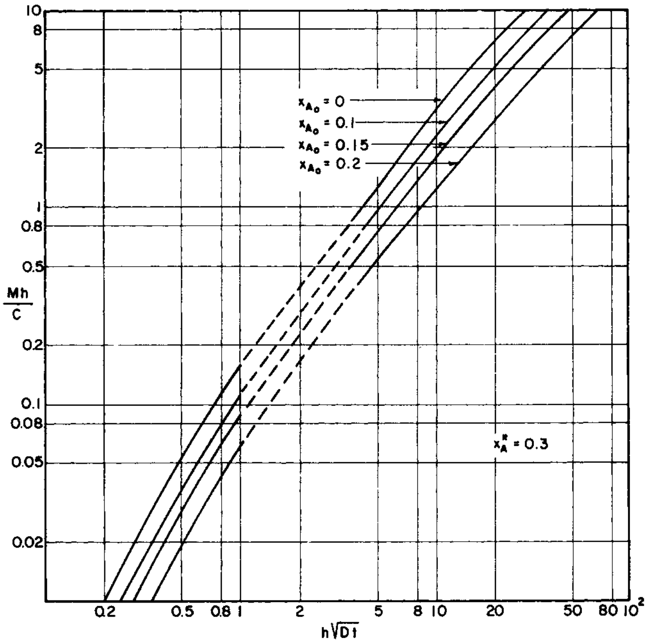

Fig. 6. Dimensionless total mass transfer as a function of dimensionless time, $h\sqrt{Dt}$.

$$f_1'(0) = -\frac{(1-\theta^*)(1-\gamma)}{\gamma} \tag{17}$$

Furthermore, by using Equations (14) and (15), we can simplify Equation (13) to

$$(1-\gamma)\,[f_k''(\xi) + 2\xi f_k'(\xi) - 2kf_k(\xi)\,] =$$
$$-\sum_{j=1}^{k-2} f_j(0)\,[f''_{k-j}(\xi) + 2\xi f'_{k-j}(\xi) - 2(k-j)f_{k-j}(\xi)]$$
$$+\sum_{j=1}^{k-1} f'_j(0)f'_{k-j}(\xi), \quad k = 1, 2, \cdots \tag{18}$$

with the boundary conditions

$$f_k(\infty) = 0 \qquad k = 1, 2 \cdots \tag{19}$$

$$f_k'(0) = \frac{-1}{\gamma}\left[\sum_{j=0}^{k-1} f_j(0)f_{k-j-1}(0) - \gamma f_{k-1}(0)\right.$$
$$\left. - \theta^* f_{k-1}(0)\right], \quad k = 2, 3 \cdots \tag{20}$$

Fortunately, we found that closed form solutions exist to the equations which constitute this system, and we list the first seven solutions as follows (36):

$$f_1(\xi) = B_1\left[\,\xi\text{erfc}\,\xi - \frac{e^{-\xi^2}}{\sqrt{\pi}}\,\right] \tag{21}$$

$$f_2(\xi) = \frac{B_2}{4}\left[\,\frac{2}{\sqrt{\pi}}\xi e^{-\xi^2} - (1+2\xi^2)\text{ erfc}\xi\,\right] + D_2\text{erfc}\xi \tag{22}$$

$$f_3(\xi) = \frac{B_3}{12}\left[\,\xi(3+2\xi^2)\text{ erfc}\xi - 2(1+\xi^2)\frac{e^{-\xi^2}}{\sqrt{\pi}}\,\right]$$
$$+ (D_3 + D_3'\xi)\text{erfc}\xi + D_3''e^{-\xi^2} \tag{23}$$

$$f_4(\xi) = \frac{B_4}{96}\left[\,\frac{2}{\sqrt{\pi}}\xi(5+2\xi^2)e^{-\xi^2}\right.$$
$$\left. - (4\xi^4 + 12\xi^2 + 3)\text{erfc}\xi\,\right] + (D_4 + D_4'\xi + D_4''\xi^2)\text{erfc}\xi$$
$$+ (D_4''' + D_4^{iv}\xi)e^{-\xi^2} \tag{24}$$

$$f_5(\xi) = \frac{B_5}{480}\left[\,\xi(4\xi^4 + 20\xi^2 + 15)\text{erfc}\xi\right.$$
$$\left. - \frac{2}{\sqrt{\pi}}(2\xi^4 + 9\xi^2 + 4)e^{-\xi^2}\,\right] + (D_5 + D_5'\xi$$
$$+ D_5''\xi^2 + D_5'''\xi^3)\text{erfc}\xi + (D_5^{iv} + D_5^{v}\xi + D_5^{vi}\xi^2)e^{-\xi^2} \tag{25}$$

$$f_6(\xi) = \frac{B_5}{5760}\left[\frac{2}{\sqrt{\pi}}(4\xi^5 + 28\xi^3 + 33\xi)e^{-\xi^2}\right.$$
$$\left. - (8\xi^6 + 60\xi^4 + 90\xi^2 + 15)\text{erfc}\xi\,\right]$$
$$+ (D_6 + D_6'\xi + D_6''\xi^2 + D_6'''\xi^3 + D_6^{iv}\xi^4)\text{erfc}\xi$$
$$+ (D_6^{v} + D_6^{vi}\xi + D_6^{vii}\xi^2 + D_6^{viii}\xi^3)e^{-\xi^2} \tag{26}$$

$$f_7(\xi) = \frac{B_7}{40320}\left[\,(8\xi^7 + 84\xi^5 + 210\xi^3 + 105\xi)\text{erfc}\xi\right.$$
$$\left. - \frac{2}{\sqrt{\pi}}(4\xi^6 + 40\xi^4 + 87\xi^2 + 24)e^{-\xi^2}\right]$$
$$+ (D_7 + D_7'\xi + D_7''\xi^2 + D_7'''\xi^3 + D_7^{iv}\xi^4 + D_7^{v}\xi^5)$$
$$\text{erfc}\xi + (D_7^{vi} + D_7^{vii}\xi + D_7^{viii}\xi^2 + D_7^{ix}\xi^3 + D_7^{x}\xi^4)e^{-\xi^2} \tag{27}$$

B_1 --- B_7, D_1 --- D_7, and those with primes, double primes, etc., are only functions of the system parameters θ^* and γ, so they can be readily calculated once we specify the system. A tabulation of the expressions for these constants is given elsewhere.*

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* Data have been deposited as document 01080 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 W. 34th St., New York 10001 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

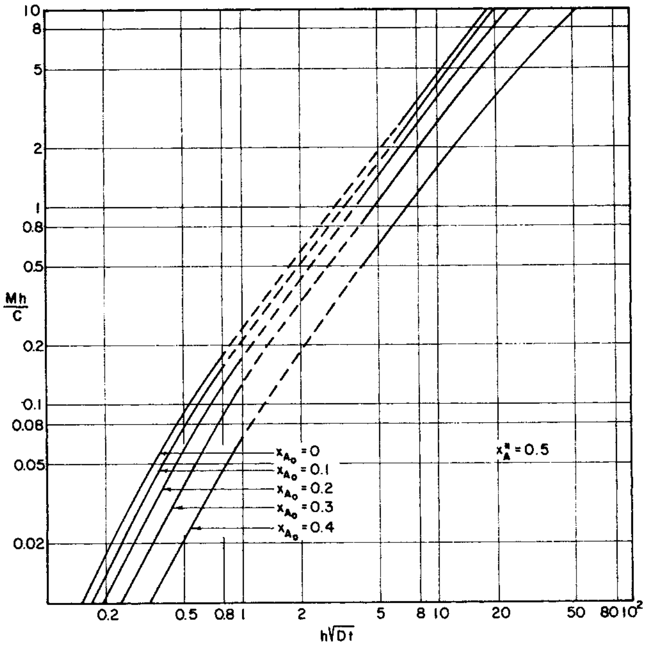

Fig. 7. Dimensionless total mass transfer as a function of dimensionless time, $h\sqrt{Dt}$.

THE OUTER SOLUTION

It is known that the unsteady state system will reach equilibrium eventually. Hence, the solution of the problem with an equilibrium interface will be expected to form the asymptotic solution of the present problem at large values of time.

For the mathematical system given by Equations (8), (9), and (10), we take the solution to be of the following form:

$$\theta(\xi,\beta) = \sum_{k=0}^{\infty} g_k(\xi)\left(\frac{\beta}{\gamma^2}\right)^{-k} \tag{28}$$

This form of solution is suggested because the interfacial concentration goes to its equilibrium value as $\beta \rightarrow \infty$, and in this event g_0 is the exact solution.

The introduction of γ^2 in the solution facilitates the numerical evaluation of the $g_k(\xi)$ functions, and its presence does not affect the differential equation. Following the same procedure as in the inner series solution, we substitute Equation (28) into Equation (8) and collect like power terms of $(\beta/\gamma^2)^{-k}$. We finally obtain the following general equation for the $g_k(\xi)$ functions:

$$\sum_{j=0}^{k} g_j(0)g''_{k-j}(\xi) - \gamma g''_k(\xi) + 2\xi\left[\sum_{j=0}^{k} g_j(0)g'_{k-j}(\xi) - \gamma g'_k(\xi)\right] - \sum_{j=0}^{k} g'_j(0)g'_{k-j}(\xi) + 2\left[\sum_{j=0}^{k-1} (k-j)g_j(0)g_{k-j}(\xi) - \gamma k g_k(\xi)\right] = 0 \quad k = 0, 1, \cdots \tag{29}$$

This expression is the same as Equation (13) except for a different sign in the last bracket. Because of this we were unable to solve for the $g_k(\xi)$ by the method used in the inner series solution. Instead, numerical methods (Runge-Kutta integration) were used for solving these equations.

The first boundary condition, Equation (9), is easily reduced to the following two by means of Equation (28):

$$g_0(\infty) = 1$$
$$g_k(\infty) = 0 \quad k = 1, 2, \cdots \tag{30}$$

Similarly, the second boundary condition, Equation (10), reduces to

$$g_0(0) = \theta^* \tag{31}$$

$$g_0'(0) = -\gamma(\theta^* - \gamma)g_1(0) \tag{32}$$

$$-g_k'(0) = \gamma\left[\sum_{j=1}^{k} g_j(0)g_{k-j+1}(0) + (\theta^* - \gamma)g_{k+1}(0)\right] \quad k = 1, 2, 3 \cdots \tag{33}$$

From Equations (29), (30), and (31) we can obtain the differential equation and boundary conditions for the zeroth order function of the series. These are

$$g_0''(\xi) + \left[2\xi - \frac{g_0'(0)}{\theta^* - \gamma}\right]g_0'(\xi) = 0$$
$$g_0(0) = \theta^* \tag{34}$$
$$g_0(\infty) = 1$$

The solution to this system can be given by the closed form expression

$$g_0(\xi) = 1 + (\theta^* - 1)\,\frac{\operatorname{erfc}\left(\xi - \frac{\kappa}{2}\right)}{\operatorname{erfc}\left(-\frac{\kappa}{2}\right)} \tag{35a}$$

where

$$\kappa = \frac{g_0'(0)}{\theta^* - \gamma} \tag{35b}$$

and this is identical to the κ associated with Arnold's solution and is given later by Equation (40).

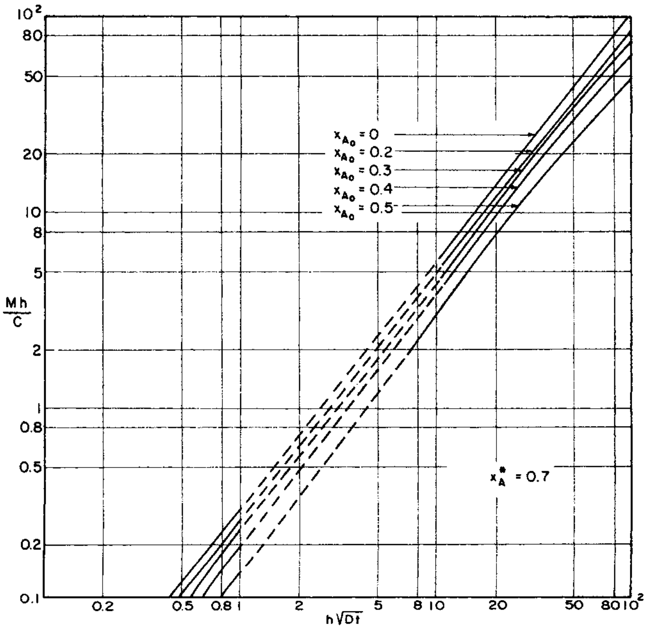

Fig. 8. Dimensionless total mass transfer as a function of dimensionless time, $h\sqrt{Dt}$.

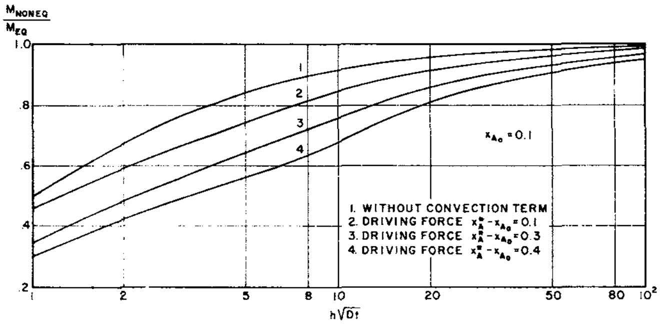

Fig. 9. Effect of nonequilibrium interface on rate of mass transfer. Ratio of total amount of mass transfer with a nonequilibrium interface to that with equilibrium at the interface as a function of dimensionless time, $h\sqrt{Dt}$.

This solution was found by Arnold (*1*) who considered convective diffusion with an equilibrium interface boundary condition. It was mentioned before that the equilibrium value will finally be reached in an unsteady state system as time goes to infinity. The fact that the zeroth order function in the series of Equation (28) is Arnold's solution indicates that the series converges to the proper limit as time becomes larger and larger. The physical interpretation of the constant κ is that it is a dimensionless molar average velocity if equilibrium exists at the interface. Clearly, the larger the flux (which implies the larger the driving force from the interface to the bulk phase), the larger the value of κ. Thus, when κ is equal to zero, corresponding to the case of very low mass flux, convection is negligible, and Equation (35*a*) then reduces to the solution that one obtains from Fick's second law for unsteady state molecular diffusion.

RESULTS AND DISCUSSION

The flux of component *A* through the interface is given by the following equation:

$$N_{Ai} = \frac{dM}{dt} = \alpha(C^*_A - C_{Ai}) \tag{36}$$

To evaluate the amount of diffusing specie transferred, first insert the inner solution, Equation (11), into the dimensionless form of Equation (36) and integrate with respect to time to obtain

$$\frac{M}{C_{A0}} = \frac{-D}{\alpha}\int_0^{\frac{\alpha^2 t}{D}} [(1-\theta^*) + 2f_1(0)\sqrt{\tau} + 4f_2(0)\tau + 8f_3(0)\tau^{3/2} + 16f_4(0)\tau^2 + 32f_5(0)\tau^{5/2} + 64f_6(0)\tau^3 + 128f_7(0)\tau^{7/2} + \cdots]d\tau$$

or

$$\frac{M}{C_{A0}} = \frac{-1}{h}\Big[(1-\theta^*)(h\sqrt{Dt})^2 + \frac{4}{3}f_1(0)(h\sqrt{Dt})^3 + 2f_2(0)(h\sqrt{Dt})^4 + \frac{16}{5}f_3(0)(h\sqrt{Dt})^5 + \frac{16}{3}f_4(0)(h\sqrt{Dt})^6 + \frac{64}{7}f_5(0)(h\sqrt{Dt})^7 + 16f_6(0)(h\sqrt{Dt})^8 + \frac{256}{9}f_7(0)(h\sqrt{Dt})^9 + \cdots\Big] \tag{37}$$

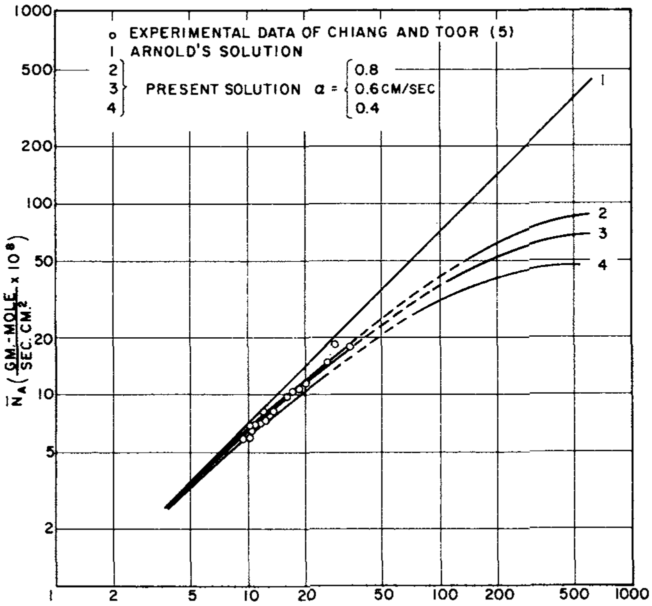

Fig. 10. Comparison of experimental data of Chiang and Toor with present analysis.

where $h = \alpha/D$.

Next the outer solution, Equation (28), is used, and the amount transferred is obtained as

$$\frac{M}{C_{A0}} = \frac{D}{\alpha}\int_{\tau_1}^{\tau}\left[\frac{\gamma^2 g_1(0)}{2\sqrt{\tau}} + \frac{\gamma^4 g_2(0)}{4\tau} + \frac{\gamma^6 g_3(0)}{8\tau^{3/2}} + \frac{\gamma^8 g_4(0)}{16\tau^2} + \ldots\right]d\tau + M_1$$

$$= \frac{-1}{h}\Big[g_1(0)\,\gamma^2\,(h\sqrt{Dt}) + \frac{1}{4}g_2(0)\,\gamma^4 \ln(h^2Dt) - \frac{g_3(0)\,\gamma^6}{4h\sqrt{Dt}} - \frac{g_4(0)\,\gamma^8}{16(h\sqrt{Dt})^2} - \frac{g_5(0)\,\gamma^{10}}{48(h\sqrt{Dt})^3} \cdots\Big] + M_1 \tag{38}$$

where $g_0(0)$ doesn't appear because it is equal to and cancels θ^*. It can be shown that

$$g_1(0) = -\frac{\kappa}{\gamma}$$

and therefore the first term of Equation (38) is identical to that of Arnold's problem, Equation (44). Some typical values of $f_k(0)$ and $g_k(0)$ are given in Tables 2 and 3.[†]

Now the problem is reduced to evaluating M_1. If Equations (11) and (28) had overlapping regions of convergence, M_1 could easily be evaluated by equating these solutions anywhere within this intersection. Unfortunately, no intersection seems to exist, and therefore it is necessary to join the short and long time solutions and evaluate M_1 by other means. That is, M_1 must be chosen so that Equations (37) and (38) can be joined smoothly and the amount of mass transferred is represented by a continuous curve. This could be done graphically, but we seek an analytical result.

To evaluate M_1 it is useful to consider the closed form solutions which exist for several special cases. These are:

1. Arnold's problem which includes V_y convection but

[†] See footnote on p. 797.

assumes an equilibrium interface. In this case the solution is

$$\frac{C_A - C_{A0}}{C_A{}^* - C_{A0}} = \frac{\operatorname{erfc}\left(\xi - \frac{\kappa}{2}\right)}{\operatorname{erfc}\left(-\frac{\kappa}{2}\right)} \tag{39}$$

where κ is defined by

$$2 + \left(\frac{\theta^* - \gamma}{\theta^* - 1}\right)\sqrt{\pi}\,\kappa\,\exp\left(\frac{\kappa^2}{4}\right)\operatorname{erfc}\left(-\frac{\kappa}{2}\right) = 0 \tag{40}$$

For small values of κ, Equation (40) reduces to

$$\kappa = \frac{2}{\sqrt{\pi}}\,\frac{(\theta^* - 1)}{\gamma - \theta^*} = \frac{2}{\sqrt{\pi}}\,\frac{x_A{}^* - x_{A0}}{1 - x_A{}^*} \tag{41}$$

For large values of κ, we get

$$\kappa = -\sqrt{\frac{2(\gamma - \theta^*)}{\gamma - 1}}, \quad \kappa < 0 \tag{42}$$

$$= -\sqrt{\frac{2(1 - x_A{}^*)}{1 - x_{A0}}}$$

and

$$\kappa = 2\sqrt{\ln\left(\frac{\pi^{-1/2}(\gamma - 1)}{(\gamma - \theta^*)}\right)}, \quad \kappa > 0 \tag{43}$$

$$\kappa = 2\sqrt{\ln\frac{1 - x_{A0}}{\sqrt{\pi}(1 - x_A{}^*)}}$$

In this case, one finds

$$\frac{M}{C_{A0}} = \kappa\,\gamma\,\sqrt{Dt} \tag{44}$$

2. When V_y convection is negligible but there is a departure from equilibrium at the interface. In this case the solution is

$$\frac{C_A - C_{A0}}{C_A{}^* - C_{A0}} = \operatorname{erfc}\frac{y}{2\sqrt{Dt}} - \exp(hy + h^2Dt)\operatorname{erfc}\left(\frac{y}{2\sqrt{Dt}} + h\sqrt{Dt}\right) \tag{45}$$

and the total amount of mass transferred is

$$\frac{M}{C_{A0}} = \left(\frac{\theta^* - 1}{h}\right)\left(e^{h^2Dt}\operatorname{erfc} h\sqrt{Dt} - 1 + \frac{2}{\sqrt{\pi}}h\sqrt{Dt}\right) \tag{46}$$

3. When V_y convection is negligible and the interface is in equilibrium. In this case the solution is

$$\frac{C_A - C_{A0}}{C_A{}^* - C_{A0}} = \operatorname{erfc}\frac{y}{2\sqrt{Dt}} \tag{47}$$

and the total amount of mass transferred is

$$\frac{M}{C_{A0}} = 2(\theta^* - 1)\sqrt{\frac{Dt}{\pi}} \tag{48}$$

Now, instead of trying to find values of M_1 by trial and error by directly attempting to construct a continuous curve, we evaluate it by assuming that the ratio of the mass transferred according to Equations (46) and (48) is the same as the ratio obtained from Equation (38) and (44) as $t \to \infty$. That is, as $t \to \infty$ the ratio of the mass transferred with an equilibrium interface to that with a nonequilibrium interface is independent of whether or not the V_y convection term is negligible in the system. This leads to

$$M_1 = -\frac{\kappa\gamma\sqrt{\pi}}{2h} \tag{49}$$

and with this value of M_1 it was found that a smooth continuous curve is obtained.

One can obtain a rapid estimate of the importance of V_y convection by forming the ratio of Equation (44) and (48) to get

$$\frac{\kappa\gamma\sqrt{\pi}}{2(\theta^* - 1)} = \frac{\kappa\sqrt{\pi}}{2(x_A{}^* - x_{A0})} \tag{50}$$

which is obviously independent of t and depends only on the parameters γ and θ^*. Figure 2 shows that the ratio of the rate of mass transfer predicted when one includes V_y to that predicted when one neglects it depends strongly on both the driving force $x_A{}^* - x_{A0}$ and the concentration level. Even with the rather small driving forces and concentration levels shown, the errors incurred by neglecting V_y convection across the interface can be much more significant than Scriven and Pigford (*30*) found to be attributable to assuming ideal flow in the jet. Much larger error would be incurred with larger driving forces.

It is found that in unsteady state mass transfer systems the assumption of thermodynamic equilibrium at the interface will be more nearly correct for large contact times. Similarly, in steady state systems such as the jet the assumption will be more valid for large values of z/U_m. Other things being equal, the deviation from thermodynamic equilibrium at the interface will be more significant when the flux passing through the interface is high. This is seen clearly in Figure 3 wherein the departure from equilibrium at the interface, denoted by $C_{A_i}/C_A{}^*$, is shown as a function of $h\sqrt{Dt}$. The departure of $C_{A_i}/C_A{}^*$ from unity is larger when $x_A{}^* - x_{A0}$ is larger, and the flux is proportional to this driving force. The shape of these curves is typical of those obtained for various values of $x_A{}^*$.

By comparing the solutions, Equations (46) and (48), of Fick's equation with and without equilibrium at the interface, we can examine the significance of interfacial resistance. Also, we can investigate the importance of interfacial resistance in the presence of a convective term by comparing the results obtained by Arnold (*1*) with those of the present analysis. The constant M_1, which equals $(-\kappa\gamma\sqrt{\pi})/(2h)$ where κ is given by Equation (40), in Equation (38) is a measure of the extent of the departure from equilibrium, Equation (44). In this sense, it is similar to the term $-(\theta^* - 1)/h$ in Equation (46) as a departure from the equilibrium solution, Equation (48). One can see that the departure from equilibrium is increased by increasing κ and γ or decreasing h. In designing experiments for the study of nonequilibrium interfaces, the value of M_1 should be considered.

In Figure 4 the effect of h (which is directly related to the interface mass transfer coefficient α) is shown for constant values of the parameters $x_A{}^*$ and x_{A0}. Four different values of h, 10, 10^2, 10^3, and 10^4 cm.$^{-1}$ are examined for which the corresponding values of α are 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1} cm./sec. if the molecular diffusivity D is taken to be 10^{-5} sq.cm./sec. (which is characteristic of liquids). α has been found experimentally to be 0.6 cm./sec. for the absorption of oxygen in water [by Chiang and Toor (*5*)]. In their work with the laminar jet, the values of contact time (time for water particle to traverse the oxygen environment) were $3 \leq h\sqrt{Dt} \leq 14$. As the values of h increase, the interfacial resistance decreases, and, consequently, the system will reach equilibrium faster for large h. The shape of the curves given by the inner and outer series solutions in Figure 4 for different values of h is nearly the same, differing only in the time they approach their equilibrium values. The sorption curve of the present problem with $h = 10^3$ can be obtained by multiplying by 10 both the ordinate M/C and the abscissa $\sqrt{Dt}$ of the sorption curve with $h = 10^4$. That is, the sorption curve with $h = 10^4$ approaches equilibrium ten times faster than the one with $h = 10^3$. The system parameters x_A^* and x_{A_0} do not influence the general shape of the sorption curves, so that any chosen values of x_A^* and x_{A_0} other than those in Figure 4 would give us the same general results.

The results of the present calculation can probably best be given in plots of dimensionless amount of mass transferred vs. dimensionless time for various x_A^* and x_{A_0}. Such plots are presented in Figures 5, 6, 7, and 8. The dashed part of the curves in these plots is the region in which the inner and outer series expansions do not converge.

The effect of a nonequilibrium interface, in terms of the rate of mass transfer as a function of driving force, is shown in Figure 9. It is seen that the importance of the nonequilibrium interface increases as $x_A^* - x_{A_0}$ increases. For example, the ratio of the mass transferred with a nonequilibrium interface to that with equilibrium at the interface is equal to 0.95 at values $h\sqrt{Dt}$ of 40, 70, and 100 for $x_A^* - x_{A_0}$ equal 0.1, 0.3, and 0.4.

The present analysis compares well with the experimental data of Chiang and Toor (5) as shown in Figure 10, where the average absorption rate per unit area is plotted against the square root of reciprocal of time. The solubility of oxygen in water is small, so the equilibrium interfacial concentration and initial concentration of oxygen in water are low. Therefore, the effect of convection is small. Results for values of the interfacial mass transfer coefficient α equal 0.4, 0.6, 0.8 cm./sec. are given. It is seen that the data points correspond most closely to the curve for $\alpha = 0.6$.

CONCLUSIONS

1. The inner and outer series solutions can be used to describe the nonequilibrium interface system when convection across the interface is significant.
2. Calculation of concentration distributions or instantaneous rates of mass transfer is straightforward, since the inner and outer solutions are independent of each other. In contrast, the analytical determination of the total amount of mass transfer (which is what one would ordinarily measure) as a function of time is complicated by the lack of an intersection wherein the inner and outer series solutions overlap and converge. This difficulty can be overcome by graphical interpolation of the concentration distribution and integration to determine the amount of mass transferred as a function of time. However, the need for graphical integration was avoided by finding $M_1 = -\kappa\gamma\sqrt{\pi}/2h$.
3. The effect of a nonequilibrium interface is greatest for small values of t in unsteady and z in steady state systems.
4. The larger the interfacial mass transfer coefficient, the smaller the time required for the interface to achieve equilibrium. This is demonstrated quantitatively in Figure 4.
5. Departure from an equilibrium interface is greatest when the driving force $x_A^* - x_{A_0}$ is largest; thus, one is most likely to observe the effect of a nonequilibrium interface with soluble gases where $x_A^* - x_{A_0}$ is large. This is also the case when convection across the interface is most important. Therefore, the effects of a nonequilibrium interface and convection across the interface should be considered simultaneously.
6. The present method of analysis can be extended to other systems such as those which occur with nonideal jets, in reverse osmosis, or with time dependent interface mass transfer coefficients as may occur when surface active agents are present.

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NOTATION

C = total concentration of the laminar liquid jet
C_A = concentration of component A (dissolved gas) in the jet
C_{A_0} = initial concentration of component A in the jet
C_{A_i} = actual concentration of component A at the jet interface
C_A^* = equilibrium concentration of component A at the jet interface
D = molecular diffusivity of component A in the jet
h = α/D
M = amount of mass transfer per unit area
M_1 = constant in Equation (38)
N = total molar flux in the jet
N_{A_i} = molar flux of component A through the jet interface
U_m = velocity of a rodlike jet
V_y = velocity normal to the surface of the jet
t = time
x_A = mole fraction of component A in the jet phase
x_A^* = θ^*/γ equilibrium mole fraction of component A at the jet interface
x_{A_0} = $1/\gamma$ initial mole fraction of component A in the jet phase
y = radial coordinate from the jet interface
z = axial coordinate from the nozzle of the jet

Greek Letters

α = interface mass transfer coefficient
β = $2\alpha\sqrt{t/D}$
γ = C/C_{A_0} reciprocal of the initial concentration
ξ = $y/2\sqrt{Dt}$
θ = C_A/C_{A_0} dimensionless concentration
θ^* = C_A^*/C_{A_0} dimensionless equilibrium concentration of component A at the jet interface
κ = dimensionless bulk velocity normal to the jet interface
τ = $\alpha^2 t/D$

Subscript

i = interface between gas and liquid jet
0 = initial state at $t = 0$

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Spray Quenching

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A study was made of spray quenching by high velocity gas atomization. A mathematical model of both high and low temperature spray quenching was developed. Data were taken for proving the validity of the model.

Experiments were performed on a vertical downward flow of air-water in a 1.0 in. diameter tube. Injection was by either of two modes. The first was a set of six peripheral liquid jets projecting water perpendicularly into the high velocity airstream. The second mode of liquid injection was by means of a 360° peripheral, annular slot, which laid down a continuous wall film at the point of injection. Air velocities of 430 and 200 ft./sec. and liquid injection rates of from 150 to 1,200 ml./min. were studied. The following physical quantities were measured: liquid fluxes, wall film flow rates, drop size distributions, and median drop size. An attempt was made to measure gas temperature in a dense spray by using two different types of temperature probes, but only liquid temperatures could be detected. A comparison of data with published data and correlations was made.

The best quenching conditions obtained were a liquid-to-gas mass ratio of 0.25, a Sauter mean drop diameter of 45 μ, and an indicated characteristic quench time of 10^{-3} sec.

Spray quenching is the process of rapidly cooling a hot gas by a liquid spray. This is accomplished by injecting liquid into a high velocity gas stream. To date, very little has been published on spray quenching. These accounts are of a highly qualitative nature and give one the impression that spray quenching is more of an art than a science.

The intent of this work was to measure characteristic quench times to gain some insight into how a spray quenching operation may be controlled.

There are a number of practical applications of high velocity atomization and spray quenching. Spray quenching may be used to stop or freeze reactions. Concentrations of a high temperature equilibrium are recovered if cooling is so fast that reversal cannot occur (except on very long time scales). Spray quenching has present-day application in missile launch systems where, at the moment of take-off and for a short time afterwards, there is a rapid efflux of hot combustion gases directed at the launch pad. The pad must be cooled during this time, usually by a liquid spraying operation. High velocity atomization is encountered in ram jet engines where the performance of the flame stabil-

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