Nonlinear Convective Diffusion: A Hyperfiltration Application

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A nonlinear unsteady state convective diffusion problem that describes the performance of a constant pressure cell is studied. The cell can be used to either determine membrane constants or to carry out batch filtration operations. It consists of a cylinder closed by a semipermeable membrane at one end and a piston at the other.

The nonlinear partial differential equation governing the system was solved by both integral methods and the use of a similarity transformation. The similarity approach formulates the solution in the form of an infinite series and reduces the problem to finding the solution of an infinite system of ordinary differential equations. The series solution can be considered to be exact but its convergence is questionable for large values of time in the event $B \neq 0$; when $B = 0$, the convergence is substantially better.

Approximate solutions obtained by integral methods were examined in detail. It was found that the results obtained by these methods can involve serious errors, under certain circumstances, and these errors seem unpredictable a priori. Consequently, it is concluded that considerable care should be taken in the use of integral methods for solving mass transfer problems in which the velocity field is coupled with the convective diffusion equation and its boundary conditions.

The numerical results obtained in this work are sufficiently comprehensive to be used, in conjunction with experimental data, to determine membrane constants which are required for the design of both continuous and batch membrane separation systems.

Increasing awareness of the importance of having an adequate water supply in the future has resulted in a flourishing of research activity on desalination during the recent years. Among the various potentially important desalination processes, the use of selective membranes for the separation of water from brine (commonly known as *hyperfiltration* or *reverse osmosis*) has attracted considerable attention. Under ordinary circumstances, if brine and pure water are placed on either side of a semipermeable membrane which allows the passage of water but not that of salt, water will flow from the pure water side to that of the brine because of the osmotic pressure effect. However, if higher pressure is exerted on the brine side and, if the pressure difference across the membrane exceeds the osmotic pressure corresponding to the concentration at the brine-membrane interface, the direction of flow will be reversed. Water will permeate through the membrane from the brine side to the pure water side and one obtains pure water from brine. This is called reverse osmosis. A main advantage of reverse osmosis processes is that the desired separation can be accomplished without change of phase as is required in other processes such as evaporation and freezing.

Although the study of the reverse osmosis process is still in a relatively early stage, a considerable number of publications have appeared in the literature concerning several aspects of the problem. Among these a substantial number of investigations concern the analysis and prediction of the behavior of continuous reverse osmosis flow systems (*1* to *6*, *9*, *10*) with different geometric configurations. In comparison, the only work done on batch systems was carried out by Dresner (*2*), who considered a system with constant water flux, which is a linear problem.

Membrane separation processes are being considered for a wide variety of applications (*8*). For a large-scale reverse osmosis installation, the process involved would, in all likelihood, be a continuous one because of its high efficiency and relatively low operating cost. On the other hand, the batch-operated process may be most suitable for small-scale and portable purposes.

As has been pointed out by Friedlander and Rickles (*8*), most of the membrane test data that have been collected over many years were obtained in batch systems. An accurate analysis of the constant pressure batch system should be useful in interpreting these data which were collected by investigators who were not always fully aware of the diffusional resistances in their apparatuses.

The nonlinear batch process, which consists of a cylinder chamber with a supported membrane at one end and a piston subjected to a constant pressure at the other, is the simplest possible system from a fluid mechanical viewpoint that one can conceive of. As can be seen by comparing Equation (4) with the equation describing reverse osmosis in a steady state, parallel-plate flow system, the batch system is mathematically identical to a plug-flow system if one interprets t as an axial distance, say Z, divided by a constant axial velocity parallel to the membrane. One can expect concentration polarization at the membrane surface to increase with time in the batch system as it does with axial distance in flow systems. Thus one would expect the batch system to be useful in many instances in which a laminar flow system is appropriate. The primary advantage that the batch system has is simplicity. Its one-dimensional nature could be a significant factor in measuring concentration polarization experimentally.

In a batch-operated reverse osmosis system, the salt concentration at the membrane surface increases with time. This accumulation of salt at the surface is due to the bulk movement of brine toward the membrane and rejection of salt at the membrane-fluid interface. Since the salt concentration at the surface increases with time, so does π. Consequently, V_w varies with time and is a function of salt concentration at the membrane surface so that the general problem is inherently nonlinear.

It seems reasonable to assume for batch-operated reverse osmosis systems that the pressure applied on the brine side (or ΔP) is constant so that the water flux produced across the membrane decreases as the operation proceeds. It is the object of this investigation to obtain a solution of such a nonlinear problem.

FORMULATION OF PROBLEM

As a model of a batch-operated, constant pressure, reverse osmosis cell, consider a cylinder which is closed at one end by a semipermeable membrane and has a piston which applies a constant pressure at the other end. A schematic diagram for such a cell is shown in Figure 1.

For practical purposes one is interested in obtaining information which relates the performance of the cell, in terms of the pure water produced, and the operating variables. The water flux produced at any time is assumed to be given by

$$V_w = A(\Delta P - \pi) \tag{1}$$

If one assumes a linear relationship between the concentration and the osmotic pressure

$$\pi = \frac{c}{c_o}\pi_o \tag{2}$$

where π_o is the osmotic pressure for a solution with the concentration c_o and π is the corresponding osmotic pressure at c, then

$$V_w = A\left(\Delta P - \frac{c_w}{c_o}\pi_o\right) \tag{3}$$

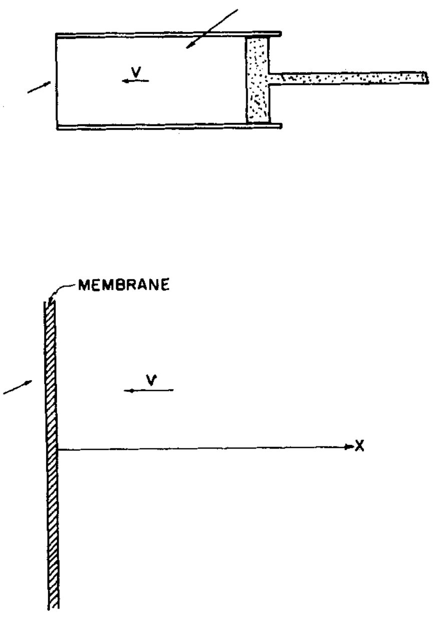

Fig. 1. Coordinate system and schematic diagram of a cell.

It is obvious that in order to obtain information on the production rate, the concentration of the brine solution at the membrane surface is needed. This can be obtained if the concentration distribution throughout the cell is known. The concentration distribution can be obtained as the solution of the proper diffusion equation which is given as

$$\frac{\partial c}{\partial t} - V_w\frac{\partial c}{\partial x} - D\frac{\partial^2 c}{\partial x^2} = 0 \tag{4}$$

if, to a good approximation, the physical properties of the brine are independent of the concentration, the diffusion is one-dimensional, and the effect of natural convection due to the density differences is negligible.

The initial condition is given as

$$c = c_o \text{ for all } x \geqq 0,\ t < 0 \tag{5}$$

The boundary condition at the membrane end can be obtained by assuming the membrane is impermeable to salt, so that

$$V_w c_w + D\left(\frac{\partial c}{\partial x}\right)_w = 0 \tag{6}$$

which yields the nonlinear boundary condition

$$A\Delta P\left[1 - \frac{\pi_o c(t,0)}{\Delta P\ c_o}\right]c(t,0) + D\left(\frac{\partial c(t,0)}{\partial x}\right) = 0 \tag{7}$$

The boundary condition at the piston end is even more complicated. First, the piston is not stationary; it moves at a velocity V_w. Furthermore, V_w is not constant but varies with time as shown in Equation (3). This moving boundary condition would inevitably introduce considerable complexity in finding the solution of this problem. On the other hand, if one assumes that the overall length of the cylinder is much greater than that of the region near the membrane where significant changes in concentration take place, one may treat the finite cell as being equivalent to a semi-infinite cylinder and therefore ignore the possible complication due to the movement of the piston. The justification of such an assumption is given later in the discussion section. Based on this assumption, the other necessary boundary condition becomes

$$c \rightarrow c_o \text{ as } x \rightarrow \infty \tag{8}$$

where c_o is the initial concentration of the brine.

Equation (4), together with the initial condition given by Equations (5) to (8), gives a complete description of the problem under consideration, and its solution would yield the concentration profile inside the cell for any given time.

It is convenient to express all quantities in dimensionless form and for this purpose, the following variables are introduced:

$$C = [c(x,t) - c_o]/c_o \tag{9}$$

$$\tau = V_o^2\ t/D \tag{10}$$

$$X = V_o x/D \tag{11}$$

$$V = 1 - \alpha C(0,\tau) \tag{12}$$

where

$$V_o = A(\Delta P - \pi_o) \tag{13}$$

$$\alpha = \pi_o/(\Delta P - \pi_o) \tag{14}$$

In terms of these dimensionless variables, one has

$$\frac{\partial C}{\partial \tau} = V\frac{\partial C}{\partial X} + \frac{\partial^2 C}{\partial X^2} \tag{15}$$

with the boundary conditions

$$C(X,0) = 0 \tag{16}$$

$$V\,[C(0,\tau) + 1] + \left(\frac{\partial C}{\partial X}\right)_{X=0} = 0 \tag{17}$$

Clearly, the system of Equations (15), (16), and (17) includes the problem Dresner considered as the special case of $\alpha = 0$, which is approached if $\Delta P >> \pi_o$.

MATHEMATICAL SOLUTION

The primary difficulty involved in the solution of Equation (15) is the presence of the nonlinear convection term as well as the nonlinear boundary condition given by Equation (17). In this investigation, it was found that this difficulty can be circumvented by using a similarity transformation which reduces Equation (15) to a system of ordinary differential equations, which can be solved numerically with the Runge-Kutta formulas. The series solution, however, was found to be valid only for relatively small time, when $B \neq 0$. Consequently, for practical purposes, approximate solutions based on integral methods were developed to extrapolate the results to relatively large values of time.

Solution by Series Expansion

A method which is frequently used for the solution of a partial differential equation involves the reduction of the partial differential equation to a system of ordinary differential equations by using suitable transformations. For the problem concerned here, one can employ the following transformations:

$$\beta = X/2\sqrt{\tau} \tag{18}$$

$$\sigma = 2\sqrt{\tau}/(1-B) \tag{19}$$

$$\omega = C + 1 = \frac{c}{c_o} \tag{20}$$

$$B = \alpha/(1+\alpha) = \frac{\pi_o}{\Delta P} \tag{21}$$

Equation (15) becomes

$$2\sigma\frac{\partial\omega}{\partial\sigma} = [2\beta + \sigma(1 - B\omega(\sigma, 0))]\frac{\partial\omega}{\partial\beta} + \frac{\partial^2\omega}{\partial\beta^2} \tag{22}$$

with boundary conditions

$$\omega(0, \beta) = 1, \ \omega(\sigma, \infty) = 1 \tag{23}$$

$$-\frac{\partial\omega(\sigma, 0)}{\partial\beta} = \sigma\omega(\sigma, 0) \quad [1 - B\omega(\sigma, 0)] \tag{24}$$

If

$$\omega = \sum_{i=0}^{\infty} \theta_i(\beta)\sigma^i \tag{25}$$

then, by substituting Equation (25) into Equation (22), the following equations are obtained:

$$\theta_o(\beta) = 1$$

$$\theta''_{i+1}(\beta) + 2\beta\theta'_{i+1}(\beta) - 2(i+1)\theta_{i+1}(\beta) = -\theta'_i(\beta) + B\sum_{j=0}^{i}\theta_j(0)\theta'_{i-j}(\beta),$$

$$i = 0, 1, 2 \ . \ . \ . \ . \ . \tag{26}$$

The boundary conditions become

$$\theta_{i+1}(\infty) = 0 \tag{27}$$

and

$$-\theta'_{i+1}(0) = \theta_i(0) - B\sum_{j=0}^{i}\theta_j(0)\theta_{i-j}(0)$$

$$i = 0, 1, 2 \ . \ . \ . \ . \ . \tag{28}$$

One of the difficulties in finding the solution of this problem is the nonlinearity due to the presence of the convective term in the diffusion equation. It is, therefore, of interest to study what effect, if any, there would be if the convective term is omitted. If the convective term is omitted, the diffusion equation reduces to

$$\frac{\partial C}{\partial\tau} = \frac{\partial^2 C}{\partial X^2} \tag{29}$$

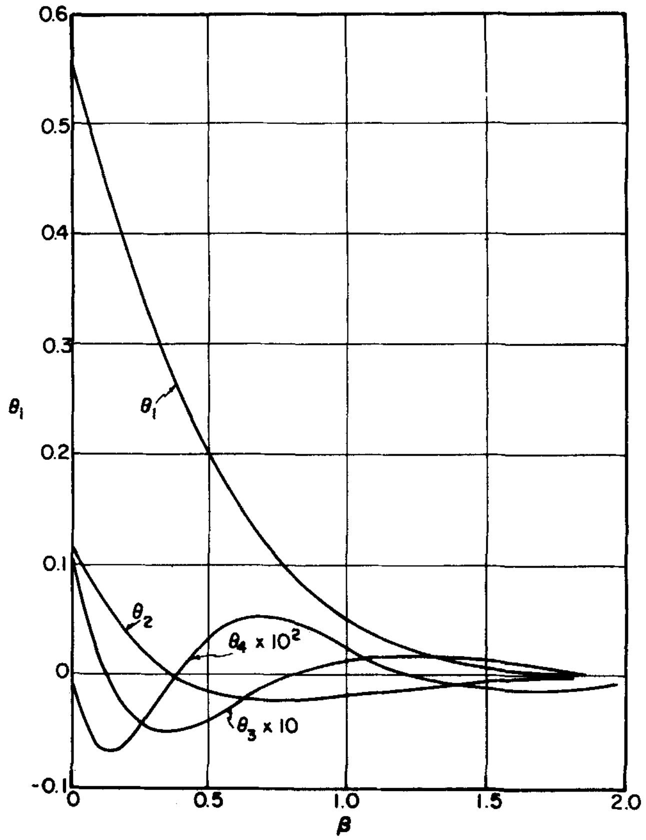

Fig. 2. θ_i (β) vs. β with convection included, P-1, for $B = 0.0$.

Using the same technique as before, we obtain a series of ordinary equations:

$$\theta_o(\beta) = 1$$

$$\theta_i''(\beta) + 2\beta\theta_i'(\beta) - 2i\theta_i(\beta) = 0, \quad i = 1, 2, \ . \ . \ . \ . \ . \ . \tag{30}$$

and the boundary conditions are the same as those in Equations (27) and (28).

The system of Equations (26), (27), and (28), as well as that related to Equation (30), was solved numerically with the Runge-Kutta method. The actual computation is processed in the following manner:

An assumed value is used for the initial condition $\theta_i(0)$. Together with the known condition of $\theta_i^1(0)$, Equation (26) can be solved to determine if Equation (27) is satisfied. In terms of actual calculation, this requires integrating to a value of β of about 2.5. Invariably, the first assumed value of $\theta_i(0)$ is inaccurate and a second guess for $\theta_i(0)$ is used to repeat the same procedure. From these two trial values, a more accurate estimate can be made by using the method of false position, and the process is

Table 1. Comparison of Excess Concentration at the Membrane $C(\tau, 0)$ Predicted by Various Methods for $B = 0.0$

σ	τ	D.R.	P.H. C	Y-1 C	Y-2 C	P-1 C
0.7071	0.1250	0.4656	0.5000	0.4332	0.4637	0.4656
1.225	0.3750	0.8999	1.000	0.7832	0.9226	0.8997
1.643	0.6750	1.316	1.500	1.063	1.385	1.315
2.000	1.000	1.720	2.000	1.283	1.851	1.719
2.315	1.339	2.116	2.500	1.454	2.320	2.115
2.598	1.687	2.507	3.000	1.586	2.790	2.506
2.858	2.042	2.895	3.500	1.686	3.261	2.892
3.098	2.400	3.278	4.000	1.761	3.733	3.276
3.323	2.761	3.660	4.500	1.816	4.205	3.657
3.535	3.125	4.040	5.000	1.856	4.678	4.036

TABLE 2. COMPARISON OF EXCESS CONCENTRATION AT THE MEMBRANE $C(\tau, 0)$ PREDICTED BY VARIOUS METHODS FOR $B = 0.25$

τ	σ	P.H.	Y-1	Y-2	P-1
0.0618	0.6628	0.3000	0.2793	0.2828	0.2870
0.2433	1.315	0.6000	0.5570	0.5642	0.5681
0.5730	2.019	0.9000	0.8449	0.8487	
1.133	2.838	1.200	1.143	1.1364	
2.108	3.872	1.500	1.448	1.427	
3.953	5.302	1.800	1.757	1.719	
7.999	7.542	2.100	2.067	2.012	
19.65	11.82	2.400	2.378	2.307	
82.84	24.27	2.700	2.689	2.603	

continued until the accuracy desired is achieved.

Theoretically, one can compute as many terms of θ_i as desired. However, the accumulated error, due to the dependence of higher order functions on those preceding them, makes this impractical. In the present work, numerical values of θ_i for i up to 7, corresponding to various values of B, were obtained and some of these results are also presented graphically in Figures 2, 3, and 4.

The numerical values of θ_i were found to decrease as i increased. It is found that the ratio of the values of θ_7 to that of θ_1 is of the order of 10^{-4} to 10^{-6}, depending upon the values of β and B. It therefore appears that in order to obtain numerical results with four significant figures, the series expression given by Equation (25) can only be used for $\sigma \lesssim 2$ in the case of $B = 0$ and for $\sigma \lesssim 1$ in other cases. From the definition of σ given by Equation (19), this implies that for relatively small values of B, the series solution can be applied for most practical situations. However, as the value of B approaches unity, it can be used only for relatively small values of time. This appears to be the most important limitation of the series expansion approach.

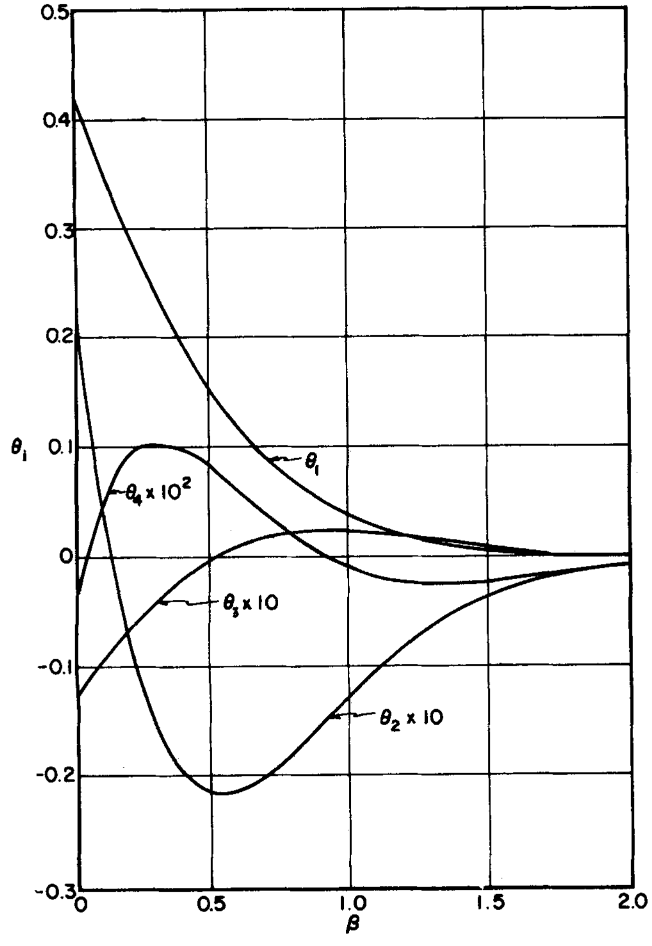

Fig. 3. $\theta_i\ (\beta)$ vs. β with convection included, P-1, for $B = 0.25$.

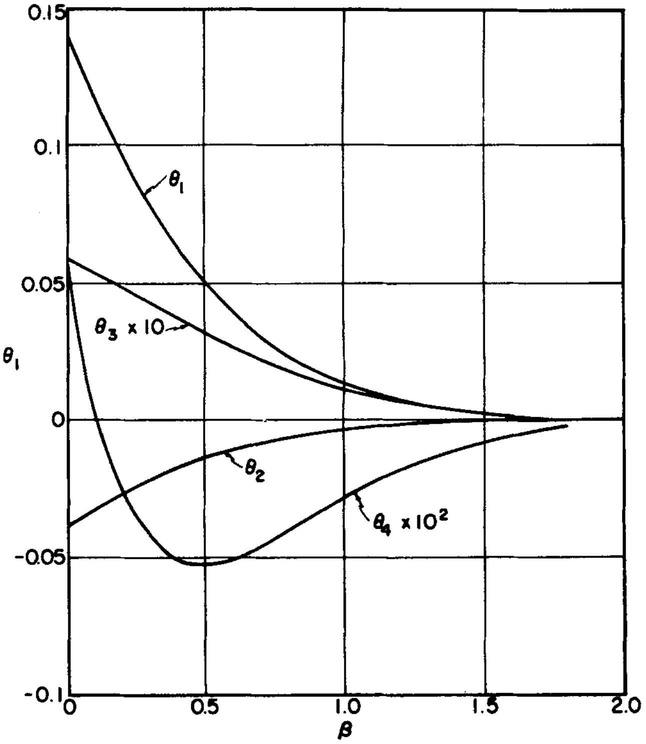

Fig. 4. $\theta_i\ (\beta)$ vs. β with convection included, P-1, for $B = 0.75$.

Approximate Solutions by Integral Methods

In order to provide information for cases when the series solution given by Equation (25) is no longer valid, the integral method of Pohlhausen (7) was used for the solution of Equation (15) by assuming the existence of a concentration boundary layer of thickness δ, which is taken to be a function of τ. Integrating Equation (15) with respect to X, from zero to δ, and using Equation (17), one gets

$$\frac{d}{d\tau}\int_0^\delta C\,dX = 1 - \alpha C(0, \tau) \qquad (31)$$

For the boundary-layer region, one can choose the following cubic equation for the concentration distribution:

$$C = C_w(a_0 + a_1\eta + a_2\eta^2 + a_3\eta^3), \quad 0 \leq \eta \leq 1 \qquad (32)$$

$$C = 0, \qquad 1 \leq \eta$$

and

$$\eta = X/\delta \qquad (33)$$

The coefficients a_0, a_1, a_2, and a_3 can be determined from the compatability conditions which require that $C = C_w$

TABLE 3. COMPARISON OF EXCESS CONCENTRATION AT THE MEMBRANE $C(\tau, 0)$ PREDICTED BY VARIOUS METHODS FOR $B = 0.50$

τ	σ	P.H.	Y-1	Y-2
0.0081	0.3605	0.1000	0.09585	0.09573
0.0362	0.7611	0.2000	0.1924	0.1915
0.0938	1.225	0.3000	0.2905	0.2880
0.2003	1.790	0.4000	0.3902	0.3856
0.3970	2.520	0.5000	0.4913	0.4844
0.7841	3.542	0.6000	0.5932	0.5844
1.656	5.147	0.7000	0.6954	0.6856
4.211	8.208	0.8000	0.7975	0.7880
18.20	17.06	0.9000	0.8991	0.8916

at $\eta = 0$ and C, $\partial C/\partial X$, and $\partial^2 C/\partial X^2$ vanish at $X = \delta$. These coefficients were found to be

$$a_0 = 1,\ a_1 = -3,\ a_2 = 3,\ a_3 = -1 \tag{34}$$

The concentration profile becomes

$$C = C_w(1-\eta)^3 = C_w(\delta - X)^3/\delta^3 \tag{35}$$

and from Equations (17) and (35), one has

$$\delta = \frac{3C_w}{(1-\alpha C_w)(C_w+1)} \tag{36}$$

If one combines Equations (31), (35), and (36), the following ordinary differential equation is obtained:

$$\frac{dC_w}{d\tau} = \frac{4(1-\alpha C_w)^3(C_w+1)^2}{3C_w\,[(1-\alpha)\,C_w+2]} \tag{37}$$

By rearranging Equation (37) and integrating, one has

$$\tau = \int_o^{C_w} \frac{3C_w[(1-\alpha)\,C_w+2]}{4(1-\alpha C_w)^3(C_w+1)^2}\,dC_w \tag{38}$$

The numerical values of the integral were obtained by using Simpson's rule with the increment of C_w taken as 10^{-2}. Values of C_w up to 90% of its asymptotic value, which is $1/B - 1$, were determined as a function of τ. Numerical results obtained according to Pohlhausen's method are given in Tables 1 to 4.

The weakest link in the Pohlhausen method is the arbitrary choice of profiles, such as that in Equation (32), which may not correspond well with that of the exact solution. In a more recent study, Yang (*11*) made the very reasonable suggestion that the accuracy of the integral solution would be improved if the solution obtained from Pohlhausen's method is considered to be a first approximation which is resubstituted into the original partial differential equation. One can apply Yang's method to the present problem to yield an equation which can be treated as a simple ordinary differential equation which may be readily solved. The solution so obtained is expected to agree much more closely with the exact solution.

One can write Equation (15) as

$$\frac{\partial^2 C}{\partial \eta^2} + P\frac{\partial C}{\partial \eta} = Q \tag{39}$$

TABLE 4. COMPARISON OF EXCESS CONCENTRATION AT THE MEMBRANE $C(\tau,0)$ PREDICTED BY VARIOUS METHODS FOR B = 0.75

τ	σ	*P.H.*	*Y*-1	*Y*-2	*P*-1
0.0010	0.2534	0.03400	0.03294	0.03281	0.03234
0.0048	0.5515	0.06800	0.06641	0.06598	0.06694
0.0130	0.9135	0.1020	0.1004	0.09960	0.10086
0.0294	1.372	0.1360	0.1347	0.1337	0.1342
0.0615	1.984	0.1700	0.1693	0.1684	
0.1286	2.869	0.2040	0.2039	0.2038	
0.2903	4.3102	0.2380	0.2385	0.2399	
0.8138	7.217	0.2720	0.2728	0.2767	
4.508	16.99	0.3060	0.3067	0.3145	

where

$$P = (V + \delta'\eta)\delta \tag{40}$$

$$Q = \delta^2(1-\eta)^3\frac{\partial C}{\partial \tau} \tag{41}$$

and the prime denotes differentiation with respect to τ.

The essential feature of this approach is that the functions P and Q are considered to be known on the basis of the results in Equations (32), (36) and (38), and are given by

$$P = r_1 + 2\,r_2\,\eta \tag{42}$$

$$Q = \frac{12C_w(1-\alpha C_w)}{(1-\alpha)C_w+2}\,(1-\eta)^3 \tag{43}$$

with

$$r_1 = \frac{3C_w}{C_w+1} \tag{44}$$

$$r_2 = \frac{6(1+\alpha C_w^2)}{(C_w+1)\,[(1-\alpha)C_w+2]} \tag{45}$$

Consequently one gets

$$C = \int_1^{\eta}\left[\exp -(r_1\xi + r_2\xi^2)\left\{\int_o^{\xi} Q\exp\,(r_1\sigma + r_2\sigma^2)\,d\sigma + K\right\}\right]d\xi \tag{46}$$

where $K = \partial C(0)/\partial\eta$ is found to be

$$K = \frac{1}{2\alpha g}\left[\left(\frac{1}{\delta g} + 1 - \alpha - 2\alpha f\right) + \sqrt{\left(\frac{1}{\delta g} + 1 - \alpha - 2\alpha f\right)^2 + 4\alpha(1+f)(1-\alpha f)}\,\right] \tag{47}$$

with

$$f = \int_1^{o} \exp\,[-(r_1\xi + r_2\xi^2)]\left\{\int_o^{\xi} Q\exp\,(r_1\sigma + r_2\sigma^2)\,d\sigma\right\}d\xi \tag{48}$$

$$g = \int_1^{o} \exp\,[-(r_1\xi + r_2\xi^2)]\,d\xi \tag{49}$$

and it is understood that C_w in Q, r_1 and r_2 is given by Equation (38). In the special case $\alpha = 0$

$$K = -\left[\frac{\delta\,(1+f)}{1+\delta g}\right] = -\delta\,(1 + C_w) \tag{50}$$

It is interesting to note that if Equation (36) is used to evaluate K, one gets the very simple result

$$K = -3C_w \tag{51}$$

One puzzling feature of Yang's approach is that Equations (47) and (51) yield values of K which agree quite well if $B > 0.25$ but the agreement breaks down rapidly well if $B \gtrsim 0.25$ but the agreement breaks down rapidly as $B \rightarrow 0$ unless τ is very small. This is particularly surprising, since, in contrast to what one would expect, Equation (46) appears to be substantially more accurate when it is used in conjunction with Equation (51). This will be discussed in more detail in later sections.

RESULTS AND DISCUSSION

A wide range of numerical results was obtained for B = 0, 0.25, 0.5, and 0.75 for the various methods described previously. In the following discussion of the Pohlhausen method, Equation (37) is abbreviated as *P.H.* The solutions obtained by Yang's approach, using Equations (47) and (51) are designated, respectively, *Y*-1 and *Y*-2, and the series solutions given by Equations (26) and (30) will be identified as *P*-1 and *P*-2, respectively.

Comparison of Results

Since the results obtained by the various methods used have certain shortcomings, it is necessary to provide some guidelines on how to choose from these various expressions for design purposes. Although there is no exact solution to the general problem considered here, an exact solution is available for the special case of $B = 0$. For $B = 0$, the problem becomes linear and the solution of Equation (15) was found to be (2):

$$C = e^{-X}(\tau + 1 - X) - (1 + \tau/2)\ \mathrm{erfc}\ (\sqrt{\tau}/2) + \sqrt{\tau/\pi}\ e^{-\tau/4} \qquad (52)$$

where

$$\mathrm{erfc}(X) = \frac{2}{\sqrt{\pi}} \int_X^{\infty} e^{-u^2}\, du \qquad (53)$$

Numerical results, obtained by the various methods, for wall concentration with $B = 0$ are compared with those of Equation (52) in Table 1. It can be seen that there is excellent agreement between the exact solution and series solution; the maximum error is not more than 0.1%, which, for practical purposes, is essentially negligible. The results obtained by using integral methods are much less satisfactory and as τ increases, the differences become more pronounced. Among the three integral methods, the solution designated Y-2 appears to be the best with a maximum relative error of 15% when the wall concentration becomes six times that in the bulk of the system. On the other hand, Y-1 is seriously in error, but the reason for this is not obvious.

Comparisons were made also for cases of $B = 0.25$, 0.5, and 0.75, and Tables 2 to 4 give the values of excess wall concentration obtained for three integral methods. Note that in each case the largest value of the excess concentration tabulated corresponds to approximately 90% of the maximum possible concentration that can exist at the membrane surface for the given value of B under consideration. It is clear that in these cases all three integral solutions agree quite well with each other and with the series solution in the region in which it is valid. It seems safe to conclude that the results obtained by using the integral methods are accurate enough for practical purposes if $B > 0$.

Discussion

Effect of Neglecting the Convective Term. It seems interesting from a physical viewpoint to determine the importance of convection in this nonlinear diffusion problem. Thus similar solutions with the omission of the convective term were obtained for $B = 0.25$ and 0.75. Comparisons of the excess wall concentration obtained by neglecting, P-2, or retaining, P-1, the convective terms were made. The agreement between these two methods for $B = 0.75$ is reasonably good but with $B = 0.25$, a substantial difference is observed and it grows with increasing time. For example, at $\sigma = 0.10$, C is 0.04255 and 0.04327 by P-1 and P-2, respectively, whereas at $\sigma = 1.0$ the values of C are 0.4337 and 0.5097. Thus in this case the relative error incurred by neglecting the convective term increases by an order of magnitude as σ increases from 0.10 to 1.0. It is expected that the differences should diminish as B approaches unity, because of the magnitude of the velocity diminishes and thus the convective term is less important. Also, the convective term increases in importance as τ increases. This occurs primarily because the molecular diffusion length is proportional to the square root of time, whereas the convective length is directly proportional to time. Since the boundary conditions remain nonlinear in the region where one can neglect the convective term without incurring serious errors, this does not represent an important computational simplification.

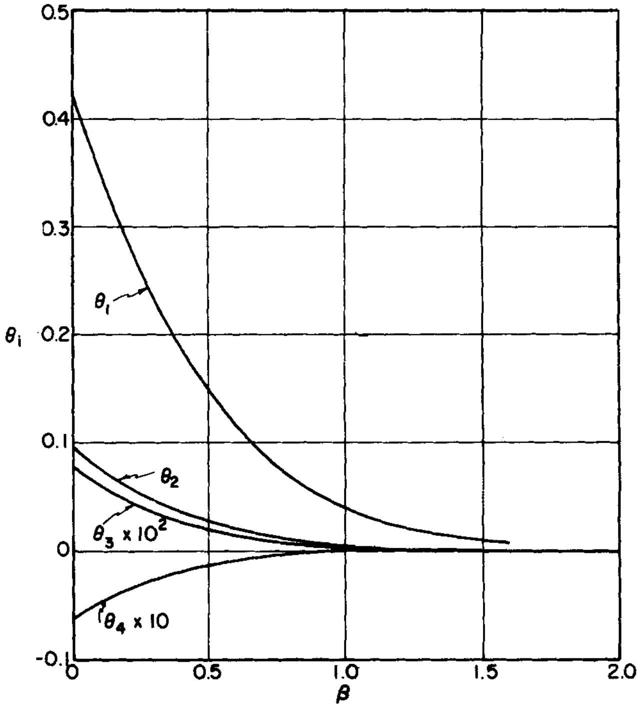

Fig. 5. θ_i (β) vs. β for case where convection is neglected, P-2, for $B = 0.25$.

The Validity of Approximating the Cell System as a Semi-Infinite Body. In applying the results of the present investigation, one should remember that two possible sources of error exist. The use of the approximate method for the solution of the diffusion equation causes one type of error. In addition, the approximation of a finite cell by a semi-infinite body obviously may result in another kind of error. The conditions under which this latter approximation is justified deserve some consideration.

From a physical point of view, the significant part of the concentration change takes place in a region close to the membrane. The thickness of this region δ is the dimensionless concentration boundary-layer thickness and the concentration of salt outside of this layer is essentially constant. Consequently, it doesn't make any difference from a practical point of view whether this part of the system is finite or not. Therefore, the approximation of a finite cell by a semi-infinite body will not introduce serious error as long as

$$\frac{x_c V_o}{D} >> \delta \qquad (54)$$

where x_c is the minimum distance between the piston and membrane.

The concentration boundary-layer thickness δ increases with time. For example, at $B = 0.25$, δ, based on the *P.H.* solution, equals 1.406, 2.727, 6.774, and 21.89 at σ equal to 1.315, 2.838, 7.542, and 24.27. At $\sigma = 24.27$, the excess concentration corresponds to 90% of its maximum possible value. Clearly, the distribution of δ with time for other values of B can be determined from Equation (36) in conjunction with Tables 1 to 4.

As a specific example of the actual size of a cell necessary for the semi-infinite body assumption to apply, assume that the salt concentration is about 4% by weight and the corresponding osmotic pressure and effective salt diffusion coefficient are approximately

$$\pi_o = 380 \text{ lb./sq.in.} = 26.8 \text{ kg./sq.cm.}$$

$$D = 1.61 \times 10^{-5} \text{ sq.cm./sec.}$$

Since it is known that a typical desalination membrane at the present time provides a water flux of approximately 10 to 20 gal./(day)(sq.ft.) when it is employed with seawater at $\Delta P = 100$ kg./sq.cm., take $V_o = 10$ gal./(day)(sq.ft.) $\simeq 4.68 \times 10^{-4}$ cm./sec., and it follows from Equation (13) that

$$A = \frac{4.68 \times 10^{-4}\ \text{cm./sec.}}{(100 - 26.8)\ \text{kg./sq.cm.}}$$

$$= 6.42 \times 10^{-6}\ \text{cc./(kg.) (sec.)}$$

Clearly $V_o = A\ \pi_{o/\alpha}$ and with Equation (54) one gets

$$x_c >> \frac{D}{A\pi_o}\alpha\delta = \frac{1.61 \times 10^{-5}}{(6.42 \times 10^{-6})(26.8)}\alpha\delta$$

$$= 9.36 \times 10^{-2}\alpha\delta\ [\text{cm.}]$$

When $\alpha = 1.0$, the maximum value of δ is 14.21; this gives a value of 1.33 for $\frac{D}{A\pi_o}\alpha\delta$. When $\alpha = 3.0$, the maximum value of δ is 8.57, and the value for $\frac{D}{A\pi_o}\alpha\delta$ becomes 3.27. Therefore the length of a test cell must be longer than 1.33 cm. when $\alpha = 1$ and longer than 3.27 cm. when $\alpha = 3$. Clearly these conditions can easily be met in practical operations.

The preceding example indicates that the infinite body assumption is quite adequate for fairly small cells when liquid phase systems are involved. In gas phase separations one would expect that the minimum dimensions required would be twenty-five to fifty times those given above.

CONCLUSIONS

1. The results of a series expansion and three solutions obtained by integral methods were compared. It was shown that the series expansion is in excellent agreement with the exact solution that can be determined for the special linear case of $B = 0$ even for rather large values of time. When $B \neq 0$, the series expansion converges well only for fairly small values of τ.
2. The integral methods may involve unacceptably large errors which cannot be predicted beforehand. It is somewhat surprising that this is dramatically demonstrated by the results for the linear case of $B = 0$ which is analogous to the case of first-order heterogeneous reaction in a flow system. Thus since large unpredictable errors were obtained in one case, integral methods should be applied with caution in general. By comparison with the series solution in the region of small τ where it converges well, and also by noting that they agree well with each other, it is concluded that the integral methods provide reasonably accurate means of extrapolating the solution to large values of τ for $B \neq 0$.
3. The relative importance of convection in the system studied decreases if the initial salt concentration of the solution increases or if the pressure drop across the membrane is decreased. Furthermore, in any particular test the relative importance of convective to diffusive effects increases with time.
4. If one assumes for mathematical purposes that the system is semi-infinite, this reduces enormously the difficulties involved in solving the problem. This assumption is reasonable for many practical purposes.
5. The numerical results of this study, together with measurements of the water throughput versus time, are sufficiently comprehensive to determine the membrane constant in a constant pressure test cell.

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NOTATION

A = membrane constant
B = $\alpha/(1 + \alpha)$
c = concentration
c_o = initial concentration
C = $(c - c_o)/c_o$ = dimensionless concentration (or excess concentration)
C_w = concentration at the membrane (or wall concentration)
D = diffusivity
$D.R.$ = Dresner's solution for $B = 0$
f, g = constants as defined by Equations (48)and (49), respectively
K = constants as defined by either Equation (50) or (51), respectively
$P.H.$ = Pohlhausen method
ΔP = pressure drop across the membrane
P-1 = series solution, Equation (25), of Equation (15)
P-2 = series solution of Equation (29)
$R.E.$ = relative percentage error
r_1, r_2 = constants as defined by Equations (44) or (45), respectively
t = time
V_o = $A(\Delta P - \pi_o)$ = interfacial velocity at the initial concentration
V_w = interfacial velocity (or permeation velocity)
V = dimensionless interfacial velocity
x = distance from the membrane
X = $V_o x/D$ = dimensionless distance
X_c = minimum distance between the piston and membrane
Y-1 = Yang's method employing Equations (46) and (47)
Y-2 = Yang's method employing Equations (46) and (51)

Greek Letters

α = $\pi_o/(\Delta P - \pi_o)$
β = $X/2\sqrt{\tau}$
δ = boundary-layer thickness
σ = $2\sqrt{\tau}/(1 - B)$
π = osmotic pressure
π_o = osmotic pressure at the initial concentration
τ = $V_o^2 t/D$ = dimensionless time
θ_i = solution of Equation (26)
η = X/δ
ω = $C + 1 = \sum_{i=0}^{\infty} \theta_i(\beta)\sigma^i$

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