Stagewise Problems Solved by Haldane's Method

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The calculus of finite differences has frequently been employed to solve the equations that arise in the stagewise processes of chemical engineering (*1* to *4*). Some equations that cannot be solved by any of the usual methods yield a series solution to a procedure devised by Haldane (*5*). For a derivation of this method the reader is referred to Haldane and to Milne-Thomson (*6*).

If the finite difference equations can be expressed in the form

$$x_{n-1} - x_n = k\phi(x_n) \tag{1}$$

then

$$N = \frac{1}{k}\int_{x_N}^{x_o} w(x, k)\, dx \tag{2}$$

in which

$$w(x, k) = \sum_{r=1}^{\infty} \frac{k^{r-1}}{r!} f_r(x) \tag{3}$$

The values of $f_r(x)$ are obtained from

$$f_1(x) = \frac{1}{\phi} \tag{4}$$

and

$$\sum_{r=1}^{s-1} \binom{s}{r} [\phi(x)]^{s-r-1} \left(\frac{d}{dx}\right)^{s-r-1} f_r(x) = 0 \tag{5}$$

From the recurrence relation one obtains

$$f_2(x) = \frac{\phi'}{\phi}$$

$$f_3(x) = -1/2\left[\frac{(\phi')^2}{\phi} + \phi''\right]$$

$$f_4(x) = \frac{(\phi')^3}{\phi} + 2\phi'\phi''$$

$$f_5(x) = \frac{1}{6}\Big[-19\frac{(\phi')^4}{\phi} - 59(\phi')^2\phi'' - \phi(\phi'')^2 + 2\phi\phi'\phi''' + \phi^2\phi^{iv}\Big]$$

A problem solved conveniently by this method is that of repeated extraction of a constant raffinate volume with equal amounts of pure solvent. The material balance for this problem is

$$x_{n-1} - x_n = \frac{E}{R} y_n \tag{6}$$

If $y_n = ax_n$ at equilibrium, the resulting equation is

$$x_{n-1} - x_n = \frac{Ea}{R} x_n \tag{6a}$$

and can be solved by other methods to obtain

$$N = \frac{\ln(x_o/x_N)}{\ln(Ea/R + 1)} \tag{7}$$

If y_n/x_n is a function of x_n, Haldane's method will yield a solution, providing the resulting series converges.

This problem was considered by Knudsen (*7*) with respect to the following equilibrium relations

1. $\dfrac{y}{x} = ax^b$

2. $\dfrac{y}{x} = d + ex$

for the first relation

$$y_n = ax_n^{b+1} \tag{8}$$

and from Equation (6)

$$x_{n-1} - x_n = \frac{Ea}{R} x_n^{b+1} \tag{9}$$

so that in Equation (1)

$$k = \frac{Ea}{R} \text{ and } \phi = x_n^{b+1}$$

Haldane solved this difference equation in his original paper, though not with chemical engineering applications in mind. The use of the first four terms of $w(x,k)$ in Equations (2) and (3) gives

$$N = \frac{1}{kb}\left[\frac{1}{x_N^b} - \frac{1}{x_o^b}\right] + [(1/2)(b+1)]\ln(x_o/x_N) - \frac{k}{12b}(b+1)(2b+1)(x_o^b - x_N^b) + \frac{k^2}{48b}(b+1)^2(3b+1)(x_o^{2b} - x_N^{2b}) + \ldots \tag{10}$$

Knudsen solved this problem numerically for the special case of $b = 1$, but Equation (10) is valid for any value of b as long as the series converges. Knudsen obtained 12.2 stages numerically for the following problem.

A solution at 20°C. containing 3.5 lb. of benzoic acid in 1,000 lb. of water is contacted with successive 200-lb. portions of benzene until 90% of the benzoic acid is removed. The equilibrium is expressed by $y = 1{,}268\ x^2$. Therefore, $R = 1{,}000$ lb.; $E = 200$ lb.; $a = 1{,}268$ and $b = 1$ from which $k = 253.6$; $x_o = 0.0035$; and $x_N = 0.00035$. The substitution of these values in Equation (10) gives the results shown in Table 1.

Table 1. The Stages Calculated by the Use of Successive Terms in Equation (10)

Term	Stages
1	10.14
2	12.44
3	12.04
4	12.24

The second equilibrium relation considered by Knudsen gives the following difference equation:

$$x_{n-1} - x_n = \frac{E}{R} x_n (d + ex_n) \tag{11}$$

The first five terms in the series solution of this equation are given below with $k = E/R$.

$$\begin{aligned} N = {} & \frac{1}{kd}\left[\ln(x_o/x_N) - \ln\frac{(d+ex_o)}{(d+ex_N)}\right] + 1/2\left[\ln(x_o/x_N) + \ln\frac{(d+ex_o)}{(d+ex_N)}\right] \\ & - \frac{k}{12}\Big[d\ln(x_o/x_N) - d\ln\frac{(d+ex_o)}{(d+ex_N)} + 6e(x_o - x_N)\Big] \\ & + \frac{k^2}{24}\Big[d^2\ln(x_o/x_N) - d^2\ln\frac{(d+ex_o)}{(d+ex_N)} + 10ed(x_o - x_N) + 8e^2(x_o^2 - x_N^2)\Big] \\ & - \frac{k^3}{720}\Big[19d^3\ln(x_o/x_N) - 19d^3\ln\frac{(d+ex_o)}{(d+ex_N)} + 270d^2e(x_o - x_N) + 409\,de^2(x_o^2 - x_N^2) + 260\,e^3(x_o^3 - x_N^3)\Big] \end{aligned} \tag{12}$$

Solving Equation (6a) by Haldane's method

$$N = \ln(x_o/x_N)\left[\frac{1}{ka} + \frac{1}{2} - \frac{ka}{12} + \frac{(ka)^2}{24} - \frac{19}{720}(ka)^3 + \ldots\right] \tag{13}$$

Comparison of Equations (7) and (13) shows that the series in brackets *is* equal to $1/\ln(ka+1)$. Combining the logarithmic terms so that the coefficients are equal to those in Equation

(13) and combining powers of x, Equation (12) becomes

$$N = \left[\frac{1}{\ln(kd+1)}\right] \ln\left[\frac{x_o(d+ex_N)}{x_N(d+ex_o)}\right] + \ln\frac{(d+ex_o)}{(d+ex_N)} - \left[\frac{ke}{2} - \frac{5}{12}k^2de + \frac{3}{8}k^3d^2e + \ldots\right](x_o - x_N) + \left[\frac{k^2e^2}{3} - \frac{409}{720}k^3de^2 + \ldots\right](x_o^2 - x_N^2) - \left[\frac{13}{36}k^3e^3 + \ldots\right](x_o^3 - x_N^3) + \ldots \quad (14)$$

This equation may be simplified by a change of variables used by Knudsen. Setting $K = Ed/R$ and $Z_n = Eex_n/R$, Equation (11) becomes

$$Z_{n-1} - Z_n = Z_n\,(K + Z_n) \quad (15)$$

Comparison of Equations (11) and (15), shows that the solution of the latter may be obtained from Equation (14) by replacing k and e by 1, d by K, and x by Z to obtain

$$N = \left[\frac{1}{\ln(K+1)}\right] \ln\left[\frac{Z_o}{Z_N}\frac{(K+Z_N)}{(K+Z_o)}\right] + \ln\frac{K+Z_o}{K+Z_N} - \left[\frac{1}{2} - \frac{5}{12}K + \frac{3}{8}K^2 + \ldots\right] \quad (16)$$

$$(Z_o - Z_N) + \left[\frac{1}{3} - \frac{409}{720}K + \ldots\right](Z_o^2 - Z_N^2) - \left[\frac{13}{36} + \ldots\right](Z_o^3 - Z_N^3) \quad (16)$$

Table 2 shows some results obtained with Equation (16). The values of N were obtained numerically by Knudsen.

Utilization of this procedure may seem uncertain in view of our inability to determine analytically the limits of convergence; also the complexity of higher terms makes the results unwieldly if their inclusion is required. The area of convergence relative to concentration and other variables may be determined by trial on the computer, or the probability of convergence can be qualitatively evaluated by noting that Equation (10) is predominately a power series in $(kbx_o)^b$, except for the logarithmic terms; and similarly, Equation (16) is a power series in K and Z_o. Therefore, small values of $(kbx_o)^b$, Z_o, and K will increase the accuracy of the method.

In view of these apparent limitations, it is very interesting to note that every example given above is represented to within about 0.2 stage by the two logarithmic terms in the series, including even the sixth example, which obviously diverges. In general, the problems worked here indicate that as long as $(kbx_o)^b$ or Z_o and K are less than 1, two terms are sufficient.

OTHER APPLICATIONS

A material balance on a countercurrent extractor with constant E and R leads to the following equation.

$$x_{n-1} = (E/R)\,y_n + [x_o - (E/R)\,y_1] \quad (17)$$

Denoting the term in brackets by C, and using the equilibrium relation

$$y_n = dx_n + eK_n^2$$

this becomes on rearrangement

$$x_{n-1} - x_n = (Ed/R - 1)\,x_n + (Ec/R)\,x_n^2 + C \quad (18)$$

Substituting K for $(Ed/R) - 1$ and Z for Eex/R gives

$$Z_{n-1} - Z_n = KZ_n + Z_n^2 + C \quad (19)$$

This differs from Equation (15) only by a constant and may be solved similarly.

It is not necessary to assume constant E and R to employ Haldane's method. For instance, if in Equation (18) it is assumed that E/R varies linearly with x, a cubic equation is obtained for ϕ to which Equations (2), (3), (4), and (5) may still be employed. Needless to say, the results obtained for countercurrent extraction may be applied to absorption and stripping problems.

For a binary distillation, material balances yield

$$Vy_n = Lx_{n-1} + Dx_D \quad (20)$$

above the feed, and

$$Vy_n = Lx_{n-1} - Bx_B \quad (21)$$

below the feed. Rearranging the first equation gives

$$x_{n-1} - x_n = y_n - x_n - (D/L)\,(x_D - y_n) \quad (22)$$

Denoting the right-hand side by ϕ and employing only the first term of Haldane's solution gives

$$N = \int_{x_f}^{x_D} \frac{dx}{\phi(x)} \quad (23)$$

This is identical to the method of Lewis (*8*). Therefore, additional terms may be used to correct Lewis' method; for instance, the second term is very simple and its inclusion yields

$$N = \int_{x_f}^{x_D} \frac{dx}{\phi(x)} + \frac{1}{2}\ln\frac{\phi(x_D)}{\phi(x_f)} \quad (24)$$

A similar equation may be obtained for the stages below the feed.

CONCLUSION

A method for obtaining series solutions for a wide variety of stagewise processes is presented. While it is impossible to determine exactly the convergence of the series, it is shown that even for series that are probably divergent, the use of the first two terms gives accurate results.

NOTATION

$a,b,d,e,$ = constants in equilibrium relations
B = bottom product flow rate
D = distillate flow rate
E = extract solution flow rate
f = functions defined by Equations (4) and (5)
k = constant in Equation (1)
K = Ed/R, or in Equation (19), $(Ed/R) - 1$
L = liquid flow rate
N = number of stages
R = raffinate solution flow rate
V = vapor flow rate
x = concentration in raffinate or liquid
y = concentration in extract or vapor
Z = $E\,ex/R$
ϕ = a single valued function of x

Subscripts

B = bottom product
D = distillate
f = feed

TABLE 2. THE STAGES CALCULATED BY THE USE OF SUCCESSIVE TERMS IN EQUATION (16)

				Terms in Equation (16)				
Z_o	Z_N	K	N	1	2	3	4	5
0.100	0.0147	0.2	9	8.68	9.01	8.97	8.98	8.98
0.912	0.1000	0.2	6	4.90	6.22	5.87	6.05	5.77
0.342	0.0401	0.2	8	7.29	8.10	7.96	7.98	7.97
0.765	0.0737	0.6	4	3.48	4.18	3.92	3.91	3.74
0.496	0.0111	0.8	6	5.64	6.11	5.91	5.88	5.82
1.138	0.0111	0.8	7	6.40	6.93	6.47	6.31	5.11
0.519	0.260	−0.2	6	4.39	6.06	5.91	6.00	5.95
1.015	0.260	−0.2	8	5.59	8.20	7.75	8.18	7.80

n = stage number
N = last stage
o = stream entering the system

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A Neglected Effect in Entrance Flow Analyses

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Flow in the entrance of a tube or channel has been the subject of numerous publications over the past one hundred years. The boundary value problem involved is the development of the well-known parabolic velocity distribution in a tube or between parallel plates, starting from a flat velocity profile. It has been suggested that this corresponds to what happens when a fluid having a very low turbulence intensity enters a tube or channel through a well-rounded converging duct, although as has been recently demonstrated by Wang and Longwell (*1*), the flat velocity profile boundary condition is definitely not a good model for the flow in which parallel plates are submerged in a fluid in uniform motion.

The hydrodynamic entry region was initially of interest in connection with viscosity measurement and has more recently been involved in attempts to establish a theory for the origin of turbulence in pipes and channels. In the meanwhile, it has provided an interesting diversion for a number of applied mathematicians. The author has been able to discover no less than twenty-five papers involving forty-three authors which deal with the theoretical analysis of laminar flow in the entrance to a channel or pipe with initially flat velocity profile. Except for the recent numerical solution of Wang and Longwell (*1*), all of these contributions have neglected a phenomenon which is of particular importance in applications of the results to stability analysis. Furthermore, this phenomenon, which may be referred to as the *persistence of parallel flows*, is of great importance in certain types of jet flows.

The model which has commonly been employed in the entry region problem for the flow close to the entrance is based on the simplified equation obtained by making boundary layer type assumptions in the equations of motion. Furthermore it is assumed that the velocity field may be represented as consisting of a core of uniform but accelerating fluid and a boundary layer at the wall. It is the author's opinion that such a model involving the hypothesis of an accelerating core cannot yield reliable information as to the details of the flow near the entrance. The argument is as follows.

Let us consider a flow of incompressible fluid in a tube or channel with the following boundary conditions:

$u = U$ at $x = 0$ (velocity initially uniform)

$u = 0$ at $r = R$ (no slip at the wall)

It may be argued from consideration of the contunity condition that a region of parallel, incompressible flow, such as we have at $x = 0$, can be altered only around its periphery. In other words, for a streamline to be deflected, fluid must flow with a velocity component normal to the direction of the parallel flow, and this can only occur where the flow is not parallel. This is the reason that there exists in a jet flow the so-called *potential core* in which the velocity is uniform. The mechanism by which the influence of the momentum gradient is transmitted into the core involves viscous shear. It must occur, then, at a finite rate depending on the viscosity of the fluid, its velocity, and the geometry of the confining walls. From an application of the Bernoulli equation to the flow in such a core, we conclude that the pressure gradient on the axis is zero up to a point at some finite value of x where the core of parallel flow is finally dissipated completely by shear at its periphery. This means that any pressure gradient measured at the wall of the entry region for small x is due entirely to radial pressure variations outside the core.

It can now be demonstrated that the existence of such a potential core in the entrance section precludes the applicability of the boundary layer model in this problem. First, the large pressure drops that have been measured at the wall in such flows (*2*) indicate the existence of a large radial pressure gradient. In addition, if the flow in a finite region in the neighborhood of the axis is just as it was at $x = 0$, and if the flow near the wall is being decelerated by viscous forces, continuity requires the existence of an intermediate region in which the velocity is higher than in the parallel flow core. The existence of such a maximum in the velocity would seem to have an extremely important effect on the stability of the flow, and stability analyses (*3, 4*), which have been based on boundary layer theory would thus seem to be of questionable validity.

Experimental measurements to date have not brought this effect to light, because they were taken either too far from the entrance or with insufficient accuracy. Wang and Longwell (*1*), however, have carefully solved, numerically, the complete set of equations for entrance flow in a channel, and their results (case 1) clearly show that for small x, the maximum in the velocity profile does not occur on the axis.

In conclusion, the author believes that if the velocity profile is flat at the entrance, there is a small but finite region near the entrance to a tube or channel in which the flow in a core of finite radius is just as it was at $x = 0$. This implies that the boundary layer type of analysis, based on the accelerating core model, is invalid for small values of x.

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