

A Theoretical and Experimental Investigation of the Effects of Horizontal Barriers in Thermal Diffusion Columns

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A theoretical and experimental investigation of the effects of horizontal barriers on the separation of binary mixtures attained in thermogravitational thermal diffusion columns was undertaken in an attempt to further the understanding of these effects. The presence of horizontal barriers serves to reduce the internal convective flow and to divide the column into a number of smaller columns with interconnecting end feeds. Equations developed from such a model serve to predict the effect of the number of barriers, temperature difference, barrier diameter, and other parameters on the steady state and transient behavior of a batch column and on the manner in which bulk flow through the column influences the steady state separation in continuous-flow columns.

Data were taken in both batch and continuous columns to test the theory. Parameters varied experimentally (with an ethanol-water system) were number of barriers, ($N = 0, 2, 4, 8, 16, 50$), temperature difference, and diameter of the cylindrical barriers. It was found that the theoretical developments were entirely adequate to explain the observed influence of number of barriers for both types of column operation. The slight dependence of steady state batch separation on temperature difference that was observed is consistent with data of other investigations, and the independence of this type of separation on barrier diameter is in agreement with theoretical predictions. The theoretical predictions with respect to changes in temperature difference and a semitheoretical analysis of the effect of barrier diameter making use of isothermal hydrodynamic determinations proved satisfactory in predicting the influence of changes in these two parameters on both the transient batch and steady state continuous-flow column operation.

Thermal diffusion has been the subject of much theoretical and experimental investigation ever since Clusius and Dickel (5) first introduced their thermogravitational column in 1938. In contrast to an apparatus utilizing the static method of thermal diffusion where there are no convection currents, the thermogravitational column multiplies the separation by means of convection currents in a manner similar to the way a countercurrent extraction cascade produces concentration differences many times greater than the difference for a single stage. As a result, although the degree of separation obtainable in an apparatus utilizing the static method is usually small, a thermogravitational column can produce separations approaching 100%. Thus, it is the thermogravitational column that has been of primary interest for the aforementioned theoretical and experimental work.

Despite the amount of theoretical and experimental work which has appeared in the literature, industry has not yet applied thermal diffusion as a method for separations. Frazier (11) has developed a number of novel end-feed systems for feeding a group of thermal diffusion columns, and Frazier's co-workers have recently reported (13) pilot-plant studies of the use of thermal diffusion as a means of increasing the viscosity index of motor oils. However, thermal diffusion is a thermodynamically irre-

versible process and requires a relatively large amount of energy for a given separation. Hence, it can be considered only for separations where the more conventional means are not economical.

Since thermal diffusion is intrinsically an expensive process, a column utilizing this method for separations must be designed for maximum efficiency. Considerable work has been done in recent years in an attempt to improve the separation ability of thermal diffusion columns. Various experimental investigators (1, 4, 6, 9, 19 to 21, 26 to 31) have tried packings, spacers, and baffles as well as other devices in the separation space in an effort to improve column performance. Most of these investigators have found increases in the separation when objects were placed in the separation space, but no general experimental agreement has been noted. These investigations were hampered by the lack of an adequate theory to predict column performance when objects were placed in the separation space. Two recent theses have helped to fill this void: Lorenz (20, 21) studied packed-column operation and found good agreement between his theory and experimental results; in addition, Boyer (2) developed a satisfactory theory to predict column performance when vertical barriers are introduced into the separation space.

The purpose of this work is to increase knowledge of the effect of barriers by making a theoretical study and experimental investigation of horizontal barriers in a parallel-plate thermogravitational thermal diffusion column. It

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was decided to extend the application of thermal diffusion theory to predict the performance of a thermogravitational column with horizontal barriers in the separation space and to obtain sufficient experimental data to test the adequacy of the theoretical developments.

THEORY

The separation obtained in a thermogravitational thermal diffusion column results from the combined effect of the flux of a given component in the horizontal direction resulting from thermal diffusion and the flow of fluid in the vertical direction as a result of natural convection. Furry, Jones, and Onsager (12) were successful in characterizing the net effect of these two factors in terms of the transport equation:

$$\tau = HC_1C_2 - K \frac{dC_1}{dy} + \sigma C_1 \quad (1)$$

Their development incorporates a large number of assumptions and some approximations. One of the most important of these is the assumption that the internal convective flow, $v(x)$, is independent of both column length and the presence of continuous feed and product drawoff.

$$v(x) = \frac{-\beta g \Delta T}{12\omega\mu} (x^3 - \omega^2 x) \quad (2)$$

Numerous experimental investigators (2, 8, 13, 15, 16, 19 to 25) have shown the theory to be generally satisfactory in explaining the operation of both batch and continuous-flow columns without barriers.

In the sections that follow, the theoretical analysis of thermal diffusion columns with horizontal barriers will be discussed. Both the batch and continuous product-removal cases will be considered. Analysis of the continuous-flow case will be restricted to steady state operation, but both transient and steady state operation of batch columns will be considered.

Steady State Batch Operation

A batch thermogravitational column without barriers (open column) and the convective flow within such a column are illustrated in Figure 1(a). For steady state operation of a batch column the bulk-flow term, σ , in Equation (1) is naturally zero, and the horizontal thermal diffusion flux and the vertical convective flows exactly balance such that the net transport, τ , is also equal to zero. For this case Equation (1) is readily integrated to yield

$$\ln \left[\frac{(C_1/C_2)_{\text{Top}}}{(C_1/C_2)_{\text{Bottom}}} \right] = \frac{HL}{K} \quad (3)$$

For relatively small separations of equicomposition mixtures ($0.7 > C_1 > 0.3$), considerable mathematical simplification results when the product C_1C_2 is treated as a constant equal to $1/4$. The comparison of the resulting theoretical equations with experimental data obtained under suitable conditions is thereby simplified. Full advantage was taken of this fact and all theoretical and experimental results herein reported are subject to the restriction

$$C_1C_2 \cong 1/4 \quad (4)$$

Under these restrictions solution of Equation (1) for the steady state batch case yields

$$(C_1)_{\text{Top}} - (C_1)_{\text{Bottom}} = \frac{HL}{4K} \quad (5)$$

or

$$\Delta_0^0 = \frac{HL}{4K} \quad (6)$$

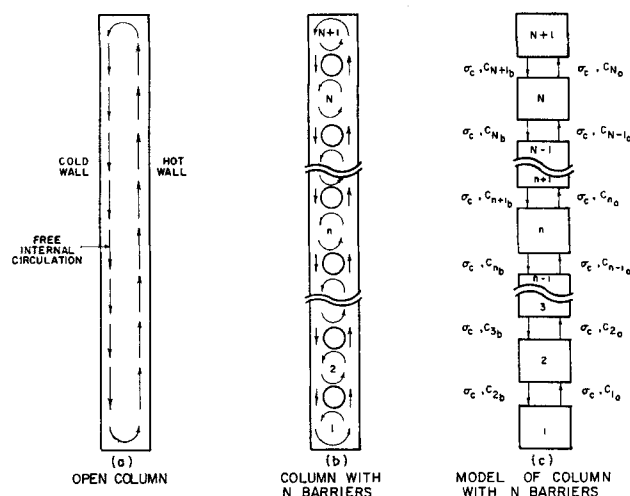


Fig. 1. Batch thermogravitational column.

where the subscript zero indicates the absence of bulk flow, and the superscript zero indicates that there are no horizontal barriers in the column.

A batch thermogravitational column with barriers is shown diagrammatically in Figure 1(b). The model that is used in the mathematical analysis of such columns is presented in Figure 1(c). The streams σ_c are all equal in amount and are caused by the fluid forced past the barriers by the convective circulation. At steady state the two streams passing any one barrier are of identical composition, and thus the total separation attained in a column with barriers is equal to the sum of the separations attained in each of the small columns:

$$\Delta_0^N = \sum \frac{H_n L_n}{4K_n} = \frac{H_N}{4K_N} \sum L_n \quad (7)$$

where the superscript N on the separation term indicates the number of horizontal barriers in the separation space, and the capital N subscript applies if the column is constructed so that values of H_n and K_n are identical for all $N + 1$ small columns.

One would expect the introduction of barriers to disturb both the velocity and temperature profile in the vicinity of each barrier and therefore reduce the effective column length in proportion to the number of barriers:

$$\sum L_n = L - Nl_r \quad (8)$$

An attempt was made to estimate the magnitude of the length correction term, l_r , on a semitheoretical basis. A value of seven plate spacings per barrier was obtained for the binary system and column operating conditions considered in this work. Although this value cannot be considered to be extremely accurate, it gives an approximate value which can be used in Equation (8) to account for the anticipated reduction in effective length.

The success of the theoretical developments of Furry, Jones, and Onsager, which are based in part on the assumption that H and K are independent of length, would lead one to assume that H and H_N as well as K and K_N are identical. When this assumption and the length correction term [Equation (8)] are applied to Equation (7) one obtains

$$\Delta_0^N = \frac{H}{4K} (L - Nl_r) \quad (9)$$

Thus one would anticipate, based on prior knowledge, that the batch separation in a column with horizontal barriers would be less than that attained in an open column.

However, numerous experimental data obtained in the course of this investigation as well as those presented by others (29, 30) demonstrate that the use of horizontal barriers in a batch column significantly increases the steady state separation attained with respect to the separation achieved in an open column. As a result, ex post facto reasoning was utilized to explain this apparent conflict with conventional theory.

As illustrated in Figure 1(b), part of the circulating fluid flows past the barriers whereas the majority of the fluid is turned around and flows back along the opposite side of the column. During this turn around, momentum is transferred to the barrier and the magnitude of the circulation within each small column is thereby reduced relative to that in the open column. This reduction of convection velocity is assumed to be linearly dependent on the number of barriers, N , in making an empirical modification of the relation for convective velocity, Equation (2):

$$v(x) = \frac{-\beta T g \Delta T}{12 \omega \mu} (x^3 - \omega^2 x) \frac{1}{(1 + bN)} \quad (10)$$

where b is an empirical momentum transfer factor.

This modified convective velocity function was used in a development paralleling that of Furry, Jones, and Onsager to develop suitable expressions for H_N and K_N as follows:

$$H_N = \frac{\alpha \beta T \rho g (2\omega)^3 B (\Delta T)^2}{6! \mu T (1 + bN)} \quad (11)$$

$$K_N = (K_c)_N + (K_d)_N \quad (12)$$

$$(K_c)_N = \frac{\beta T^2 \rho g^2 (2\omega)^7 B (\Delta T)^2}{9! D \mu^2 (1 + bN)^2} \quad (13)$$

$$(K_d)_N = 2\omega \rho B D \quad (14)$$

These relations reduce to those presented by Furry, Jones, and Onsager when $N = 0$.

With liquids the vertical diffusion term as represented by $(K_d)_N$ is rarely of importance and can be ignored in calculating K_N . When Equations (11) to (14) are substituted into Equation (7), one obtains the final expression for the steady state separation attained in a batch column with reservoirs:

$$\Delta_0^N = \frac{126 \alpha D \mu (L - Nl_r) (1 + bN)}{\beta T g (2\omega)^4 T} \quad (15)$$

This result is equivalent to

$$\Delta_0^N = \frac{H}{4K} (L - Nl_r) (1 + bN) \quad (16)$$

for $K_d \ll K_c$.

Comparison of Equation (16) with Equation (6) yields

$$\Delta_0^N / \Delta_0^0 = (1 + bN) \left(\frac{L - Nl_r}{L} \right) \quad (17)$$

Transient Batch Case

The diagrams presented in Figures 1(a) to 1(c) apply equally well for the unsteady state operation of a batch column. The general transport equation of Furry, Jones, and Onsager can be written for the batch case ($\sigma = 0$)

$$\tau_1 = HC_1C_2 - K \frac{\partial C_1}{\partial y} \quad (18)$$

The transient behavior of a thermal diffusion column without barriers can be analyzed when the transport equation is combined with the continuity conditions for a differential length of column:

$$m \frac{\partial C_1}{\partial t} = \frac{\partial^2 C_1}{\partial y^2} K - \frac{\partial (C_1 C_2)}{\partial y} H \quad (19)$$

Von Halle (31) has obtained a general solution to an equation of the same form as Equation (19). In addition, Powers has presented restricted solutions of Equation (19) (23, 24). One of these restricted solutions will be presented here because it applies to the restricted experimental region investigated ($C_1 C_2 \cong 0.25$), and because the final equation is much simpler than Von Halle's general solution. Powers' solution is

$$\frac{\Delta_0^0}{\Delta_\infty^0} = \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{e^{-\frac{(2n+1)^2 \pi^2 K}{L^2 m} t}}{(2n+1)^2} \right] = f(\xi) \quad (20)$$

where ξ is a dimensionless time quantity defined by

$$\xi = \frac{\pi^2 K t}{L^2 m} \quad (21)$$

Thus, the transient behavior of a column with no bulk flow and with no objects in the separation space can be predicted through use of Equation (20). This equation [or Equation (21)] predicts that the relaxation time of an open column is proportional to the square of the column length.

It might be possible to analyse the transient behavior of a batch thermogravitational column with barriers without making additional assumptions, but such an analysis would be tedious and one would expect the results to be cumbersome. Instead considerable simplification was obtained with the assumption that each of the small columns formed by the barriers attained steady state separation instantaneously. This assumption is reasonable in that the time to reach equilibrium is proportional to the square of the column length. Thus, in a column with four barriers (and therefore five small columns) each small column will reach equilibrium approximately twenty-five times as fast as a corresponding open column five times as long. It is to be anticipated that a column with barriers will approach steady state at a slower rate than even the open column, and therefore this simplifying assumption is justifiable except in the extreme cases in which the column contains only one or two barriers or no barrier at all.

In carrying out the analysis using the basic assumption of instantaneous equilibrium in each of the small columns, it was further assumed that the columns are initially all filled with a solution of uniform concentration, C_F . At time zero plus, all of the small columns have attained their equilibrium separation and the difference in concentration between the top and bottom of each small column will remain constant from then on. One component will be enriched at the top and stripped at the bottom such that the streams of equal total amount, σ_e , which pass the barriers in opposite directions will serve to produce a net upward transport of the enriched component. As a result, although the concentration difference in any small column remains constant, the average concentration in the small column will change with time.

The equilibrium concentration difference in a small column is designated as Δ_n and Δ_B if the lengths of the small columns are identical. (The assumption of equally spaced barriers is incorporated in the developments that follow.) The analysis is further simplified when one takes advantage of symmetry relations about the midpoint of the column. The center column is therefore divided in two and has a constant separation with respect to the feed composition equal to $\Delta_B/2$.

In any column, n , in the enriching section with end feeds such as shown in Figure 1(c), a material balance around the column gives

$$\rho V \frac{d\bar{C}_n}{dt} = \sigma_c (C_{n+1b} + C_{n-1o} - C_{no} - C_{nb}) \quad (22)$$

in which \bar{C}_n refers to the average concentration in column n . Solution of Equation (1) subject to the restriction $C_1 C_2 \cong 1/4$ results in a linear concentration gradient at steady state such that \bar{C}_n is also equal to the concentration at the midpoint of the column. In addition, the concentration differences in each column, Δ_B , have been assumed to be the same for all N columns and to be independent of time. As a result

$$C_{no} = \bar{C}_n + \frac{\Delta_B}{2} = \bar{C}_n + \frac{\Delta_\infty^N}{2(N+1)} \quad (23)$$

$$C_{no} = C_{nb} + \frac{\Delta_\infty^N}{(N+1)} \quad (24)$$

$$C_{n+1o} = C_{n+1b} + \frac{\Delta_\infty^N}{(N+1)} \quad (25)$$

where Δ_∞^N is the steady state batch separation for the column with N equally spaced barriers. Substitution of Equations (23) to (25) into Equation (22) yields

$$\frac{dC_{no}}{dt} = R (C_{n+1o} + C_{n-1o} - 2C_{no}) \quad (26)$$

where the simplification

$$R = \sigma_c / \rho V \quad (27)$$

has been introduced. Equation (26) describes the transient behavior of the concentration at the top of column n in the enriching section as a function of the overhead concentrations in columns $(n+1)$ and $(n-1)$. In the developments that follow the secondary subscript o will be dropped as all concentrations in Equation (26) refer to the top or overhead concentrations.

There are two columns above and two columns below the point of symmetry (the x -axis) of any column which do not satisfy Equation (26): the uppermost (or bottom-most) column which has no streams entering or leaving one end of the batch column and the center column (cut by the x -axis) which is but one-half as long as the other columns. For the uppermost column a material balance yields

$$\frac{dC_{n+1}}{dt} = R \left[C_n - C_{n+1} + \frac{\Delta_\infty^N}{(N+1)} \right] \quad (28)$$

and for the center column

$$C_1 = C_F + \frac{\Delta_\infty^N}{2(N+1)} \quad (29)$$

When a solution is obtained from these equations, advantage is taken of the assumption of symmetry about the midpoint in the column in that the total separation between the top and bottom of the entire column, Δ , is equal to $2(C_e - C_F)$ where C_e refers to the concentration at the top of the uppermost column.

To solve the above equations, it is convenient to remove them from the time domain by use of the Laplace transformation. The Laplace transform of Equation (26) is

$$C_n(S) = \frac{R}{S+2R} \left[C_{n+1}(S) + C_{n-1}(S) + \frac{\Delta_\infty^N}{2R(N+1)} \right] + \frac{C_F}{S+2R} \quad (30)$$

Similarly, the transform of Equation (28) is

$$C_{n+1}(S) = \frac{R}{S+R} \left[C_n(S) + \frac{\Delta_\infty^N (S+2R)}{2RS(N+1)} \right] + \frac{C_F}{S+R} \quad (31)$$

and of Equation (29) simply

$$C_1(S) = \frac{C_F}{S} + \frac{\Delta_\infty^N}{2S(N+1)} \quad (32)$$

Thus, for any number of equally spaced horizontal barriers, N , a system of equations will result consisting of

$\left(\frac{N-2}{2} \right)$ equations of the type given by Equation (30),

one equation of the type given by Equation (31), and one equation of the type given by Equation (32). It is comparatively easy to solve the system of equations for small N , but the problem becomes progressively more difficult as N gets larger. The problem essentially is one of finding the inverse transform of the solved system of equations. The inverse of the solution places it again in the time domain and gives the desired time-dependent solution. In general, finding the inverse transform entails finding the roots of a $(N/2)$ th order polynomial where N is again the number of barriers. Values of N of zero, two, four, eight, and sixteen were considered in the transient runs with barriers. For $N = 0, 2$ and 4 the roots of the polynomial are easily determined. For instance, for $N = 2$ the system of equations is

$$C_2(S) = \frac{R}{S+R} \left[C_1(S) + \frac{\Delta_\infty^N (S+2R)}{6RS} \right] + \frac{C_F}{S+R} \quad (33)$$

$$C_1(S) = \frac{C_F}{S} + \frac{\Delta_\infty^{N=2}}{6S} \quad (34)$$

A combination of Equations (33) and (34) yields

$$\left[C_2(S) - \frac{C_F}{S} \right] = \frac{\Delta_\infty^{N=2}}{6S} \left[\frac{S+3R}{S+R} \right] \quad (35)$$

and the inverse of Equation (35) yields

$$\frac{\Delta}{\Delta_\infty^{N=2}} = \frac{1}{3} + \frac{2}{3} (1 - e^{-Rt}) \quad (36)$$

For $t = 0$, $\Delta/\Delta_\infty^{N=2} = 0.33$ which results from the assumption of instantaneous equilibrium.

It is not necessary that N be an even number as implicitly assumed. If an odd number of barriers are equally spaced, however, one barrier would fall on the x -axis, and all $(N+1)$ columns formed by the N barriers (N odd) would be of equal length. Consequently, the case with N equally spaced barriers (N odd) would yield a system of

$\left(\frac{N-1}{2} \right)$ equations of the type given by Equation (30),

and one equation of the type given by Equation (31).

The solutions of all such developments are of the general form

$$\frac{\Delta}{\Delta_\infty^N} = \frac{1}{N+1} + \frac{N}{N+1} \left[1 - \sum_{i=0}^J a_i \exp(-b_i Rt) \right] \quad (37)$$

where $J = N/2$ for even values of N , and $J = (N+1)/2$

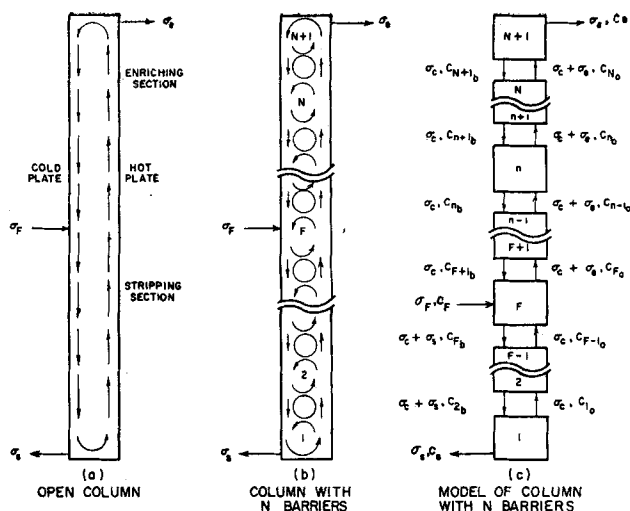


Fig. 2. Continuous-flow thermogravitational column.

for N odd. Only the first term of the series contributes materially to the form of the transient curve for $t > 0$, but the constants for the first two terms are included in Table 1 which summarizes the results.

The results of applying these relations for $N = 0, 1$ and 2 [see Equation (36)] emphasize the error introduced by the assumption of instantaneous equilibrium in the small columns.

$$\underline{N = 0} \quad \Delta/\Delta_\infty^0 = 1.0 \quad (38)$$

$$\underline{N = 1} \quad \Delta/\Delta_\infty^1 = \frac{1}{2} + \frac{1}{2} (1 - e^{-Rt}) \quad (39)$$

Thus application of Equation (37) to an open column ($N = 0$) predicts that the entire column attains equilibrium separation instantly, and it would be preferable to use Equation (20) in this case. For $N = 1$ it is predicted that one-half of the final separation is attained instantaneously, and similarly Equation (36) predicts an initial separation $1/3$ of that of the final separation. Equation (20) can be utilized to approximate the error introduced by the assumption of instantaneous equilibrium in the preceding development with the assumption that Equation (20) describes the transient behavior of each of the small columns formed by the barriers. In this way a value for zero plus can be estimated. This correction will be discussed in more detail in connection with the interpretation of experimental results.

It is, of course, not necessary that the barriers be equally spaced in the column as assumed. However, there is no apparent advantage in spacing them otherwise, and the theoretical development is more involved for unequal spacing.

Steady State Continuous Flow Case

Under conditions of continuous flow, feed is added to the center of the column, and overhead and bottom prod-

TABLE 1. VALUES OF COEFFICIENTS OF THE FIRST TWO TERMS IN THE FINITE SERIES OF EQUATION (37)

N	a_0	a_1	b_0	b_1
0	0	0	0	0
1	1	0	1	0
2	1	0	1	0
4	0.947	0.053	0.382	2.618
8	0.893	0.085	0.121	1.00
16	0.96	0.02	0.034	0.265

ucts are removed continuously from the ends of the column as illustrated in Figure 2. In almost any conceivable industrial application, the flow case is the one of primary interest because very little product can be obtained under batch conditions.

Under steady state conditions $\tau = \sigma_e C_e$ in the enriching section of a continuous-flow column. For the case $C_1 C_2 \cong 1/4$, it is reasonable to operate a column so that $L_e = L_s = L/2$ and $\sigma_e = \sigma_s = \sigma$. Under these conditions, solution of the transport equation [Equation (1)] for an open column yields a relation between the separation measured between the two ends of the open column and the flow rate:

$$\Delta = \frac{H}{2\sigma} (1 - e^{-\frac{\sigma L}{2K}}) \quad (40)$$

Now consider the case of a column with N equally spaced horizontal barriers. Figure 2 shows a situation similar to that in Figure 1 for a batch column. As in the batch case, it is assumed that a column with N equally spaced barriers performs effectively in the same manner as the sum of the separations given by the $(N + 1)$ small columns. For the flow case, in addition to the flow, σ_e , brought about by the convective circulation, there is a bulk flow of σ_s through each column above the feed point, and a flow of σ_s through each column below the feed point.

It is assumed that σ_e joins the stream σ_e flowing upward near the hot plate in the enriching section and that σ_s joins the stream σ_e flowing downward near the cold plate is the stripping section. In other words, it is assumed that the addition of bulk flow does not oppose the convective flow. It is further assumed that the addition of bulk flow does not alter the velocity distribution, $v(x)$, for the batch case [given by Equation (10)]. A similar assumption originally was made by Jones and Furry (18), and it has been proven satisfactory except for high flow rates (22, 25).

The concentration difference between the overhead and bottom streams which leaves each of the small columns with end feeds [see Figure 2(c)] is given by a modification of Equation (40). For a column, n , in the enriching section of a column in which the barriers are equally spaced

$$\Delta_{Be} = (C_{n0} - C_{nb}) = \frac{H_{Ne}}{4\sigma_e} \left[1 - e^{-\frac{\sigma_e L}{K_{Ne}(N+1)}} \right] \quad (41)$$

where L is the total column length, and the length of a small column is given by $L/(N + 1)$. Thus, if the composition leaving the bottom of the column, C_{nb} , is known, then the overhead composition, C_{n0} , can be calculated from Equation (41). As a result Equation (41) serves as a function directly analogous to the equilibrium relations in an ideal stage distillation calculation. However, it should be noted by inspection of Equation (41) that the concentration difference is flow-rate dependent whereas such is not the case in making ideal stage distillation calculations.

It is assumed that the feed is entered into the middle of a small column whose total length is equal to that of the other $N + 1$ small columns. As a result a special equation is developed for the enriching half of the feed column:

$$\Delta_{Le} = (C_{Fo} - C_F) = \frac{H_{Ne}}{4\sigma_e} \left[1 - e^{-\frac{\sigma_e L}{2K_{Ne}(N+1)}} \right] \quad (42)$$

Material balances made around each of the columns provide the additional relations required for determination of the difference between the outlet concentration, C_e , and that of the feed C_F . Thus for the top column ($N + 1$)

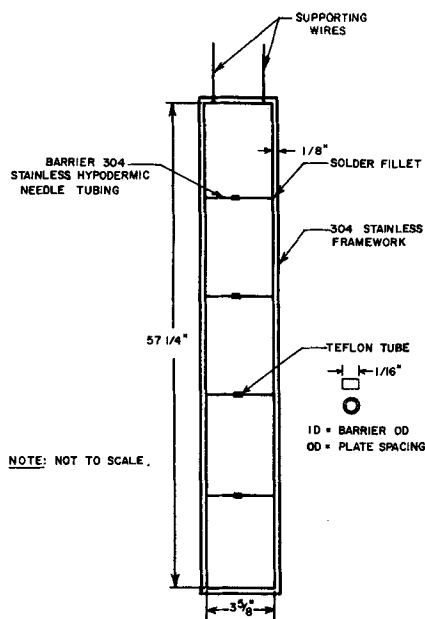


Fig. 3. Barrier framework with four barriers.

$$(\sigma_c + \sigma_e) C_{N0} = \sigma_c C_{N+1b} + \sigma_e C_e \quad (43)$$

and for the general enriching section column, n ,

$$\sigma_c C_{n+1b} + (\sigma_c + \sigma_e) C_{n-10} = \sigma_c C_{nb} + (\sigma_c + \sigma_e) C_{n0} \quad (44)$$

The general solution of Equations (41) to (44) is expressed as follows:

$$\Delta_e \equiv C_e - C_F = \Delta_{Le} + \Delta_{Be} \sum_{i=1}^I \zeta_e^i \quad (45)$$

where $I = N/2$ if N is an even number and

$$\zeta_e \equiv \frac{\sigma_c}{\sigma_c + \sigma_e} \quad (46)$$

In the general case it would be necessary to analyse the stripping section separately to obtain an expression for Δ_s similar to Equation (45) in which case the total separation, Δ^N , is given by

$$\Delta^N = \Delta_e + \Delta_s \quad (47)$$

For the special case in which the enriching and stripping sections are identical and $\sigma_e = \sigma_s = \sigma$, $\Delta_e = \Delta_s$

$$\Delta^N = 2 \left[\Delta_L + \Delta_B \sum_{i=1}^I \zeta^i \right] \quad (48)$$

where Equations (41), (42), and (46) serve to define Δ_L , Δ_B , and ζ in terms of $\sigma = \sigma_e = \sigma_F/2$.

The preceding development is based on the assumption of an even number of barriers. If an odd number of equally spaced barriers is used, one barrier is at the feed point, and hence all $N + 1$ columns are of the same length. As a result $\Delta_L = 0$, and Equation (48) applies with $I = (N - 1)/2$ for N odd.

The development also assumes that the barriers are equally spaced in the column. There appears to be no advantage to be gained by unequal spacing, and therefore special equations were not developed to handle this more general case.

Flow of Fluid Past the Barriers: Evaluation of σ_c

The magnitude of the flow past the barriers, σ_c , greatly influences both the transient behavior of batch columns [Equations (27) and (37)] and the steady state separa-

tion obtained in columns with continuous feed and product removal [Equations (46) and (48)]. Factors which influence this important term are considered below.

Preliminary considerations indicate that the flow past the barriers should be influenced by the geometry of the barriers, the properties of the fluid, and the magnitude of the convective circulation. A measure of the convective circulation was determined with the average value of the convective velocity over half of the distance between the plates as obtained by integration of the velocity distribution function [Equation (10)]:

$$F \equiv \rho \omega \bar{v} = \rho \int_0^\omega \left[-\frac{\beta \tau g \Delta T}{12 \omega \mu (1 + bN)} (x^3 - \omega^2 x) \right] dx \quad (49)$$

$$= \frac{\beta \tau g \rho (2\omega)^3 \Delta T}{384 \mu (1 + bN)} \quad (50)$$

where F is the mass flow rate per unit column width.

Further, a product form was assumed to relate σ_c to the convective circulation, F , in terms of a coefficient, c , which is assumed to be a function of the barrier geometry and fluid properties only:

$$\sigma_c = cF \quad (51)$$

Rather than attempt to calculate c from first principles, it was decided to evaluate one value of c in order to correlate experimental data obtained at one barrier-diameter to plate-spacing ratio and to use the results of hydrodynamic model studies in an attempt to predict the influence of a change in that ratio. It was assumed that values of c would be inversely proportional to cylindrical drag factors (17) (all barriers were cylindrical in form) determined for cylinders placed between two parallel plates. These model studies and interpretation of the results will be considered briefly when the interpretation of data obtained with different barrier-diameter to plate-spacing ratios are discussed.

EXPERIMENTS

Equipment

The thermogravitational column and most of the auxiliary equipment used in this work with horizontal barriers was the same as described in detail by Boyer (2). Therefore, only the equipment peculiar to this investigation will be described here.

Horizontal Barrier Systems: A barrier framework (see Figure 3) was fabricated from 304 stainless steel sheet. Horizontal barriers were fabricated from 304 stainless steel hypodermic needle tubing. The barriers were soldered, equally spaced (with one exception) between the top and bottom of the barrier framework. The solder joints were scraped and sanded flush with the frame, and all joints were cleaned thoroughly with cotton and distilled water to remove traces of acid flux and bits of excess solder.

The barriers were centered in the framework so that when installed in the column they were positioned equidistant from both plates. A small Teflon tube with an outer diameter equal to the plate spacing and an inner diameter which was the same as the barrier's outer diameter was positioned on each barrier to help prevent contact of the barrier with the plates as a result of the possible bowing of the barrier. (See Figure 3).

The inner dimensions of the barrier framework defined the working volume and were held constant during all runs at a width of 9.21 cm., a length of 145 cm., and thickness (plate spacing) of 0.0794 cm. The working volume was sealed by cutting a gasket from a sheet of 1/8-in. thick sponge neoprene and fitting it around the framework. Strips of stainless steel of thickness equal to that of the barrier framework were placed along the bolt holes to prevent bowing of the plates when the bolts which secure the framework and water jackets in place were tightened.

In previous investigations with parallel-plate columns (2, 22) a gasket was compressed between the transfer plates and served the dual purpose of sealing and defining the working volume. A characteristic of gaskets that hampered these previous experimental investigations is gasket creep or plastic deformation. Since the degree of creep is largely dependent on the characteristics of a particular gasket, it was therefore difficult to reproduce the same working volume (in particular, the same plate spacing) each time a new gasket was installed. In addition, the creep is a function of time, and unless one waits a considerable period for a gasket to settle, the working volume will change during the course of a run. The framework method of sealing the working volume and defining the plate spacing described in the preceding paragraph did not suffer from such experimental difficulties and was utilized for all experimental runs with horizontal barriers and for all of the open column runs that were used for comparison with the barrier data. The thickness of the barrier framework established reproducibly the plate spacing within the limits of accuracy of measurement of this important variable.

Procedure

The reader is referred to the thesis of Boyer (2) or to that of Fleming (10) for the general procedure followed in obtaining experimental data for this investigation with horizontal barriers. Parameters varied in this work included the number of barriers, barrier diameter, temperature difference between the plates, and bulk flow rate. Both transient and steady state data were obtained for the batch case, but only steady state data were taken for the continuous flow case.

EXPERIMENTAL RESULTS AND THEIR INTERPRETATION

The majority of the experiments carried out in connection with this study were designed to test the theoretically predicted effect of the insertion of horizontal barriers on the operating characteristics of batch and continuous-flow thermogravitational thermal diffusion columns. In addition, experiments were carried out to check the predicted influence of changes in the temperature gradient through the fluid and of changes in the diameter of the cylindrical barriers.

Number of Barriers

Experimental data were obtained on the steady state and transient behavior of batch columns and on the influence of bulk flow rate on the separation in a continuous flow column in which 0, 2, 4, 8, 16 and 50 barriers had been inserted.

Steady State Batch. According to Equation (17), the separation attained at steady state in a batch column will be influenced by the combined effect of a length correction term $(L - Nl_r)$ and reduced convective circulation $(1 + bN)$. A value of $l_r = 7(2\omega) = 0.55$ cm. as discussed previously was used in an attempt to correlate the data. Values of b were determined by comparing the open-column steady state separation with the separations obtained at steady state in columns with two and four barriers. (All data for $\Delta T = 26.7^\circ\text{C}$.) The average of the two values thus determined was used together with $l_r = 7(2\omega)$ in Equation (17) to predict the effect of adding additional barriers. Excellent agreement was found between theory and experiment* as illustrated by the solid line and circular data points on Figure 4. The small value of $b = 0.035$ which applies indicates that the decrease in convective velocity caused by a single barrier is not great.

Additional strong support is afforded by a similar treatment of the experimental data of Treacy and Rich (30) as illustrated by the triangular data points and dashed line on Figure 4.

* Complete experimental data has been deposited as document 7655 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for \$2.50 for photoprints or \$1.75 for 35-mm. microfilm.

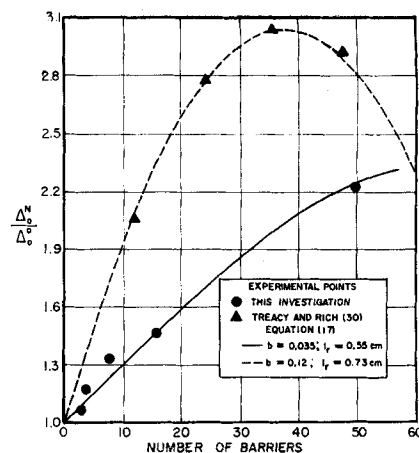


Fig. 4. Steady state batch separation as a function of the number of barriers.

Transient Batch. Typical data on the transient behavior of an open column are presented as open circles in Figure 5. For an open column Equation (20) together with a value of K calculated from Equation (12) serves to correlate the data very well.*

Although horizontal barriers serve to increase the steady state separation as illustrated in Figure 4, the time required to attain steady state is also increased. The major influence of the number of barriers on the transient time is predicted by Equation (37) in which an important secondary effect results from the fact that σ_c (and therefore $R[\text{Equation (27)}]$) is slightly influenced by N [Equations (50) and (51)]. Thus the transient behavior of a batch column with N barriers can be calculated if a value of the flow past the barriers, σ_c , is known.

Rather than attempt to predict such a value from first principles, empirical values of σ_c which provided good fits of the experimental data were determined by trial and error. The nature of the agreement between the calculated and experimental values is illustrated in Figure 5 for a column with four barriers (solid circles).

The insert on Figure 5 illustrates the magnitude of the error introduced with the assumption of instantaneous equilibrium in the $(N + 1) = 5$ small columns. Thus it takes about 20 min. for a column of length $L_N = L/(N + 1)$ to reach 95% of the steady state separation in contrast to approximately 1,900 min. for the entire column with four barriers to attain the same percentage approach to

* This is a fortunate coincidence because in general it is necessary to use empirical values of K (and H) to correlate experimental transient (and steady state) data. A procedure for accomplishing this has been described in detail by Powers (24).

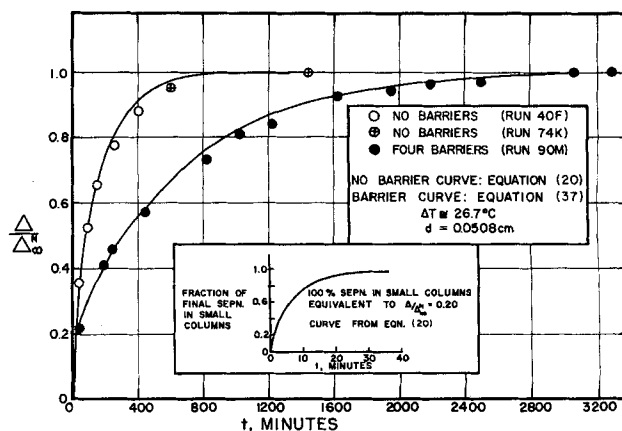


Fig. 5. Influence of the presence of barriers on the approach to equilibrium.

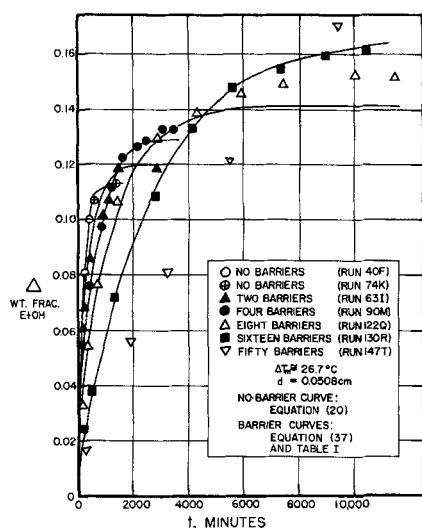


Fig. 6. Summary of transient runs.

equilibrium. Although the error was therefore very small ($\cong 1\%$), a correction was made to account for this error by considering that $t = 0$ in Equation (37) occurred at the time the small column attained 95% of its steady state value (20 min. in this case). Note that approximately 1/5 of the equilibrium separation was attained in this time in agreement with Equation (37).

Although the influence of the initial time correction was negligible in most cases it was incorporated in determining empirical values of σ_c for each transient run made with different numbers of barriers. These empirical values of σ_c represent the data very well over the transient periods involved and are listed in the top portion of Table 2.

A combination of Equations (50) and (51) predicts that σ_c should be inversely proportional to $(1 + bN)$ and directly proportional to ΔT .

$$\sigma_c \propto \frac{\Delta T}{(1 + bN)} \quad (52)$$

Therefore, the product $\sigma_c (1 + bN)$ should be a constant for any series of runs in which ΔT is maintained constant. Values of this product are indeed constant within the limits of accuracy of the data as illustrated by the numbers appearing in Table 2.

Use was made of this fact to correlate all of the data obtained at the higher temperature difference ($\Delta T = 26.7^\circ\text{C.}$) for which all variables other than number of barriers were held constant. The value of σ_c determined

to provide a fit of the data for a column with four barriers (Figure 5) was used in combination with Equations (52), (37), (27), and (16) to predict curves corresponding to all other values of N . The results are presented in Figure 6. In brief, the data for 0, 2, 4, 8, and 16 barriers are all well correlated by use of only two empirical parameters: b , the empirical momentum transfer term used to correlate the steady state separation data and one value of σ_c , the flow rate past the barriers, as determined to fit the transient data for a column with four barriers.

Data obtained during the initial phases of a transient study of a column with 50 barriers are included in Figure 6. The equipment malfunctioned before steady state conditions had been reached. For this reason and because a computer solution would have been required to find the roots of the 25th-order polynomial involved, no theoretical curve was calculated for the 50-barrier case.

When the number of horizontal barriers in a column of fixed length is varied, there is a change in the length of the $(N + 1)$ small columns formed by the N barriers according to the model used as the basis for the theoretical developments presented previously. Thus effective column lengths varying from 2.84 cm. (50 barriers) to 145 cm. (open column) were used in this study. Other investigators (8, 9, 13, 16, 25) have considered column length as a parameter, but the most extensive study reported previously (8) was limited to a factor of five in length variation. The greater variation in column length encountered in the present investigation focused attention on the usually negligible end effects and decreased convective circulation.

Steady State Continuous Flow. Equation (48) and associated equations predict the influence of flow rate and number of barriers on the steady state separation achieved in a continuous-flow thermogravitational column. From this equation [and the corresponding one for an open column, Equation (40)] one would expect the separation to decrease monotonically with increasing flow rate and to decrease at a faster rate as the number of barriers in the column is increased.

Experimental data obtained in an open column are presented as open circles in Figure 7. Equation (40) incorporating theoretical values of H and K calculated from Equations (11) and (12) serves to correlate the data very well.*

The magnitude of the flow past the barriers, σ_c , plays a dominant role in determining the effect of flow rate on separation in a column with barriers in much the same way that the transient behavior of batch columns is like-

* In general it is necessary to use empirical values of H and K to obtain good agreement between calculated and experimental results such as discussed by Powers and Wilke (25).

TABLE 2. EMPIRICAL VALUES OF σ_c AND CALCULATED VALUES OF THE PRODUCTS $\sigma_c(1 + bN)$ AND $\sigma_c(1 + bN)/\Delta T$

N	$\Delta T = 26.7^\circ\text{C.}$			$\Delta T = 13.4^\circ\text{C.}$		
	σ_c	$\sigma_c(1 + bN)$	$\left[\frac{\sigma_c(1 + bN)}{\Delta T} \right] 10^3$	σ_c	$\sigma_c(1 + bN)$	$\left[\frac{\sigma_c(1 + bN)}{\Delta T} \right] 10^3$
Transient batch						
2	0.070	0.075	2.8	0.028	0.030	2.2
4	0.070	0.080	3.0	0.030	0.036	2.7
8	0.060	0.077	2.9			
16	0.051	0.080	3.0	0.024	0.037	2.8
Steady state continuous flow						
2	0.13	0.14	5.2	0.070	0.075	5.6
4	0.13	0.15	5.5	0.067	0.076	5.7
8	0.115	0.15	5.5			
16	0.095	0.15	5.5	0.048	0.075	5.6
50	0.053	0.15	5.5			

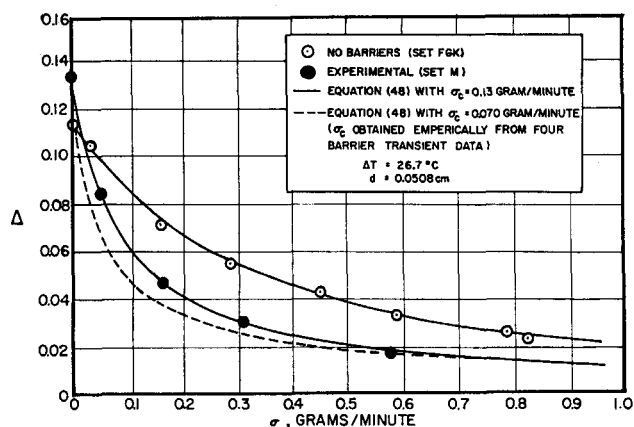


Fig. 7. Influence of flow rate and barriers on steady state separation.

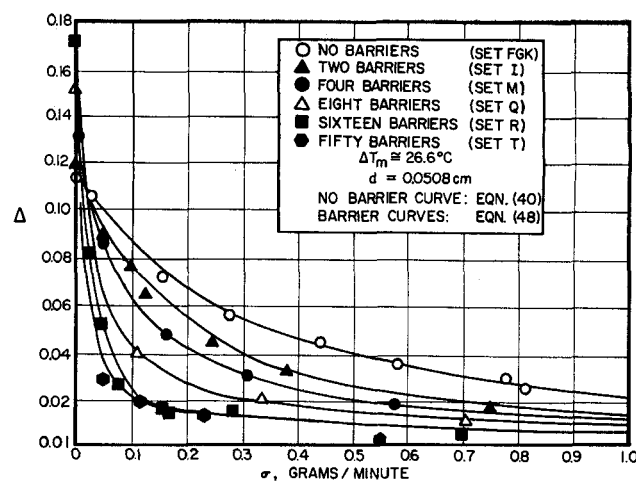


Fig. 8. Summary of continuous-flow runs.

wise controlled by σ_c . As a result one might expect that the value of σ_c determined empirically to fit the transient data would also serve to correlate the steady state continuous data. Such was not the case as is illustrated by the dashed line in Figure 7. Instead the empirical value of σ_c that served to correlate the steady state flow data (solid line) was almost twice as large as the value determined from the transient data for a column with the same number of barriers (four). Any correction that might be applied in an attempt to take into account the assumption that the bulk flow does not oppose the flow past the barriers [see Figure 2(c)] causes a greater rather than a lesser disparity between calculated and experimental results. It is possible that the presence of bulk flow through the column changes the hydrodynamic flow pattern in the vicinity of the barriers, but no attempt was made to account for such a change theoretically.

Instead values of σ_c were determined individually to provide a good fit for each set of experimental data. The nature of the fit in each case was similar to that illustrated for the four-barrier case in Figure 7. The values of σ_c thus determined are listed in the bottom portion of Table 2. As was the case with values obtained to fit individual transient batch curves, values of σ_c from the individual steady state continuous-flow curves were found to be inversely proportional to $(1 + bN)$ at constant values of other parameters as demonstrated by the constancy of the product $\sigma_c (1 + bN)$.

Use was made of this fact to correlate all of the data obtained at the higher temperature difference ($\Delta T = 26.7^\circ\text{C}$.) for which all parameters other than number of barriers were held constant. The value of σ_c determined to provide a fit of the data for a column with four barriers (Figure 7) was used in combination with Equations (52), (48), and associated equations to predict curves corresponding to all other values of N . In applying these equations it should be noted that Δ_L and Δ_B as well as ζ are all

functions of the bulk-flow rate, σ , in accordance with Equations (41), (42), and (46), respectively. The results are presented in Figure 8. In brief, the data for 0, 2, 4, 8, 16, and 50 barriers are all well correlated by use of only two empirical parameters: b , as determined from steady state batch data and one value of σ_c as determined to fit the steady state continuous-flow data for a column with four barriers.

Inspection of Figure 8 reveals that the separation in columns with barriers is less than that in the open column at all bulk-flow rates greater than approximately 0.02 g./min. Thus the use of barriers in this case would allow greater separations than the open column only for very low flow rates. (No experimental points were obtained between zero and 0.02 g./min.)

Temperature Difference

A limited number of experiments were carried out at a temperature difference of 13.4°C . to compare with the more extensive results at $\Delta T = 26.7^\circ\text{C}$. which have been described above.

Steady State Batch. Consideration of Equations (6) and (15) indicates that the steady state separation in a batch column without or with horizontal barriers should be independent of the temperature difference, ΔT . Data obtained to check this effect (and the effect of barrier diameter to be discussed later) are presented in Table 3.

Although the theory is qualitatively correct in that a change in ΔT by a factor of two does not result in a big change in separation, the separations at the lesser ΔT are generally less than those at the greater ΔT . The results of the present investigation indicate that the steady state batch separation is proportional to $(\Delta T)^{0.088}$. Other investigators (2, 14, 15, 23, 24) have made similar observations.

Transient Batch and Steady State Continuous Flow. According to the theoretical developments presented in this article, both the transient batch and the steady state continuous-flow behavior of thermogravitational columns with horizontal barriers is strongly influenced by the flow past the barriers, σ_c . Furthermore, it is to be anticipated that σ_c is directly proportional to ΔT in accordance with Equation (52). In order to test this, prediction values of $[\sigma_c(1 + bN)/\Delta T]$ were calculated and are presented in Table 2. The values of this group are all very close to 2.85 for the transient batch data, and similarly they are well represented by a value of 5.55 for the steady state continuous-flow case which strongly supports the assumptions incorporated in the development of Equations (50) and (51).

TABLE 3. COMPARISON OF STEADY STATE BATCH SEPARATIONS. TEMPERATURE DIFFERENCE AND BARRIER DIAMETER AS PARAMETERS

Barrier diameter cm.	Barrier-diameter to plate-spacing ratio	Separation—wt. frac. ethanol	
		$\Delta T = 26.7^\circ\text{C}$.	$\Delta T = 13.6^\circ\text{C}$.
0	0	0.1132	0.1020
0.0508 ^a	0.643	0.1330	0.1233
0.0635 ^a	0.803	0.1286	0.1226

^a = column with four barriers.

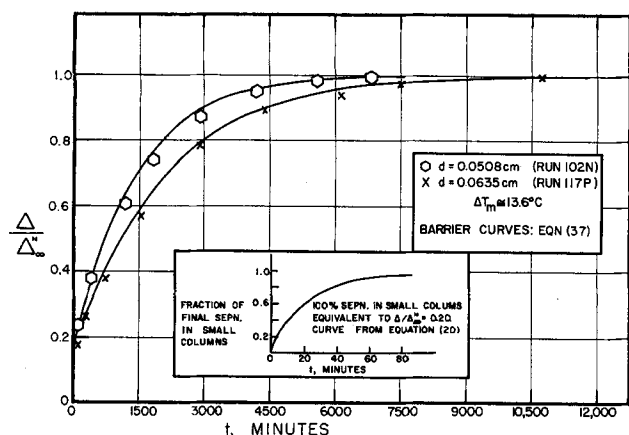


Fig. 9. Influence of barrier diameter on approach to equilibrium.

The value of 2.2 for σ_c , which was selected to fit the data obtained on the transient behavior of a batch column with two barriers at $\Delta T = 13.4^\circ\text{C}$, is in marked disagreement with the other values. Although there is no way to be certain, this particular discrepancy might have resulted from a pinhole leak in a feed port in the column. The presence of a leak was definitely established in a subsequent run and was repaired at that time.

Barrier Diameter

The effect of barrier diameter was treated semitheoretically by assuming the coefficient c which appears in Equation (51) to be inversely proportional to the cylindrical drag factors for isothermal flow past cylinders placed with their axes parallel to two flat plates and perpendicular to the direction of fluid flow. The cylindrical drag factors were determined in a plastic hydrodynamic model with the same cylinder-diameter to plate-spacing ratio as was used in the thermal diffusion column (see Table 3) but with a considerably greater distance between the plates. The drag owing to the flat plates (7) was subtracted from the total observed pressure drop to arrive at a value for the head loss owing to the presence of the cylinder. In this way it was determined that the ratio of the drag coefficient of the larger to the smaller cylinder was 1.49.

Steady State Batch. When Equation (16) was developed, it was assumed that at steady state the streams that flow past any barrier are equal in amount and of the same composition. This will be true independent of the size of the barrier (unless the barrier diameter equals or exceeds the plate spacing), and therefore theory predicts the steady state separation to be independent of the barrier diameter if all other variables are held constant.

Data obtained to test this prediction are included in Table 3. Whereas the assumption does not apply in the limit $d \rightarrow 0$, because no momentum transfer occurs at this limit, the data presented in Table 3 for a column with four barriers show little effect of barrier diameter on steady state batch separation. Data at both temperature differences display a slightly reduced separation at the higher barrier-diameter to plate-spacing ratio but the difference is not great enough nor the data extensive enough to warrant any conclusion in conflict with the theoretical predictions.

Transient Batch and Steady State Continuous Flow. When the barrier-diameter to plate-spacing ratio is increased, the rate of flow past the barriers, σ_c , should decrease and thereby increase the transient time in a batch column and decrease the separation achieved in a continuous-flow column at any given flow rate. Both of these qualitative predictions are supported by the experimental

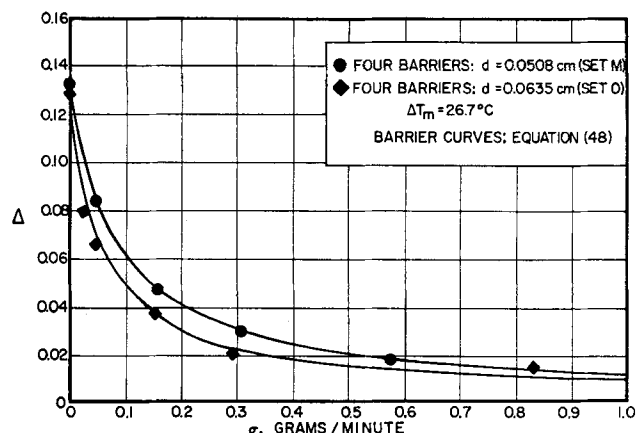


Fig. 10. Influence of barrier diameter on steady state separation in a continuous-flow column.

results illustrated by Figures 9 and 10. (The inset portion of Figure 9 is used to establish zero time for the columns as discussed previously.) The effect of increased barrier diameter was estimated quantitatively from the data obtained with the smaller diameter barriers by applying Equations (50) and (51) and assuming the coefficient c to be inversely proportional to the cylindrical drag coefficients as determined in the isothermal hydrodynamic model discussed previously. The excellent correspondence between the calculated values (solid lines) and the experimental results obtained in both transient batch and steady state continuous-flow cases gives strong support to the use of this method of accounting for the result of changing the barrier-diameter to plate-spacing ratio.

SUMMARY

The representation of a thermogravitational thermal diffusion column with horizontal barriers by use of a model consisting of individual columns with interconnecting end feeds yields mathematical equations which predict the effect of the number of barriers and other operating variables on the operation of both batch and continuous-flow columns. Experimental data obtained on both types of columns to determine the effect of number of barriers, temperature difference, and diameter of the cylindrical barriers were found to be in direct correspondence with the theoretical predictions, especially when the decrease in internal circulation due to the presence of the barriers was taken into account.

ACKNOWLEDGMENT

The financial support of the National Science Foundation through a research grant and of the Celanese Corporation Fellowship is gratefully acknowledged. Mr. John Samaska prepared the figures.

NOTATION

- b = empirical factor to account for momentum loss due to presence of barriers
- b = subscript to identify streams leaving the bottom of a column
- B = column width
- c = coefficient in Equation (51)
- C_1 = concentration of component 1
- C_2 = concentration of component 2
- C_e = concentration of component 1 leaving the enriching section
- C_s = concentration of component 1 leaving the stripping section

C_F = concentration of component 1 in the feed
 d = barrier diameter
 D = diffusion coefficient
 e = subscript to identify variables in the enriching section ($y > 0$)
 F = convective flow rate per unit column width [Equation (50)]
 g = local acceleration of gravity
 g_c = dimensional constant
 H = $\frac{\alpha \beta_T \rho g (2\omega)^3 B (\Delta T)^2}{6l\mu T}$
 H_N = term defined by Equation (11)
 i = index number
 I = $N/2$ for N even, $(N-1)/2$ for N odd
 J = $N/2$ for N even, $(N+1)/2$ for N odd
 K = $\frac{\beta_T \rho g^2 (2\omega)^7 B (\Delta T)^2}{9lD\mu^2} + 2\omega DB\rho$
 K_N = term defined by Equation (12)
 $(K_c)_N$ = term defined by Equation (13)
 $(K_d)_N$ = term defined by Equation (14)
 l_r = length of disturbance created by a single horizontal barrier
 L = total column length ($L = L_e + L_s$)
 m = solution per unit length of column
 n = subscript identifying a general column formed between two barriers
 n = index number [Equation (20)]
 N = number of horizontal barriers
 N = subscript which applies when all small columns are identical
 o = subscript to identify streams leaving the top of a column
 P = pressure
 R = dimensionless flow in transient equation [Equation (27)]
 s = subscript to identify variables in the stripping section ($y < 0$)
 S = Laplace transform variable
 t = time
 T_H, T_C = temperature of hot and cold plates, respectively
 \bar{T} = mean operating temperature
 $v(x)$ = general velocity distribution function
 \bar{v} = average velocity over half the column width
 V = volume of column
 x = axis normal to plates
 y = axis parallel to plates in the direction of convective circulation

Greek Letters

α = thermal diffusion coefficient
 β_T = change in density with temperature = $-\frac{\partial \rho}{\partial T}$
 Δ = total column separation (enriching minus stripping composition)
 Δ_B = separation in any column, n , defined by Equation (41)
 Δ_L = separation in center column cut by x -axis, defined by Equation (42)
 Δ_0^N = separation with no bulk flow and N barriers
 Δ_∞^N = steady state batch separation (at infinite time) with N barriers
 ΔT = temperature difference between plates
 ζ = dimensionless flow in continuous-flow equation [Equation (46)]
 μ = coefficient of viscosity
 ξ = dimensionless time quantity defined by Equation (21)
 ρ = density

σ = average mass flow rate passing through the column
 σ_c = mass flow past barriers brought about by convective circulation
 σ_e = enriching section bulk-flow rate
 σ_s = stripping section bulk-flow rate
 τ = net transport of component 1 passing through a cross section of the column normal to the walls
 2ω = distance between the hot and cold plates

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