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PERIODIC COUNTERCURRENT PROCESSES

by

Robert A. May

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I. INTRODUCTION

Most chemical processes today are designed to operate in the steady state and often elaborate steps are taken to insure that the desired steady state is reached and maintained. Unsteady state processes are usually considered to be inferior to steady state processes in most respects. However, considerable evidence—both theoretical and experimental—exists in the literature which indicates that the performance of many processes can be significantly improved by controlled unsteady state operation. In most cases the controlled unsteady state is the result of variations of one or more of the control variables of the process or of externally applied pulsations or vibrations.

Many examples of the beneficial effects resulting from externally applied vibrations and pulsations of controlled intensity are available. The large increase in heat transfer from a wire resulting from vibrations [11] may be cited as one example of the improvement in an engineering process obtained by this type of unsteady state operation. Baird [1] has reviewed the past research on the effects of vibrations and pulsations on various chemical engineering operations. The details of these effects will not be described here since this type of unsteady state operation is not closely related to the present work.
Many chemical processes, either steady or unsteady state, are characterized by a set of state variables and a set of control variables together with certain relations which describe the process in terms of these variables. If the control variables are constant with time, the process will in general reach a steady state after sufficient time. If the control variables are not constant with time the process will in general be unsteady state. In particular, if the control variables are periodic functions of time it may be expected that the process will also be periodic.

Experimental studies concerning periodic operation have been carried out for numerous processes including distillation [6,15,13], extraction [2,21,25], absorption [26], ion exchange [24], crystallization [14], and particle separation [19]. These studies have shown conclusively that the performance of many chemical engineering processes can be significantly improved, at least on the laboratory scale, by periodic operation. For example Gaska [6] and McWhirter [15], working under the direction of Cannon, observed large increases in both the efficiency and capacity of a small laboratory column when operated periodically. The details of these experimental studies will not be given here since they are not closely related to the theoretical development presented in this work.

Several theoretical analyses concerning the periodic operation of certain chemical processes have appeared in the literature. The general theory of periodic processes has been considered by Horn and Lin [10], who have derived equations which can be used to optimize periodic processes by the method of hill climbing...
in function space and have given necessary conditions for an optimal period. These authors also show the similarity between recycle and periodic processes and present a numerical method for the solution of periodic problems. The special example of a chemical reaction process carried out in a continuously operated tank reactor with periodic temperature control is used to illustrate the theory. Mathematical analyses of periodic reactor operation have also been published by Douglas [4,5] for stirred tank reactors, and by Gore [7] for fixed-bed reactors.

Periodic operation of countercurrent flow multistage separation processes has been considered by McWhirter and Lloyd [16], Chien, Sommerfeld, Schrod, and Parisot [3,23], Belter and Speaker [2], Robinson and Engel [20] and Horn [8,9]. The work presented here will be concerned only with this type of process, and is based on the previous work by Horn.

The periodic operation of a countercurrent process is the result of the manner in which the different phases are transported through the column. That is, the flow of the different phases may be considered to be the control variables and periodic transport of the different phases will in general result in the overall process being periodic.

Consider the countercurrent stagewise process represented schematically in Figure 1. When operated in the conventional (steady-state) manner, the light phase is continuously introduced into the first stage and withdrawn from the last stage. The heavy phase enters the last stage continuously and is removed
from the first stage. The same process can be operated periodically in the following way. During a time interval of length $\tau$ the light phase is transported to the right while the heavy phase is stationary. The heavy phase is then transported to the left for a time interval of length $t'$, the light phase being stationary during this interval. Repetition of this sequence results in the process being periodic.

Different modes of periodic operation can be obtained, depending on how the phases are transported. For example, another mode of operation would be to alternately transport each phase in batches, allowing the contents of each stage to equilibrate between the transport of the different phases. Horn [8], in a paper dealing with the basic theory of continuous and periodic countercurrent processes, has shown that a process operated periodically in this manner has the same separating ability as a conventional column with twice the number of stages.

This work will be primarily concerned with the specific mode of operation described below which could easily be applied in the case of distillation or absorption. Previously published work has shown that the performance of a countercurrent process can be improved by operating the process periodically in the following manner. One of the phases is transported uniformly in one direction; the other phase is transported periodically in batches in the other direction. In this work only cases will be considered where the mass holdup of the uniformly transported phase in a stage is negligible. This would be the case, for instance, in distillation
or absorption if the vapor phase is transported uniformly. Batch-wise and uniformly transported phases are called liquid and vapor, respectively.

In the papers published previously, the case has been studied in which piston flow can be assumed for the liquid phase during the time of down transport. That is, there is no mixing between the liquids belonging to different stages during that time. Horn [9] used the method of generating functions (z-transforms) to derive simple and accurate asymptotic formulas for the stage efficiency, which show that the performance of a column can be improved considerably by periodic operation. These asymptotic expressions are valid for columns with either a finite or infinite number of stages. Particularly simple relations were obtained for the important special case of difficult separations.

Computer simulations of a periodically operated column have been carried out by McWhirter and Lloyd [16] and by Sommerfeld, Schrodt, Parisot and Chien [3, 23]. Sommerfeld et al also present an asymptotic expression for the stage efficiency of a column with an infinite number of stages. Robinson and Engel [20] have also derived an asymptotic expression for the stage efficiency, but like the expression derived by Sommerfeld et al, this expression is valid only for a column with an infinite number of stages.

In this work the asymptotic expressions derived by Horn [9] are investigated in detail. Numerical results obtained by these equations are presented and the accuracy of the expressions is investigated. The effect of mixing during the down transport of
liquid is studied by modeling each stage during the time of down transport with a series of well stirred tanks. In this way an asymptotic expression for the stage efficiency of a periodically operated column with many stages is derived for the case of difficult separations. Numerical results concerning columns with a small number of stages are also given.

In the remainder of this chapter some of the basic equations which will be needed later are given. Consider again the stagewise apparatus shown in Figure 1 through which two binary phases -- called liquid and vapor -- flow in opposite directions with average molar (mass) flow rates $p$ and $q$, respectively. One of the components is called the reference component and its mole (mass) fraction in the liquid and vapor phase is denoted by $x$ and $y$, respectively.

In this work it is assumed that $p$ and $q$ can be considered constant over the entire column and that the equilibrium relation between $x$ and $y$ is approximately linear, i.e.

$$y = Kx \quad (1.1a)$$

or

$$y = Kx + L \quad (1.1b)$$

Both of these assumptions are justified in the case of difficult separation problems where (for steady state) each stage represents but a small step in the McCabe-Thiele type diagram. This is the case, for example, when a very high purity of one of the components is desired or when the boiling points and other physical properties of the components are close together.
In the mathematical analysis which follows it is sufficient to consider the equilibrium relation to be given by equation (1.1a) since, except for the case \( K = 1 \) which requires special treatment, Equation (1.1b) is transformed into a form identical to Equation (1.1a) by a translation of the coordinates, i.e.

\[
x' = x - \frac{L}{1-K}, \quad y' = y - \frac{L}{1-K}
\]  

(1.2)

It is assumed that the resistance to mass transfer in a stage can be adequately represented by a Murphree efficiency \( \epsilon \) so that the relation between composition of the vapor leaving a stage and the liquid in the stage is given by

\[
y_{v} = \epsilon K x_{v} + (1 - \epsilon) y_{v-1}
\]  

(1.3)

This assumption is well founded in the case of steady state operations but is not valid for unsteady state processes unless the holdup of one of the phases in the stage is negligible (see Appendix I).

For a column operated in the conventional manner the material balance equations together with Equation (1.3) yield the following difference equation.

\[
x'_{v+1} = [1 + \epsilon(1 - \gamma)] x_{v} = -\gamma x_{o} + x_{1} \epsilon
\]  

(1.4)

\( x_{o} \) is related to the composition of the vapor entering the bottom of the column by

\[
y_{o} = K x_{o}
\]  

(1.5)

and the separation factor \( \gamma \) is defined by

\[
\gamma = \frac{K_{a}}{p}
\]  

(1.6)
The solution of Equation (1.4) is the well known Kremser Equation.

\[ x_e = \frac{\gamma x_0 - x_1}{\gamma - 1} + (x_1 - x_0) \frac{\gamma}{\gamma - 1} \left[ 1 + (\gamma - 1) \phi \right]^{N_e} \]  \hspace{1cm} (1.7)

Here \( x_e \) refers to the composition of the liquid entering the top stage \( N_e \).

If the column is operated by transporting the vapor phase continuously in one direction and the liquid phase periodically in the other direction, the liquid composition in each stage during the time in which only vapor is transported is described by a differential equation. If perfect mixing is assumed in each stage during this time and if the vapor holdup is negligible so that Equation (1.3) can be used, then a mass balance on the \( \nu \)th stage yields

\[ \frac{dx_v}{dt} = q(y_{v-1} - y_v) \quad \nu = 1, 2, \ldots, N_p \]  \hspace{1cm} (1.8)

The initial condition of Equation (1.8) is given by the liquid composition at the end of the down transport period. It is assumed that the time required for the down transport of liquid is short so that changes in composition due to vapor flow can be neglected during this time. The approach to the periodic state for the case of a four stage absorption (stripping) column with plug flow during the time of liquid transport, obtained by computer simulation, is shown in Figure 2. For the case shown in the figure, the initial conditions of Equation (1.8) are given by \( x_{\nu}(0) = x_{\nu+1}(\tau) \) where \( \tau \) corresponds to the length of the period during which there is no transport of liquid.
If for two columns, each with two inputs and two outputs, the same relation between the two inputs and one of the outputs is valid, then the columns behave identically regardless of the way in which the two columns are operated or the way in which the ends of the columns are connected with the environment. When comparing the performance of two columns which are operated in different manners, the practical basis for comparison is the ratio of the number of stages required by the two columns in order to accomplish a given separation. The ratio \( N_e/N_p \) of the number of stages required by the two processes is called the relative overall stage efficiency. Equation (1.7) is used to compare the performance of a periodically operated column with the corresponding steady state column.
FIG. 2 - APPROACH TO PERIODIC STATE OF A FOUR STAGE COLUMN WITH NO REFERENCE COMPONENT INITIALLY IN THE COLUMN. VALUES OF THE PARAMETER ARE $\gamma = 0.75$, $\varepsilon = 1.0$, $\eta = 1.0$, $k = 1.5$, $\gamma = 0.6$, $x = 0.0$
II. STAGE EFFICIENCY OF A PERIODICALLY OPERATED COLUMN WITH NO MIXING DURING THE TIME OF LIQUID TRANSPORT.

A. Introduction

The stage efficiency of a periodically operated column in which no mixing between the liquids of different stages takes place is studied in this chapter. In this case, at the end of each cycle \( t = \tau \) a fraction \( \eta \) of the liquid holdup of each stage is transferred batchwise to the stage below and mixed there with the remaining fraction \( (1 - \eta) \) of the liquid holdup of that stage. Since the completion of the down transport corresponds to the beginning of a new cycle, the down transport is described by the relation

\[
x_v(0) = \eta x_{v+1}(\tau) + (1 - \eta)x_v(\tau)
\]

This equation together with Equations (1.3) and (1.8) describes the periodic state of the column.

Horn [9] used the method of generating functions (z-transform) to derive an asymptotic expression for the stage efficiency of a periodically operated column with no mixing. In this chapter, values of the stage efficiency are calculated using this expression and exact values are calculated by expanding the generating function by means of a digital computer. Estimates of the very small error of the asymptotic equation are also given. The location in the complex plane of the roots of the characteristic equation, which determines the accuracy of the asymptotic equation, is also investigated. We begin with a brief review of Horn's work in order to provide a basis for the work in this chapter.
B. The Asymptotic Equation

Using generating functions, Horn [9] demonstrated that for the case in which piston flow can be assumed for the liquid phase during the time of down transport, the relative overall stage efficiency of a column with \( N_p \) states can be obtained by cutting a fictitious column with infinitely many stages. The generating functions for a column with infinitely many stages are defined by

\[
u(z,t) = \sum_{\nu=1}^{\infty} x_{\nu}(t) z^{\nu} \tag{2.2a}\]

and

\[
u(z,t) = \sum_{\nu=1}^{\infty} y_{\nu}(t) z^{\nu} \tag{2.2b}\]

The generating functions transform Equations (1.3) and (1.8), which describe the column during the time when only vapor is transported, into a first order ordinary differential equation for \( u(z,t) \). The solution of this equation under consideration of the periodicity condition (Equation (2.1)) is

\[
u(z,\tau) = x_o \frac{z}{1 - z} + w(z)[x_1(\tau) - x_o] \tag{2.3a}\]

where

\[
w(z) = \frac{\eta z \exp f(z)}{[\eta + z(1-\eta)] \exp f(z) - z} \tag{2.3b}\]

and

\[
f(z) = \frac{\gamma \eta(z - 1)}{1 - (1 - \gamma)z} \tag{2.3c}\]

Here \( x_o \) is defined as in Equation (1.5) and \( x_1(\tau) \) refers to the composition of the liquid which is removed from the bottom of the column at the end of the period. The separation factor \( \gamma \) in this
case is defined as
\[ \gamma = \frac{K_0 \tau}{\| V \|} \] (2.4)

This definition of \( \gamma \) is equivalent to that given previously for a conventional column (Equation (1.6)) since in both cases \( \gamma \) denotes the equilibrium constant times the ratio of the vapor transported per cycle to the liquid transported per cycle.

After consideration of the definition of the generating function, expansion of Equation (2.3) in powers of \( z \) yields an expression for the composition \( x_e \) of the liquid entering the column at stage \( N_p \), which is identical in form to Equation (1.7) for a conventional column. These two expressions provide a comparison between two columns -- one with \( N_e \) stages and operated in a conventional manner, the other with \( N_p \) stages operated periodically with identical performance and the same Murphree efficiency \( \varepsilon \). In this manner Horn [9] obtained the following relation for the relative overall stage efficiency \( N_e/N_p \)
\[ \frac{N_e}{N_p} = \frac{1}{N_p} \frac{\ln \frac{1}{\gamma \left[ 1 + (\gamma-1) \sum A_{N_p} e \right]} \right]}{\ln \left[ 1 + (\gamma-1)\varepsilon \right]} \] (2.5)

where \( A_{N_p} + 1 \) is the \((N_p+1)\)th coefficient in the Taylor Expansion of \( w(z) \)
\[ w(z) = \sum_{\nu=1}^{\infty} A_{\nu} z^{\nu} \] (2.6)

Equation (2.5) is exact provided that the coefficients \( A_{\nu} \) can be determined exactly. Analytical determination of these coefficients by differentiation of \( w(z) \) is not practical even for small \( \nu \), but with the aid of a digital computer exact calculation is
possible. Results obtained by this method will be presented later.

Horn [9] applied the residue theorem to the function \( w(z)/z^{\nu+1} \) and obtained the following asymptotic relation for the coefficients \( A_{\nu} \)

\[
A_{\nu} = -\sum_{j} \frac{\varnothing(z_j)}{\psi'(z_j)} \cdot \frac{1}{z_j^{\nu+1}} + \frac{1}{2\pi i} \oint_{C} \frac{w(z)}{z^{\nu+1}} \, dz
\]  

(2.7)

[\( \psi'(z_j) \neq 0, \quad i = \sqrt{-1} \)]

where \( \varnothing \) and \( \psi \) are the numerator and denominator of the function \( w(z) \) defined by Equation (2.3b), i.e.

\[
\varnothing = \eta \cdot z \exp f(z)
\]  

(2.8a)

\[
\psi = [\eta + z(1 - \eta)] \exp f(z) - z
\]  

(2.8b)

\[
\psi' = d\psi/dz
\]  

(2.8c)

The quantities \( z_j \) in Equation (2.7) denote the roots of the characteristic equation

\[
\psi(z_j) = 0
\]  

(2.9)

and the summation is taken over all characteristic roots within a closed contour \( C \) which encircles the origin.

Using this expression for the coefficients \( A_{\nu} \), Horn [9] showed that an excellent asymptotic approximation of the stage efficiency is given by

\[
\frac{N_c}{N_p} = S + \frac{B}{N_p}
\]  

(2.10a)

where

\[
S = -\frac{\ln C}{\ln [1 + (\gamma - 1)\varepsilon]}
\]  

(2.10b)
and

\[ B = \frac{-\ln\left\{ \left[ 1 - \gamma e^{2\zeta} \frac{\eta + \zeta(1 - \eta)}{[1 - (1 - \varepsilon)\zeta]^{2}} \right] \frac{\gamma}{\gamma - 1} \right\}}{\ln[1 + (\gamma - 1)e]} \]  

(2.10c)

and \( \zeta \) is the real root differing from unity of the characteristic equation. Furthermore, for \( \varepsilon \eta \neq 1 \) the bilinear transformation

\[ Z = e^{\frac{\eta + z(1 - \eta)}{1 - z(1 - \varepsilon)}} \]  

(2.11a)

\[ z = \frac{-\varepsilon \eta + Z}{\varepsilon(1 - \eta) + (1 - \varepsilon)Z} \]  

(2.11b)

transforms the characteristic equation into

\[ \exp^{\alpha \gamma (Z - 1)} = 1 + \alpha - \alpha/Z \]  

(2.12a)

where

\[ \alpha = \frac{\varepsilon \eta}{1 - \varepsilon \eta} > 0 \]  

(2.12b)

The real root differing from unity of the transformed characteristic equation for \( \varepsilon \eta \neq 1 \) and of the characteristic equation for \( \varepsilon \eta = 1 \) has been calculated with the aid of a digital computer by means of a Newton-Raphson technique. The results are given in Table 1.

The term \( S \) of the asymptotic equation, which represents the limiting value of the overall stage efficiency for a column with a large number of stages, has been calculated from the characteristic roots given in Table 1. The results of these calculations are shown in Figure 3.

For the purpose of representation, the term \( B \) in the asymptotic expression is more conveniently written as
\[ B = -B' \frac{1}{\ln[(1 + (\gamma - 1)\varepsilon)]} \]  \quad (2.13a)

\[ B' = \frac{1}{\ln\gamma} \ln \left\{ [1 - \gamma Z_1 \frac{Z_1 - \varepsilon\eta}{1 - \varepsilon\eta}] \frac{\gamma}{\gamma - 1} \right\} \]  \quad (2.13b)

\( Z_1 \) is the real root different from unity of the transformed characteristic equation (Equation (2.12)). It depends on \( \gamma \) and \( \varepsilon\eta \).

Values of \( B' \) are shown in Figure 4.

Figures 3 and 4 are a useful appendix to the theory of periodic countercurrent processes developed by Horn [9]. With the aid of these figures it is possible to estimate rapidly and accurately the advantage of periodic operation for specific cases.

C. Accuracy of the Asymptotic Equation

Exact values of the relative overall stage efficiency are calculated by expanding \( w(z) \) (see Equation (2.3)) in a Taylor's series. The coefficients \( \lambda_\nu \) in this expansion are used in Equation (2.5) to calculate the stage efficiency.

The general expansion of \( w(z) \) in a Taylor's series for the coefficients \( \lambda_\nu \) is not practical even for a small number of stages, but the expansion can be carried out for specific cases with the aid of a digital computer. In order to accomplish the desired expansion one must have available a library of subroutines for addition, subtraction, multiplication and division of power series. With such a library of subroutines, \( f(z) \) can be expanded in a power series to give

\[ f(z) = b_0 + b_1 z + b_2 z^2 + \ldots \]  \quad (2.14)
Table 1. Real Characteristic Roots Different From 1.

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<td>0.9605</td>
<td>0.5770</td>
</tr>
<tr>
<td>1.40</td>
<td>0.7294</td>
<td>0.7464</td>
<td>0.7657</td>
<td>0.7875</td>
<td>0.8123</td>
<td>0.8405</td>
<td>0.8729</td>
<td>0.9098</td>
<td>0.9520</td>
<td>0.4890</td>
</tr>
<tr>
<td>1.50</td>
<td>0.6844</td>
<td>0.7043</td>
<td>0.7269</td>
<td>0.7525</td>
<td>0.7817</td>
<td>0.8150</td>
<td>0.8529</td>
<td>0.8960</td>
<td>0.9449</td>
<td>0.4172</td>
</tr>
<tr>
<td>1.60</td>
<td>0.6449</td>
<td>0.6675</td>
<td>0.6931</td>
<td>0.7222</td>
<td>0.7553</td>
<td>0.7930</td>
<td>0.8359</td>
<td>0.8844</td>
<td>0.9390</td>
<td>0.3580</td>
</tr>
<tr>
<td>1.70</td>
<td>0.6102</td>
<td>0.6350</td>
<td>0.6633</td>
<td>0.6955</td>
<td>0.7322</td>
<td>0.7740</td>
<td>0.8212</td>
<td>0.8745</td>
<td>0.9341</td>
<td>0.3088</td>
</tr>
<tr>
<td>1.80</td>
<td>0.5793</td>
<td>0.6062</td>
<td>0.6370</td>
<td>0.6720</td>
<td>0.7120</td>
<td>0.7573</td>
<td>0.8085</td>
<td>0.8660</td>
<td>0.9298</td>
<td>0.2676</td>
</tr>
<tr>
<td>1.90</td>
<td>0.5516</td>
<td>0.5805</td>
<td>0.6135</td>
<td>0.6511</td>
<td>0.6940</td>
<td>0.7427</td>
<td>0.7975</td>
<td>0.8587</td>
<td>0.9262</td>
<td>0.2328</td>
</tr>
<tr>
<td>2.00</td>
<td>0.5268</td>
<td>0.5574</td>
<td>0.5924</td>
<td>0.6325</td>
<td>0.6701</td>
<td>0.7298</td>
<td>0.7878</td>
<td>0.8523</td>
<td>0.9231</td>
<td>0.2032</td>
</tr>
</tbody>
</table>

The columns headed from 0.1 to 0.9 contain the value \(z_1\) of the root in the transformed plane. The column headed 1.0 contains \(ζ\).
FIG. 3 - LIMITING VALUES OF RELATIVE OVERALL STAGE EFFICIENCY FOR $\varepsilon = 1.0, 0.8, 0.6, 0.4, 0.2$
\( \varepsilon = 0.8 \)
\( \epsilon = 0.6 \)

\( \eta = 1.0 \)

\( 0.8 \)

\( 0.6 \)

\( 0.4 \)

\( 0.2 \)

\[ (N_\epsilon / N_\rho)_8 \]

\[ \gamma \]
FIG. 4 - THE VALUE OF $B'$ IN LOGARITHMIC SCALE AS FUNCTION OF $\epsilon \eta$ AND $\mu$
TABLE 2

Exact and Approximate Stage Efficiencies for $\zeta = 0.8$, $\eta = 1.0$

<table>
<thead>
<tr>
<th>$N$</th>
<th>$\gamma = 0.5$</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Exact value)</td>
<td>1.3252</td>
<td>1.3497</td>
<td>1.3657</td>
<td>1.3765</td>
<td>1.3840</td>
<td>1.3894</td>
<td>1.3934</td>
<td>1.3965</td>
<td>1.3989</td>
</tr>
<tr>
<td></td>
<td>(Asymp. value)</td>
<td>1.2439</td>
<td>1.3311</td>
<td>1.3601</td>
<td>1.3747</td>
<td>1.3834</td>
<td>1.3892</td>
<td>1.3933</td>
<td>1.3965</td>
<td>1.3989</td>
</tr>
<tr>
<td>$\gamma = 1.5$</td>
<td>(Exact value)</td>
<td>1.7026</td>
<td>1.7645</td>
<td>1.7928</td>
<td>1.8079</td>
<td>1.8171</td>
<td>1.8232</td>
<td>1.8275</td>
<td>1.8308</td>
<td>1.8333</td>
</tr>
<tr>
<td></td>
<td>(Asymp. value)</td>
<td>1.6705</td>
<td>1.7621</td>
<td>1.7926</td>
<td>1.8079</td>
<td>1.8171</td>
<td>1.8232</td>
<td>1.8275</td>
<td>1.8308</td>
<td>1.8333</td>
</tr>
</tbody>
</table>
With the coefficients in the expansion of \( f(z) \) known, \( \exp f(z) \) can be expanded to give

\[
\exp f(z) = c_0 + c_1 z + c_2 z^2 + \ldots \tag{2.15}
\]

It is shown in Appendix II that the coefficients \( c_j \) in the expansion of \( \exp f(z) \) are related to the coefficients \( b_j \) in the expansion of \( f(z) \) by the recurrence relations

\[
c_0 = \exp b_0 \tag{2.16a}
\]

\[
c_j = \sum_{k=0}^{j-1} \frac{(j - k)/j}{c_k b_{j-k}} \tag{2.16b}
\]

Once the expansion of \( \exp f(z) \) has been carried out, the expansion of \( w(z) \) is completed by further use of the subroutines mentioned previously. When the expansion is completed the resulting coefficients are used in Equation (2.5) to calculate the value of the relative overall stage efficiency.

Some typical results of the exact calculation are given in Table 2. These values should be compared to the values obtained by the asymptotic equation which are also given in Table 2. It is seen that the difference between the asymptotic and exact values is insignificant if the number of stages is greater than 2 or 3. The accuracy of the asymptotic equation is better demonstrated by Figure 5 where the error in the asymptotic values for a particular case is shown as a function of the number of stages. The error is here defined to be simply the difference between the exact and asymptotic value.

If the number of stages is greater than 2 or 3, the asymptotic equation is sufficiently accurate for all practical purposes and
the relative overall stage efficiency can be easily calculated from the values of S and B given in Figures 3 and 4. A digital computer must be used for the exact calculation. In addition, the direct calculation suffers badly from round off error if the number of stages is large.

The difficulty in the exact calculation is brought out by examining the behavior of the coefficients \( A_\nu \) in the expansion of \( w(z) \) for large \( \nu \). In Appendix III it is shown that for \( \gamma > 1 \) the following relation is true

\[
\lim_{\nu \to \infty} A_\nu = \frac{1}{1 - \gamma} \quad (\gamma < 1)
\]  

(2.17)

For \( \gamma > 1 \) the magnitude of the coefficients increases with increasing \( \nu \). In either case Equation (2.5) becomes indeterminate for large \( \nu \). In practice it is difficult to calculate columns with more than about 15 stages using the direct method even with double precision calculations.

The above discussion concerning the difficulty in the direct calculation of the stage efficiency serves only to emphasize the value of the asymptotic equation and the quantities S and B given in Figures 3 and 4.

D. The Characteristic Equation

Although an accurate estimate of the error involved in the asymptotic equation is difficult to obtain, a qualitative idea of the accuracy can be gained by investigating the position of the roots of the characteristic equation (Equation (2.9)) in the complex plane. Horn [9] has shown that there are two and only two
FIG. 5-ERROR OF ASYMPTOTIC EQUATION IN LOG SCALE FOR $\varepsilon = 0.2$, $\eta = 1.0$ AS FUNCTION OF $N_p$
real roots of the characteristic equation. One of these roots is equal unity and for the other real root $\zeta$ the following relations hold:

$$\zeta > 1 \quad \text{for } \gamma < 1 \quad (2.18a)$$

$$\zeta < 1 \quad \text{for } \gamma > 1 \quad (2.18b)$$

For $\gamma = 1$ the root $z = 1$ is a double root. Furthermore, the modulus $R$ of the complex root nearest the origin is greater than the modulus of either of the real roots. That is

$$R > \max (1, \zeta) \quad (2.19)$$

If the contour $C$ in Equation (2.7) is taken to be a circle about the origin of radius $R$, then the summation in this equation has only two terms corresponding to the real roots 1 and $\zeta$ and the integral can be estimated by

$$\left| \frac{1}{2\pi i} \oint_C \frac{w(z)}{z^{\nu+1}} \, dz \right| \leq \frac{M}{R^\nu} \quad (2.20)$$

The coefficients $A_\nu$ are thus given by

$$A_\nu = \frac{1}{1 - \gamma} + \frac{1}{1 - \gamma \varepsilon^2 \zeta} \frac{1}{\eta + \zeta(1 - \eta)} \cdot \frac{1}{\varepsilon^{\nu-1} + \text{Exp.}} \quad (2.21)$$

The term denoted by Exp. in Equation (2.21) represents the contribution from the contour integral. It decreases faster with $\nu$ than the second term on the right hand side, as can be seen from Equations (2.19) and (2.20). Thus of particular importance is the modulus of the complex root of the characteristic equation nearest the origin in relation to the largest of the real roots 1 and $\zeta$. The error in the asymptotic equation is approximately proportional to the reciprocal modulus of this root to the power $N_p$. 
Horn [9] has shown that all complex roots of the characteristic equation (which occur in conjugate pairs) must lie inside a circle with center on the real axis and passing through the points \( z = 0 \) and the largest of the two real roots. In this section it will be shown that all complex roots must lie outside a circle of radius

\[
\rho_H = \frac{1}{2} \frac{1 + \frac{1 - \varepsilon}{\gamma \eta}}{\ln \frac{1}{1 - \varepsilon \eta}}
\]  

(2.22)

(see Figure 6) again with center on the real axis and passing through the point \( z = 0 \).

There are infinitely many complex roots inside the half crescent region formed by the two circles described above. This region can be divided into subregions, \( R_n \), each of which contains one and only one complex root. The subregions are defined with the aid of two additional circles of radius

\[
\rho_n = \frac{1}{2} \frac{\gamma \eta^2 \varepsilon}{(1 - \varepsilon)^2} \frac{1}{2 \pi n} \]

(2.23a)

and

\[
\rho'_n = \frac{1}{2} \frac{\gamma \eta^2 \varepsilon}{(1 - \varepsilon)^2} \frac{1}{(2n + \frac{1}{2}) \pi}
\]

(2.23b)

\( n = \pm 1, \pm 2, \ldots \)

respectively; each with center on the vertical line \( x = 1/(1 - \varepsilon) \) and passing through the point \((1/(1 - \varepsilon), 0)\). Each subregion, \( R_n \), is then determined by the intersection of two half crescent regions as illustrated in Figure 6 in which the first two complex roots have been calculated for the case \( \gamma = 1.5, \varepsilon = 0.9 \) and \( \eta = 0.8 \).
FIG. 6 - LOCATION OF THE COMPLEX ROOTS OF THE CHARACTERISTIC EQUATION FOR $\gamma = 1.5$, $\epsilon = 0.9$, $n = 0.8$
THE REGIONS $R_n$ ARE SHADED
In this case it is seen that the modulus of the complex root nearest the origin is much larger than the larger of the two real roots. This in turn implies that the asymptotic equation should be very accurate even for a small number of stages.

As \( \varepsilon \) approaches unity, \( (\gamma \neq 1) \), the circles defined with the aid of Equations (2.22) and (2.23) become straight lines. In this case the subregions \( R_n \) are rectangular and are defined by the relations

\[
\max(1, \zeta) < \text{Re}(z) < 1 + \frac{1}{\gamma \eta} \ln \left[ \frac{1}{1 - \eta} \right] \quad (2.24a)
\]

\[
\frac{2n\pi}{\gamma \eta} < \text{Im}(z) < \frac{(2n + 1/2)\pi}{\gamma \eta} \quad (2.24b)
\]

The special case \( \varepsilon = 1 \) and \( \eta = 1 \) has been discussed by Horn [8] previously.

The remainder of this section will be concerned with proving the above statements concerning the roots of the characteristic equation. For \( \varepsilon \gamma \neq 1 \) it is convenient to consider the roots of the transformed characteristic equation (Equation (2.12)) or equivalently the zeroes of the function

\[
\Psi(Z) = \exp^{\alpha \gamma (Z - 1)} - (1 + \alpha) + \alpha/Z \quad (2.25)
\]

and then relate these values to the characteristic roots in the \( z \)-plane by means of the bilinear transformation --- Equation (2.11).

Real and imaginary parts of the variable \( Z \) are denoted by \( X \) and \( Y \) respectively, i.e.

\[
Z = X + iY \quad (2.26)
\]

In the following discussion it is sufficient to consider only positive \( Y \) since the complex roots occur in conjugate pairs. It
has been shown previously [9] that the transformed characteristic equation has only two real roots $X_0$ and $X_1$ and these roots satisfy the relations

$$X_0 = 1, \quad X_1 > 1 \quad \text{for} \quad \gamma < 1 \quad (2.27a)$$

$$X_1 = 1, \quad X_0 < 1 \quad \text{for} \quad \gamma > 1 \quad (2.27b)$$

and for any complex root $Z_c$, the real part $X_c$ must satisfy the relation

$$X_c > X_1 \quad (2.28)$$

Consideration of Equation (2.25) shows that the real part of any complex root must also satisfy the relation

$$X_c \leq 1 + \frac{1}{\alpha \gamma} \ln(1 + \alpha) \quad (2.29)$$

Equation (2.29) can be established by examining the functions

$$F_1(Z) = \exp^{\alpha \gamma (Z - 1)} \quad (2.30)$$

and

$$F_2(Z) = 1 + \alpha - \alpha / Z \quad (2.31)$$

The image of a line of constant $X$ under $F_1(Z)$ is a circle about the origin of radius (see Figure 7)

$$r = \exp^{\alpha \gamma (X - 1)} \quad (2.32)$$

Under $F_2(Z)$, the image of a line of constant $X$ is a circle with center on the real axis, passing through the point $(1 + \alpha, 0)$ and lying to the left of the line $\text{Re}(F_2) = 1 + \alpha$ as indicated in Figure 7. From the figure it is evident that the two circles do not intersect unless $X$ satisfies Equation (2.29). Since $F_1(Z)$ and $F_2(Z)$ are the left and right hand sides of the transformed
FIGURE 7 - IMAGE OF A LINE OF CONSTANT X IN THE $F_1$ (SOLID) OR $F_2$ (DASHED) PLANE.

FOR $X < 1 + \frac{1}{a\gamma} \ln (1 + \alpha)$ THE CIRCLES INTERSECT.

FOR $X = 1 + \frac{1}{a\gamma} \ln (1 + \alpha)$ THE CIRCLES ARE TANGENT AT THE POINT $[1 + \alpha, 0]$.

FOR $X = 1 + \frac{1}{a\gamma} \ln (1 + \alpha)$ THE CIRCLES DO NOT INTERSECT.
characteristic equation, it follows that Equation (2.29) must be satisfied for any complex root.

Equation (2.25), written in terms of real and imaginary parts is

\[ Y(Z) = U + i \, V \]

(2.33a)

where

\[ U = \exp^{\alpha \gamma (X-1)} \cos(\alpha \gamma Y) - (1 + \alpha) + \frac{\alpha X}{X^2 + Y^2} \]

(2.33b)

and

\[ V = \exp^{\alpha \gamma (X-1)} \sin(\alpha \gamma Y) \cdot \frac{\alpha Y}{X^2 + Y^2} \]

(2.33c)

For positive \( Y \) and values of \( X \) satisfying Equation (2.28), \( U \) and \( V \) cannot be simultaneously zero unless \( Y \) satisfies the relation

\[ \frac{2\pi n}{\alpha \gamma} < Y < \frac{(2n + 1/2)\pi}{\alpha \gamma} \quad n = 1, 2, \ldots \]

(2.34)

It follows from Equations (2.28), (2.29) and (2.34) that the complex roots of the transformed characteristic equation must lie in certain rectangular regions of the \( Z \)-plane. With the help of the principle of the argument, it will now be demonstrated that each of these (infinitely many) regions contains one and only one root.

The principle of the argument is a theorem from complex variable theory [18] which allows one to determine the number of zeroes and poles of a function inside a closed contour \( C \) in the complex plane by examining the behavior of the function along the contour. If the function \( Y(Z) \) is not zero at any point on the contour, then the principle of the argument is

\[ \frac{1}{2\pi i} \oint_C [\text{Arg} \, Y(z)] = (Q - P) \]

(2.35)

Here \( Q \) is the number of zeroes and \( P \) is the number of poles of
\( \mathcal{Y}(Z) \) inside the contour and \( \Delta_c [\text{Arg } \mathcal{Y}(Z)] \) represents the change in the argument of \( \mathcal{Y}(Z) \) as the contour is traversed in the positive (counterclockwise) direction.

In the case of Equation (2.25) the only pole in the finite \( Z \)-plane is at the origin. Thus, if the contour does not encircle the origin, the principle of the argument for this case reduces to

\[
\frac{1}{2\pi} \Delta_c [\text{Arg } \mathcal{Y}(Z)] = Q \tag{2.36}
\]

With the exception of the case \( n = 0 \), which requires special consideration, the contours \( c_n \) in Equation (2.36) will be chosen as indicated in Figure 8a. It has already been shown that there can be no roots with real part greater than

\[
x^* = 1 + \frac{1}{\alpha \gamma} \ln(1 + \alpha) \tag{2.37}
\]

In the figure the rectangular region has been extended to

\[
x^{**} = 1 + \frac{1}{\alpha \gamma} \ln(1 + \alpha) + \sigma/\alpha \gamma \tag{2.38}
\]

by adding the term \( \sigma/\alpha \gamma \) to \( x^* \). The constant \( \sigma \) will be defined later and is introduced for convenience.

To apply Equation (2.36), the behavior of \( \mathcal{Y}(Z) \) as \( Z \) travels around the closed curve \( c_n \) must be investigated. The reader may verify that for \( n > 0 \) and any value of \( \sigma > 0 \), the signs of the real and imaginary parts of \( \mathcal{Y}(Z) \) at the points (1) through (4) on \( c_n \) are as indicated below.
FIGURE 8 - THE CLOSED CONTOURS $C_n$ USED TO ISOLATE THE ROOTS OF THE TRANSFORMED CHARACTERISTIC EQUATION BY THE PRINCIPLE OF TO THE ARGUMENT.

(a) $n > 0$    (b) $n = 0$
Table 3. *Sign of the Real and Imaginary Parts of $Y(Z)$*

*At the Points Indicated on the Contour $C_n$ (Figure 8)*

<table>
<thead>
<tr>
<th>Point 1</th>
<th>Point 2</th>
<th>Point 3</th>
<th>Point 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Real Part, $U$</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Imag. Part, $V$</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

As $Z$ varies along $C_n$ from point (1) to point (2), $V$ is always negative while $U$ changes from negative to positive (see Figure 9). It may be possible for $U$ to change signs more than once as $Z$ moves along this part of the contour, but even if this should happen there must be a net increase in the argument of $Y(Z)$ since $V$ remains negative.

The choice (see Appendix IV)

$$\sigma = \ln \frac{2}{\sqrt{3}}$$

(2.39)

is sufficient to insure that as $Z$ moves along $C_n$ from point (2) to point (3), $U$ and $V$ change in such a manner that

when $V = 0$, then $U > 0$  \hspace{1cm} (2.40a)

and when $U = 0$, then $V > 0$  \hspace{1cm} (2.40b)

since at point (3) $U < 0$ and $V > 0$, conditions (2.40) are sufficient to insure that there is a net increase in the argument of $Y(Z)$ as $Z$ changes from point (2) to point (3). Furthermore, as $Z$ travels along $C_n$ from point (3) to point (4) and then from point (4) to point (1), the contour in the $Y(Z)$-plane must close while $U$ remains negative. The resulting contour in the $Y(Z)$-plane must be of the general shape of that shown in Figure 9. From the figure it is seen that as $Z$ progresses around the contour $C_n$
the corresponding contour in the \( \Psi(Z) \)-plane encircles the origin one time, and from Equation (2.36) it follows that each contour \( C_n \) with \( n > 0 \) contains one and only one zero of the function \( \Psi \) or equivalently one and only one root of the transformed characteristic equation.

The procedure outlined above must be modified slightly in order to determine the number of zeroes of \( \Psi \) inside the rectangular region adjacent to the real axis. In this case the contour \( C_0 \) is deformed slightly to take into account the zero of \( \Psi(Z) \) at \( Z = X_1 \) (see Figure 8b). For \( Z \) near \( X_1 \) the contour is taken as a circular arc of radius \( \delta \). Thus, along the portion of the contour from point (5) to point (1) in Figure 8b \( Z \) is given by

\[
Z - X_1 = \delta \exp^{i\theta}
\]

where

\[
\delta \ll 1
\]

For \( Z \) on this portion of the contour, \( \Psi(Z) \) may be expanded in a Taylor's series about the real zero \( X_1 \) to yield

\[
\Psi(Z) = \frac{d\Psi}{dZ} \bigg|_{X_1} \delta \exp^{i\theta} + \frac{1}{2!} \left( \frac{d^2\Psi}{dZ^2} \right)_{X_1} \delta^2 \exp^{i2\theta} + 0(\delta^3)
\]

Now for real \( Z \), i.e. \( Z = X \)

\[
\left( \frac{d\Psi}{dZ} \right)_{X} = \alpha \gamma \exp^{\alpha \gamma(X-1)} - \frac{\alpha}{X^2}
\]

Equation (2.43) has only one zero and this zero must lie between \( X_0 \) and \( X_1 \) (for \( \gamma \neq 1 \)). This fact, together with the observation that the right-hand side of Equation (2.43) is positive for large \( X \), leads to the relation
FIGURE 9 - CONTOUR IN THE $\Psi(Z)$-PLANE CORRESPONDING TO THE CONTOUR $C_n (n > 0)$ IN THE Z-PLANE SHOWN IN FIGURE 8a
\[
\frac{dy}{dz} \bigg|_{x_1} > 0 \quad (\gamma \neq 1) \quad (2.44)
\]

For \( \gamma = 1 \), \( x_1 \) is a double root and the relations

\[
\frac{dy}{dz} \bigg|_{x_1} = 0 \quad (\gamma = 1) \quad (2.45)
\]

\[
\frac{d^2y}{dz^2} \bigg|_{x_1} > 0 \quad (\gamma = 1) \quad (2.45b)
\]

hold. It follows from Equations (2.42), (2.44), and (2.45) that

for \( Z \) on the portion of the contour from point (5) to point (1), \( \Psi(Z) \) behaves like

\[
\Psi(Z = x_1 + \delta \exp^{i\theta}) \approx \pm (\nu\delta\exp^{i\theta}) \quad (\gamma \neq 1) \quad (2.46a)
\]

or

\[
\Psi(Z = x_1 + \delta \exp^{i\theta}) \approx (\nu\delta^2\exp^{i2\theta}) \quad (\gamma = 1) \quad (2.46b)
\]

The discussion of the behavior of \( \Psi(Z) \) around the rest of the contour is similar to that given before for \( n > 0 \). The general shape of the contour in the \( \Psi(Z) \)-plane is shown in Figure 10. In the figure the portion of the contour near the origin has been exaggerated. From the figure it is seen that as the contour in the \( Z \)-plane is closed by going from point (5) to point (1), the corresponding contour in the \( \Psi(Z) \)-plane is closed without encircling the origin and, therefore, it follows from the principle of the argument that there are no zeroes of \( \Psi(Z) \) inside the rectangular strip adjacent to the real axis.

It has been shown that the complex roots of the transformed characteristic equation must lie in the rectangular regions of the \( Z \)-plane defined by Equations (2.28), (2.29), and (2.34). Further-
FIGURE 10 - CONTOUR IN THE $\Psi(Z)$-PLANE
CORRESPONDING TO THE CONTOUR $C_0$ IN THE $Z$-PLANE IN
FIGURE 8b.
(a) for $\gamma \neq 1$ and (b) for $\gamma = 1$
more, the principle of the argument has shown that -- except for
the region adjacent to the real axis which contains no complex
roots -- each of these regions contains one and only one root. The
regions in the $z$-plane corresponding to these rectangular regions
in the $z$-plane are determined by means of Equation (2.11). From
this equation it can be shown that for $\varepsilon \neq 1$, a line $X = \text{constant}$
in the $z$-plane transforms into a circle in the $z$-plane with center
on the real axis and passing through the point $(1/(1-\varepsilon), 0)$ whose
equation is

$$
[x - \frac{1}{1/(1-\varepsilon)} - r_x]^2 + y^2 = r_x^2
$$

where

$$
r_x = \frac{1}{2} \cdot \frac{\varepsilon}{(1-\varepsilon)^2} \cdot \frac{1 - \varepsilon \eta}{x-1 + \frac{1-\varepsilon}{1-\varepsilon}}
$$

Similarly, a line of $Y = \text{constant}$ in the $z$-plane ($\varepsilon \neq 1$) transforms
into a circle in the $z$-plane with center on the line $x = 1/(1-\varepsilon)$
and passing through the point $(1/(1-\varepsilon), 0)$ with equation

$$
[x - \frac{1}{1/(1-\varepsilon)}]^2 + (y - r_y)^2 = r_y^2
$$

where

$$
r_y = \frac{1}{2} \cdot \frac{\varepsilon(1 - \varepsilon \eta)}{(1-\varepsilon)^2 y}
$$

For $\varepsilon = 1$ ($\eta \neq 1$) the following relations are valid

$$
x = (X - \eta)/(1 - \eta)
$$

$$
y = Y/(1 - \eta)
$$

The statements made earlier concerning the location of the roots of
the characteristic equation follow directly from Equations (2.47)
and (2.48) or Equation (2.49) along with Equations (2.28), (2.29)
and (2.34).
III. THE EFFECT OF MIXING ON PERIODIC COUNTERCURRENT PROCESSES

A. Introduction

In the preceding chapter the stage efficiency of a periodically operated countercurrent process was studied for the case in which piston flow can be assumed for the liquid phase during the time of down transport. That is, there is no mixing between the liquids belonging to different stages during that time. In practice, a column can be operated in a formally equivalent manner if the liquid is transported in the following way. At the end of the period the bottom stage is emptied first, then the liquid in the stage above is transferred to the stage below, and so on, until the top stage is emptied. The top stage is then filled with fresh liquid phase (absorption) or is allowed to fill continuously with liquid from the condenser (distillation). With this method, mixing during the time of down transport can be completely avoided, but this kind of operation may be difficult in practice. If the liquid flows simultaneously in every stage mixing cannot be avoided; that is, the piston flow assumption is never actually realized.

In this chapter, the effect of mixing on the stage efficiency of a periodically operated column is investigated by modeling each stage, during the time of liquid transport, by a set of well stirred mixers in series. Complete mixing is assumed in the remainder of the period. The time \( t' \) of the down transport is assumed to be short compared to the remaining time \( \tau \) of the period.
B. General Theory of Periodically Operated Columns

Several methods have been employed to calculate the asymptotic behavior for periodically operated columns with no mixing. Horn [9] used the z-transform in order to obtain the following equation

\[
\frac{N\varepsilon}{N} = S + \frac{B}{N} + \text{Exp.}
\]  (3.1)

The results of the last chapter show that the exponential terms denoted by Exp. can be disregarded for columns with more than 2 or 3 stages. The quantities \( S \) and \( B \) depend on the separation factor \( \gamma \), the Murphree efficiency \( \varepsilon \), and the transport number \( \eta \). The method of the z-transform also shows that the general solution of the linear column equation is of the form

\[
x_{\gamma}(t) = \sum_{j=0}^{\infty} c_j f_j(t) a_j
\]  (3.2)

where the functions \( f_j(t) \) are certain eigenfunctions and the magnitudes \( a_j \) are the (infinitely many) roots of a transcendental eigenvalue equation. This equation always has a root \( a_0 = 1 \) corresponding to a column which is in complete equilibrium and a real root \( a_1 \) different from unity. The other roots are complex. It is the root \( a_1 \) which governs the behavior of the column for a large number of stages. The term \( S \) of Equation (3.1) is given by

\[
S = \frac{\ln a_1}{\ln[1 + (\gamma-1)\varepsilon]}
\]  (3.3)
The coefficients $c_j$ have also been determined by the $z$-transform for some particular processes [9]. The coefficient $c_1$ is directly connected with $B$ of Equation (3.1) and the coefficients $c_j$ with $j > 1$ appear in the exponential terms of Equation (3.1) and are thus of no great importance.

A cross flow column is formally equivalent to a periodically operated column with no mixing and transport number of unity [20]. Lewis [12], in his treatment of a cross flow column, intuitively assumed the correctness of the above statements concerning the eigenfunctions and therefore determined only the eigenfunction for $j = 1$ (but not $c_1$). The same treatment was used by Robinson and Engel [20] for the solution of more general problems in connection with periodic operations. This corresponds to calculation of the quantity $S$ in Equation (3.1). This quantity which gives the stage efficiency for a column with a large number of stages was also estimated for some processes by Sommerfeld et al [3,23]. In these references columns with a small number of stages were also calculated by numerical methods and the approach to the periodic state was simulated. Values of $S$ and $B$ for a certain class of processes have been determined by Horn [9] and in this work in the previous chapter.

For the problems considered in this chapter, the determination of $c_1$ and consequently $B$ is considerably more difficult than in the case where there is no mixing and where $\eta \leq 1$ which has been treated previously. Therefore, only $a_1$ will be determined but estimates of $B$ will be given by calculating columns with
various numbers of stages numerically. Only the important case of
difficult separations will be considered; that is where $\gamma$ is
close to unity.

C. The Basic Equations of the System

When the down transport of the liquid takes place, each
stage is divided into $m$ tanks, each of which has the volume $V/m$
(Figure 11). At the beginning of the down transport all conцен-
trations in these tanks are equal and equal to $x_{\gamma}(\tau)$. Thus,

$$
\xi_{\gamma j}(0) = x_{\gamma}(\tau) \quad j = 1, 2, \ldots, m \quad (3.4)
$$

The down transport is then described by the following differential
equations.

$$
\frac{V}{m} \frac{d\xi_{\gamma 1}}{dt} = -p \xi_{\gamma 1} + p\xi_{\gamma + 1 1} \quad (3.5a)
$$

$$
\frac{V}{m} \frac{d\xi_{\gamma j}}{dt} = -p[\xi_{\gamma j} - \xi_{\gamma j-1}] \quad j = 2, \ldots, m \quad (3.5b)
$$

In these equations $\xi$ and $p$ denote the composition and flow rate,
respectively, of the liquid during the down transport period. If $t'$
is the time of the down transport, the composition after mixing
is given by

$$
x_{\gamma}(0) = \frac{1}{m} \sum_{j=1}^{m} \xi_{\gamma j}(t') \quad (3.6)
$$

It will be assumed that

$$
t' \ll \tau
$$

so that the change of the composition of liquid due to vapor flow
during the down transport can be neglected.
FIGURE II - SCHEMATIC OF THE STIRRED TANK MODEL
USED TO REPRESENT THE DOWN TRANSPORT
OF LIQUID.
EACH TANK HAS VOLUME \( V/m \)
During the time in which there is only vapor transport the column is described by Equations (1.3) and (1.8), i.e.

\[
\frac{dx_v}{dt} = -q (y_v - y_{v-1}) 
\]  \hspace{1cm} (3.7a)

\[
y_v = Kx_v + (1 - \varepsilon) y_{v-1} \hspace{1cm} (3.7b)
\]

The periodicity condition is already implicit in the notation if \( x_v(0) \) and \( x_v(\tau) \) of Equations (3.6) and (3.4) are identical to the initial \( (t = 0) \) and end values \( (t = \tau) \) of the variable \( x_v \) in Equation (3.7).

The transport number \( \eta \) is defined as

\[
\eta = \frac{p t'}{V} \hspace{1cm} (3.8)
\]

This definition of the transport number is equivalent to that given previously for the case of plug flow. In both cases \( \eta \) denotes the ratio of the liquid transported per cycle to the liquid holdup of a stage. In this chapter \( \eta \) will be allowed to take on all positive values \( (0 \leq \eta < \infty) \) instead of only values between 0 and 1 as was the case in the previous chapter.

The separation factor \( \gamma \) is defined as

\[
\gamma = \frac{Kq\tau}{p t'} \hspace{1cm} (3.9)
\]

This definition is also equivalent to the previous definitions for a conventional column (Equation (1.6)) and a periodically operated column with no mixing (Equation (2.4)). In all cases \( \gamma \) denotes the equilibrium constant times the ratio of the vapor transported per cycle to the liquid transported per cycle.
D. The Eigenvalue Equation

In order to obtain the eigensolutions appearing on the right hand side of Equation (3.2) we shall determine solutions of the form

\[
\begin{align*}
x_\nu(t) &= a^\nu f(t) \\
y_\nu(t) &= a^\nu g(t) \\
\xi_{\nu j}(t) &= a^\nu h_j(t)
\end{align*}
\]  

(3.10a) (3.10b) (3.10c)

Putting Equation (3.10c) into Equation (3.5) under consideration of Equation (3.8) yields

\[
\begin{align*}
\frac{dh_1}{dt} &= \frac{\eta m}{t'} (-h_1 + a h_m) \\
\frac{dh_j}{dt} &= \frac{\eta m}{t'} (-h_j + h_{j-1}) & j = 2, 3, \ldots, m
\end{align*}
\]  

(3.11a) (3.11b)

The initial conditions are given by

\[
h_j(0) = f(\tau)
\]  

(3.12)

and from Equation (3.6) it follows that

\[
f(0) = \frac{1}{m} \sum_{j=1}^{m} h_j(t')
\]  

(3.13)

It is evident that for a given \( f(\tau) \) the quantity \( f(0) \) can be calculated by integration of the differential Equations (3.11a) and (3.11b). Since the differential equations are linear and homogeneous, the ratio \( f(0)/f(\tau) \) is determined by Equations (3.11) through (3.13) as a function of \( \eta, m, \) and \( a \). The ratio does not depend on \( t' \) as can be seen if \( t/t' \) is introduced as a new independent variable. The quantity \( f(0)/f(\tau) \) will be denoted by \( \xi \). Thus,
\[ f(0)/f(\tau) = \hat{\eta}(\eta, m, a) \quad (3.14) \]

Putting Equation (3.10a) and (3.10b) into Equation (3.7) yields

\[ \frac{df}{dt} = -q(1 - 1/a) g \quad (3.15a) \]

\[ g = \varepsilon K f + \frac{1}{a} \left( 1 - \varepsilon \right) \frac{1}{a} g \quad (3.15b) \]

Elimination of \( g \) from Equations (3.15a) and (3.15b) yields a homogenous first order differential equation for \( f \)

\[ \frac{df}{dt} = \frac{\varepsilon \eta (1 - a)}{a - (1 - \varepsilon)} \cdot \frac{f}{\tau} \quad (3.16) \]

which can be integrated easily. The result is given by

\[ f(\tau) = f(0) \exp \left[ \frac{\varepsilon \eta (1 - a)}{a - (1 - \varepsilon)} \right] \quad (3.17) \]

From Equations (3.14) and (3.17) the eigenvalue equation for \( a \) follows

\[ \hat{\eta}(\eta, m, a) = \exp \left[ \frac{\varepsilon \eta (a - 1)}{a - (1 - \varepsilon)} \right] \quad (3.18) \]

These ideas are easily illustrated for the special case of complete mixing (\( m = 1 \)) during the time of down transport. In this case it follows from Equations (3.11) through (3.14) that

\[ \hat{\eta}(\eta, 1, a) = \exp [\eta(a - 1)] \quad (3.19) \]

and therefore the eigenvalue equation for this case is

\[ \exp[\eta(a - 1)] = \exp \left[ \frac{\varepsilon \eta (a - 1)}{a - (1 - \varepsilon)} \right] \quad (3.20) \]

This equation is satisfied whenever \( a \) satisfies the equation

\[ \frac{\eta(1 - a)}{a - (1 - \varepsilon)} \left[ 1 + (\eta - 1)\varepsilon - a \right] = \pm 2\pi i n \quad n = 0, 1, \ldots \quad (3.21) \]
Equation (3.21) has two real roots

\[ a_0 = 1 \]  

(3.22a)

and

\[ a_1 = 1 + (\gamma - 1) \varepsilon \]  

(3.22b)

and infinitely many complex roots. For the case \( \gamma = 1 \), the root \( a = 1 \) is a double root. The distribution in the complex number plane of the roots of the eigenvalue equation is shown schematically in Figure 12.

From Equations (3.3) and (3.22b) it follows that the quantity \( S \) in Equation (3.3), which represents the limiting value of the relative overall stage efficiency for a column with infinitely many stages, is equal to unity in the case of complete mixing during the time of down transport. Numerical results to be presented later (see Figure 14) show that for a column with a finite number of stages and complete mixing the relative overall stage efficiency is less than unity.

This result shows that the advantages to be gained by periodic operation are nullified in the case of complete mixing and indicates the importance of plug flow during the liquid transport period. McWhirter [15], in his experimental studies with a small (6 inch) diameter laboratory column, found that the plug flow assumption was fairly realizable and obtained high stage efficiencies by periodic operation. On the other hand, pilot plant experiments by Schrodt, Sommerfeld, Martin, Parisot, and Chien [3,23] on a fifteen tray distillation column, twelve inches in diameter, failed to show an increased efficiency when operated periodically and indicate
FIGURE 12 - SCHEMATIC REPRESENTATION OF THE DISTRIBUTION IN THE COMPLEX \( \alpha \)-PLANE OF THE ROOTS OF THE EIGENVALUE EQUATION FOR THE CASE \( m = 1 \)
that liquid mixing during the time of down transport may be an important factor in a column of industrial size.

E. **Some Properties of the Function \( \psi(\eta, m, a) \)**

The solution of Equations (3.11) through (3.14) and the resulting eigenvalue equation for general \( \gamma \) and finite \( m \geq 1 \) is very difficult. Consequently, the remainder of this chapter will be concerned primarily with the important special case of difficult separations (\( \gamma \approx 1 \)). In what follows, the function \( \psi(\eta, m, a) \) (see Equation (3.14) for \( a = 1 \) and in the neighborhood of \( a = 1 \) will be of particular interest.

The function \( \psi(\eta, m, a) \) for \( a \approx 1 \) can be easily investigated by means of the Laplace transform. The Laplace transform of Equation (3.11) with initial conditions given by Equation (3.12) is

\[
(s + \eta m/t')H_1 - (a\eta m/t')H_m = f(\eta) \tag{3.23a}
\]

\[
-(\eta m/t')H_{j-1} + (s + \eta m/t')H_j = f(\eta) \tag{3.23b}
\]

\( j = 2, 3, \ldots, m \)

Here \( H_j \) denotes the Laplace transform of \( h_j \), i.e.,

\[
H_j = \int_0^\infty h_j(t) \exp^{-st} \, dt
\]

The quantities of interest, namely \( \psi(\eta, m, 1), \frac{d\psi}{da} \bigg|_{a=1} \) and \( \frac{d^2\psi}{da^2} \bigg|_{a=1} \) can be determined by differentiating Equation (3.23) with respect to \( a \) twice, taking the limit as \( a \) goes to 1, and summing the appropriate equations to form the desired quantities before inverting the transforms. Differentiation of Equation (3.23)
twice yields, after taking the limit as $a$ goes to 1
\[ (s + \tau m/t')H_{1}^{(1)} - (\tau m/t')H_{m}^{(1)} = (\tau m/t')H_{m}^{(1)} \]
\[ - (\tau m/t')H_{j-1}^{(1)} + (s + \tau m/t')H_{j}^{(1)} = 0 \quad j = 2, \ldots, m \]  
(3.24)

and
\[ (s + \tau m/t')H_{1}^{(2)} - (\tau m/t')H_{m}^{(2)} = (2\tau m/t')H_{m}^{(1)} \]
\[ - (\tau m/t')H_{j-1}^{(2)} + (s + \tau m/t')H_{j}^{(2)} = 0 \quad j = 2, \ldots, m \]  
(3.25)

The superscripts in these equations denote differentiation with respect to $a$ and all quantities are evaluated at $a = 1$.

Summation of Equations (3.23) (setting $a = 1$) yields, after consideration of the definition of $\hat{g}$ (see Equation (3.14)),
\[ \hat{g}(\tau, m, 1) = L^{-1} \left\{ 1/s \right\}_{t=t'} \]  
(3.26)

Here $L^{-1}\{F(s)\}$ denotes the inverse Laplace transform of $F(s)$. Proceeding in a similar manner, it follows from Equations (3.24) and (3.25) that
\[ \frac{d\hat{g}}{da} \bigg|_{a=1} = \frac{\tau}{f(\tau) t'} \cdot L^{-1} \{H_{m}/s\} \bigg|_{t=t'} \]  
(3.27)

and
\[ \frac{d^{2}\hat{g}}{da^{2}} \bigg|_{a=1} = \frac{2\tau}{f(\tau) t'} \cdot L^{-1} \{H_{m}^{(1)}/s\} \bigg|_{t=t'} \]  
(3.28)

The quantities $H_{m}$ and $H_{m}^{(1)}$ appearing in these equations can be determined from Equations (3.23) and (3.24). Equation (3.23) yields
\[ H_{m} = f(\tau) \frac{D_{1}}{D} \]  
(3.29)

and from Equation (3.24)
\[ H_m^{(1)} = \frac{D_2}{D} \]  

(3.30)

where \( D, D_1, \) and \( D_2 \) are the determinants

\[
D = \begin{vmatrix}
(s+\tau_m/t') & 0 & 0 & \cdots & 0 & (-\tau_m/t') \\
(-\tau_m/t') & (s+\tau_m/t') & 0 & \cdots & 0 & 0 \\
0 & (-\tau_m/t') & (s+\tau_m/t') & \cdots & 0 & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
0 & 0 & 0 & \cdots & (-\tau_m/t') & (s+\tau_m/t')
\end{vmatrix} \tag{3.31}
\]

\[
D_1 = \begin{vmatrix}
(s+\tau_m/t') & 0 & 0 & \cdots & 0 & 1 \\
(-\tau_m/t') & (s+\tau_m/t') & 0 & \cdots & 0 & 1 \\
0 & (-\tau_m/t') & (s+\tau_m/t') & \cdots & 0 & 1 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
0 & 0 & 0 & \cdots & (-\tau_m/t') & 1
\end{vmatrix} \tag{3.32}
\]

\[
D_2 = \begin{vmatrix}
(s+\tau_m/t') & 0 & 0 & \cdots & 0 & (\tau_m/t')H_m \\
(-\tau_m/t') & (s+\tau_m/t') & 0 & \cdots & 0 & 0 \\
0 & (-\tau_m/t') & (s+\tau_m/t') & \cdots & 0 & 0 \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
0 & 0 & 0 & \cdots & (-\tau_m/t') & 0
\end{vmatrix} \tag{3.33}
\]
The determinant $D$ can be evaluated easily by expanding in terms of the minors of the first row. The result is

$$D = (s + \eta m/t')^m - (\eta m/t')^m$$  \hspace{1cm} (3.34)

Expansion of $D_1$ in terms of the minors of the first row yields

$$D_1 = (s + \eta m/t')\begin{vmatrix} (s + \eta m/t') & 0 & \ldots & 0 & 1 \\ (-\eta m/t') & (s + \eta m/t') & \ldots & 0 & -1 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \ldots & (\eta m/t') & 1 \end{vmatrix} + (\eta m/t')^{m-1}$$  \hspace{1cm} (3.35)

An inductive argument then leads to the conclusion that

$$D_1 = (s + \eta m/t')^{m-1} + (\eta m/t')(s + \eta m/t')^{m-2} + \ldots + (\eta m/t')^{m-2}(s + \eta m/t') + (\eta m/t')^{m-1}$$  \hspace{1cm} (3.36)

which can be written in the form

$$D_1 = (s + \eta m/t')^m - (\eta m/t')^m$$  \hspace{1cm} (3.37)

Expansion of the determinant $D_2$ in terms of the minors of the last column leads directly to the relation

$$D_2 = (\eta m/t')^m$$  \hspace{1cm} (3.38)

Equations (3.27) and (3.28) together with Equations (3.29), (3.30), (3.34), (3.37), and (3.38) yield the desired transforms

$$\frac{d\delta}{da} \bigg|_{a=1} = \frac{\eta}{t} L^{-1} \left[ 1/s^2 \right] \bigg|_{t=t'}$$  \hspace{1cm} (3.39)

$$\frac{d^2\delta}{da^2} \bigg|_{a=1} = \frac{2\eta}{t} L^{-1} \left[ \frac{1}{s^2} \cdot \frac{1}{[(st'/\eta m) + 1]^{m-1}} \right] \bigg|_{t=t'}$$  \hspace{1cm} (3.40)
Expressions for $\mathcal{E}(\eta, m, 1)$ and $\left.\frac{d\mathcal{E}}{da}\right|_{a=1}$ follow directly from Equations (3.26) and (3.39). Thus,

$$\mathcal{E}(\eta, m, 1) = 1$$  \hspace{2cm} (3.41)

$$\left.\frac{d\mathcal{E}}{da}\right|_{a=1} = \eta$$  \hspace{2cm} (3.42)

Expressions for $\left.\frac{d^2\mathcal{E}}{da^2}\right|_{a=1}$ can be obtained from Equation (3.40) quite easily for the special cases $m = 1$ and $m = \infty$.

For the case $m = 1$

$$\left.\frac{d^2\mathcal{E}}{da^2}\right|_{a=1} = \left[\frac{\eta}{t}\right]^2 \cdot L^{-1}\left\{\frac{2}{s^3}\right\}|_{t=t'}$$  \hspace{2cm} (3.43)

which is easily inverted to give

$$\left.\frac{d^2\mathcal{E}}{da^2}\right|_{a=1} = \eta^2$$  \hspace{2cm} (3.44)

Taking the limit as $m \to \infty$ in Equation (3.40) gives

$$\lim_{m \to \infty} \left.\frac{d^2\mathcal{E}}{da^2}\right|_{a=1} = 2L^{-1}\left\{\frac{1}{s^2} \cdot \frac{\exp(-s)}{1 - \exp(-s)}\right\}|_{t=\eta}$$  \hspace{2cm} (3.45)

In going from Equation (3.40) to Equation (3.45), the relations

$$\lim_{m \to \infty} \left(\beta/m + 1\right)^m = \exp^\beta$$  \hspace{2cm} (3.46)

and

$$L^{-1}\{F(s/\beta)\} = \beta f(\beta t)$$  \hspace{2cm} (3.47)

have been used. Equation (3.45) can be inverted to yield

$$\lim_{m \to \infty} \left.\frac{d^2\mathcal{E}}{da^2}\right|_{a=1} = k[2\eta - (k + 1)]$$

$$k \leq \eta \leq k + 1; \hspace{1cm} k = 0, 1, 2, \ldots$$  \hspace{2cm} (3.48)

For finite $m > 1$ it is convenient to use Equation (3.47) again and write Equation (3.40) in the form

$$\left.\frac{d^2\mathcal{E}}{da^2}\right|_{a=1} = \frac{2}{m} \cdot L^{-1}\{F(s)\}|_{t=\eta m}$$  \hspace{2cm} (3.49a)
with
\[ F(s) = \frac{1}{s^2} \frac{1}{(s + 1)^m - 1} \] (3.49b)

\( F(s) \) has a third order pole at \( s = 0 \) and \( m - 1 \) first order poles at
\[ s_k = -[1 - \cos(2k\pi/m)] + i \sin(2k\pi/m) \] (3.50)
\[ k = 1, 2, \ldots, m-1 \]

\( F(s) \) can be expanded in terms of partial fractions to give (see Appendix V)
\[ F(s) = \frac{m^2-1}{12m} \cdot \frac{1}{s} - \frac{m-1}{2m} \cdot \frac{1}{s^2} + \frac{1}{m} \cdot \frac{1}{s^3} + \sum_{k=1}^{m-1} \frac{M_k}{s - s_k} \] (3.51)

where
\[ M_k = -\frac{1}{2m} \cdot \frac{1}{1 - \cos(2k\pi/m)} \] (3.52)

Equation (3.51) can be inverted easily to give the desired expression for \( \frac{d^2 \hat{\phi}}{da^2} \bigg|_{a=1} \). Thus
\[ \frac{d^2 \hat{\phi}}{da^2} \bigg|_{a=1} = \Lambda(\eta, m) \] (3.53a)

where
\[ \Lambda(\eta, m) = \frac{1}{6} \left( \frac{m^2}{m} - 1 \right) - \frac{m - 1}{m^2} \eta + \eta^2 - \rho_m(\eta) \] (3.53b)

For even \( m \)
\[ \rho_m = \frac{1}{2m^2} \exp(-2\eta m) + \frac{1}{2} \sum_{k=1}^{(m-2)/2} \frac{\exp[-\eta m (1 - \cos(2k\pi/m))] \cdot \cos(\eta m \sin(2k\pi/m))}{1 - \cos(2k\pi/m)} \] (3.53c)
and for uneven \( m \)

\[
\rho_m = \frac{2}{m^2} \sum_{k=1}^{(m-1)/2} \left[ \frac{\exp[-\eta_0(1-\cos(2k\pi/m))] \sin(2k\pi/m)}{1 - \cos(2k\pi/m)} \right] (3.53d)
\]

F. The Asymptotic Stage Efficiency for Difficult Separations \((\gamma \ll 1)\)

From Equation (3.41) it follows that for any \( \gamma, \varepsilon, \) and \( \eta \), one solution of the eigenvalue equation (Equation (3.18)) is given by

\[
a = 1
\]

By using Equation (3.42) it can be seen that for \( \gamma = 1 \) the root \( a = 1 \) is a double root. By expanding the left side of Equation (3.18) with respect to \((a - 1)\) and the right side with respect to \((a - 1)\) and \((\gamma - 1)\) and using Equation (3.53) it can be seen that for \( \gamma \) close to 1 the real root \( a_1 \) is also close to 1 and is given by

\[
a_1 - 1 = \frac{2\varepsilon \eta}{\varepsilon \Lambda + \eta(2 - \varepsilon \eta)} (\gamma - 1) + 0 [\gamma - 1]^2 \] (3.54)

By putting this into Equation (3.3) and by taking the limit as \( \gamma \to 1 \) one obtains

\[
S_{\gamma = 1} = \frac{2\eta}{\varepsilon \Lambda + \eta(2 - \varepsilon \eta)} \] (3.55)

By means of this equation the asymptotic stage efficiency for difficult separations \((\gamma \ll 1)\) can be calculated easily. All equations in the remainder of this section and the next refer to the case \( \gamma = 1 \) and hence the subscript \( \gamma = 1 \) will be dropped for brevity. For the graphical representation of results it is convenient to use the function
\[ \Omega_m(\eta) = (\eta^2 - \Lambda)/\eta \] (3.56)

which is related to \( S \) by

\[ \frac{2}{\varepsilon} \left[ 1 - \frac{1}{S} \right] = \Omega_m(\eta) \] (3.57)

In Figure 13 \( \Omega_m(\eta) \) is represented graphically for various \( m \).

In order to cover the interval \( 0 \leq \eta < \infty \) the function has been plotted against \( \eta/(1 + \eta) \). The curve for \( m = \infty \) which is shown in the diagram corresponds to piston flow in each stage. This case has been treated already by Horn [9] for \( \eta \leq 1 \) and by Robinson and Engel [20] for unrestricted \( \eta \).

It can be seen that \( \Omega_m(\eta) \) varies between 0 and 1 and consequently \( S \) varies between 1 and \( 2/(2 - \varepsilon) \) For given \( \varepsilon \) the asymptotic stage efficiency \( S \) increases with increasing \( \Omega_m(\eta) \).

Thus, the larger \( m \), the larger is the asymptotic stage efficiency for given \( \varepsilon \) and \( \eta \). In order to make \( \Omega_m(\eta) \), and consequently \( S \), maximal by choice of \( \eta \) one can set \( \eta = 1 \) for \( m = \infty \) (the values \( m = 2, 3, \ldots \) are also possible in this case) and for finite \( m \geq 1 \), at least up to 20, \( \eta \) should be made as large as possible. From Equations (3.53), (3.56) and (3.57) it is seen that

\[ \lim_{\eta \to \infty} S = \frac{2^m}{2^m - \varepsilon(m-1)} \] (3.58)

As noted before, for \( m = 1 \) there is no influence of \( \eta \) on the asymptotic stage efficiency which equals 1 in this case.
G. **Columns With a Finite Number of Stages**

The value $S$ which has been calculated in the previous section gives the stage efficiency for columns with very many stages ($N_p \to \infty$). In order to study how this value is approached, absorption columns (equivalent to stripping columns) have been calculated numerically by the following method. The Equations (3.5) can be integrated easily analytically. In this way it is possible to express $x_{\nu}(0)$ as a linear combination of the $x_{\mu}(\tau)$ with $\nu \leq \mu \leq N_p + 1$ where $x_{N_p + 1}(\tau)$ represents the composition of the liquid entering the column. The coefficients of the linear combination are elementary functions of $\eta$. Similarly, by integrating Equations (3.7) analytically, $x_{\nu}(\tau)$ can be expressed as a linear combination of the $x_{\mu}(0)$ with $0 \leq \mu \leq \nu$. The coefficients are elementary functions of $\gamma$, $\epsilon$, and $\eta$. Combining both relations gives a set of linear equations in the unknown variables $x_{\nu}(0), 1 \leq \nu \leq N_p$. The details of this calculation will be investigated in the following chapter.

After the periodically operated column has been calculated, the number of stages $N_e$ of a conventional column with the same overall performance and Murphree efficiency $\epsilon$ is determined. The stage efficiency is then the ratio $N_e/N_p$. This stage efficiency is plotted against $1/N_p$ (see Figures (14) - (16)) since $N_e/N_p$ becomes linear in $1/N_p$ for $N_p \to \infty$ according to Equation (3.1).

These calculations confirmed the general theory excellently as can be seen from Figures (14) through (16). In these figures
the values \( S \) calculated from Equations (3.53) and (3.55) are plotted on the ordinate \((1/N_P = 0)\). It can be seen that these asymptotic points lie on the straight lines extrapolating the points corresponding to finite but large \( N_p \) calculated numerically. Values of \( B \) can be estimated from the slopes of these straight lines.

All \( B \) values calculated are negative and are cetaris paribus the smaller the larger \( \eta \) (see Figures (14) - (16)). This agrees with the results for \( m = 0 \) and \( 0 \leq \eta \leq 1 \) which have been obtained by Horn [9] previously. In this case,

\[
B = -\frac{1}{3} \cdot \frac{\varepsilon \eta^2}{(2 - \varepsilon \eta)^2} \tag{3.59}
\]

This equation shows that \( B \) decreases with increasing \( \eta \) for given \( \varepsilon \). All numerical calculations indicate that this is also true for finite \( m \) but no proof of this is available. Since \( B \) apparently decreases with increasing \( \eta \) and since for systems with \( m \leq 10 \) (see Figure (13)) \( S \) increases with increasing \( \eta \) it can be expected that the stage efficiency has a maximum as a function of \( \eta \) for certain systems. This conjecture is born out by the results shown in Figure (17). Here the stage efficiency has been calculated for \( m = 4 \) and for various \( N_p \) as a function of \( \eta \).

It can be seen that the \( \eta \) corresponding to the maximum stage efficiency may be larger than 1. Obviously, this is not possible in the case \( m = \infty \). In this case \( N_{e'}/N_p \) is given by Horn [9]

\[
N_{e'}/N_p = \frac{2}{2 - \varepsilon \eta} - \frac{1}{3N_p} \cdot \frac{\varepsilon \eta^2}{(2 - \varepsilon \eta)^2} \quad 0 \leq \eta \leq 1 \tag{3.60}
\]
FIGURE 14 - Relative overall stage efficiency for $\gamma = 1$, $\epsilon = 1$ of a periodically operated absorption column with a finite number of stages and complete mixing; i.e., $m = 1$, during the time of liquid transport. The value for the asymptotic efficiency, $S$, is 1 in this case.
FIGURE 15 - Relative overall stage efficiency for $m=4$, $\gamma=1$, $\epsilon=1$ of a periodically operated absorption column with a finite number of stages. Values of $S$ calculated from Equations 3.53 and 3.55 are plotted on the ordinate ($1/N_p = 0$).
FIGURE 16 - Relative overall stage efficiency for $\gamma = 1$, $\varepsilon = 1$ of a periodically operated absorption column with a finite number of stages and plug flow; i.e., $m = \infty$, during the time of liquid transport. The value for the asymptotic efficiency, $S$, is 2 in this case.
FIGURE 17- Relative overall stage efficiency for $m = 4$, $\gamma = 1$, $\varepsilon = 1$ of a periodically operated absorption column with various numbers of stages as a function of $\eta$. 

$1 - \lambda (p_N / \theta_N)$
The exponential terms have been neglected here which is entirely justifiable for $N_p > 2$. It is easy to show that the right-hand side of this equation increases monotonously with increasing $\eta$ in the interval [0,1]; hence the maximum of the stage efficiency for $m = \infty$ occurs at $\eta = 1$. This fact has also been demonstrated by Sommerfeld et al [3,23] by carrying out numerical calculations for a column with $N_p = 5$. However, as has been mentioned before, in a column in which mixing occurs it is quite possible that the optimum $\eta$ (maximizing $N_e/N_p$) may be larger than 1.
IV. NUMERICAL CALCULATION OF STAGE EFFICIENCY

A. Introduction

In the preceding chapter the general theory of periodically operated columns was developed and an analytical expression for the stage efficiency was given for the case of difficult separations. Results of numerical calculations were also presented which confirmed the general theory excellently. In this chapter the method used to obtain these numerical results is explained. In addition, more justification of the general theory is given by simulating a periodically operated column for particular cases and comparing the results with those obtained by using only the first two eigenfunctions.

B. Numerical Calculation of the Overall Stage Efficiency

The relative overall stage efficiency of a column with a finite number of stages is calculated by first calculating the performance of a periodic column with \( N_p \) stages and then determining the number of stages, \( N_e \), of a conventional column with the same performance and Murphree efficiency \( \varepsilon \). The stage efficiency is then the ratio \( N_e/N_p \) of the number of stages required by the two processes. Direct calculation of the performance of a periodic column is not difficult for specific cases, but does require the use of a digital computer. Except for the special case \( \gamma = 1 \), the performance of a conventionally operated column with Murphree efficiency \( \varepsilon \) is determined by the Kremser equation, i.e.

\[
\frac{x_1 - x_0}{N_e + 1} + (x_1 - x_0) \frac{\gamma}{\gamma - 1} [1 + (\gamma - 1)\varepsilon]^{N_e} \tag{4.1a}
\]
For the special case $\gamma = 1$, the performance is determined by

$$x_{N_p+1} = x_1 + \varepsilon N_e (x_1 - x_0) \tag{4.1b}$$

In this chapter it is shown that for a periodically operated column the quantities $x_o, x_1, x_{N_p+1}$ can be related to one another by an equation of the form

$$(x_1 - x_{N_p+1}) = G \cdot (x_o - x_{N_p+1}) \tag{4.2}$$

Comparison of Equations (4.1) and (4.2) yields the desired expressions for the relative overall stage efficiency

$$\frac{N_e}{N_p} = \frac{1}{N_p} \ln \left( \frac{\nu G}{\gamma (1 - G)} \right) \tag{4.3a} \quad (\gamma \neq 1)$$

or

$$\frac{N_e}{N_p} = \frac{1}{N_p} \cdot \frac{G}{\varepsilon (1 - G)} \tag{4.3b} \quad (\gamma = 1)$$

C. A Linear Equation for the Initial Composition

In order to calculate the periodic state of a column, the initial composition of each stage must be chosen correctly. One method of calculating the correct initial compositions is to simulate the approach to the periodic state. This was done for a particular case in Chapter 1. Another method will be described here.

During the time in which only vapor is transported, the column is described by Equations (1.3) and (1.8). The solution of this set of linear differential equations will be discussed later and
is of the form

$$\mathbf{x}(t) - x_o = \mathbf{C}(t) [\mathbf{x}(0) - x_o] \quad (4.4)$$

In this equation $\mathbf{x}$ is the $N_p$-dimensional composition vector whose

$\nu$th element is $x_{\nu}(t)$. $\mathbf{C}(t)$ is an $(N_p \times N_p)$ matrix function of
time which will be calculated later. It is a function of $\gamma$, $\epsilon$, $\eta$ and the ratio $t/\tau$. $\mathbf{x}(0)$ represents any arbitrary initial comp-
position and not necessarily the initial condition which corresponds
to the periodic state.

In a similar manner, Equation (3.5) which describes the column
during the time of liquid transport, can be integrated analytically.
The compositions in the $(m \cdot N_p)$ stirred tanks used to simulate the
down transport of liquid are given by an equation of the form

$$\mathbf{\xi}(t) - x_{N_p+1} = \mathbf{Q}(t) [\mathbf{\xi}(0) - x_{N_p+1}] \quad (4.5)$$

$\mathbf{\xi}(t)$ is the $(m \cdot N_p)$-dimensional vector function of time whose

elements are the compositions of the stirred tanks

$$\mathbf{\xi}(t) = [\xi_{1m}(t), \ldots, \xi_{11}(t), \xi_{2m}(t), \ldots, \xi_{Nm}(t), \ldots, \xi_{N_p}(t)]$$

(4.6)

The double subscripts on the elements of $\mathbf{\xi}$ should not be confused
with the subscripts of an $(N_p \times m)$ matrix. $\mathbf{Q}(t)$ is an $(m \cdot N_p)$
$x (m \cdot N_p)$ matrix function of time.

The average composition in each stage during the time of down
transport is then given by

$$\mathbf{\Xi}(t) - x_{N_p+1} = \mathbf{Q}(t)[\mathbf{\Xi}(0) - x_{N_p+1}] \quad (4.7)$$

The elements of $\mathbf{\Xi}(t)$ are formed from the elements of $\mathbf{\xi}(t)$ by
the relation

$$\Xi(t) = \frac{1}{\mu} \sum_{\mu=1}^{m} \xi_{\mu}(t)$$

(4.8)

and the elements of the $N_p \times N_p$ matrix function $\Xi(t)$ are certain combinations of the elements of $\mathcal{Q}(t)$.

The vectors $\mathbf{x}_0$ and $\mathbf{x}_{N_p+1}$ in these equations are constant vectors, every element of which is equal to $\mathbf{x}_0$ or $\mathbf{x}_{N_p+1}$ and whose dimension is $N_p$ or $m \cdot N_p$ depending on the equation.

The approach to the periodic state can be simulated using Equations (4.4) and (4.7). Starting from an arbitrary initial condition, Equation (4.4) is used to calculate the initial condition for Equation (4.7). Equation (4.7) in turn is then used to calculate a new initial condition for the next cycle, and so on until the periodic state is reached.

Equations (4.4) and (4.7) can also be used to calculate the initial conditions corresponding to the periodic state directly.

This initial condition is denoted by $\mathbf{x}^P(0)$. Since

$$\Xi(0) = \mathbf{x}(\tau)$$

(4.9)

it follows from Equations (4.4) and (4.9) that

$$\Xi(0) - \mathbf{x}_{N_p+1} = \mathcal{Q}(\tau)[\mathbf{x}^P(0) - \mathbf{x}_{N_p+1}] - [\mathcal{Q}(\tau) - \mathcal{I}][\mathbf{x}_0 - \mathbf{x}_{N_p+1}]$$

(4.10)

Equations (4.7), (4.10) and the periodicity condition

$$\Xi(t') = \mathbf{x}^P(0)$$

(4.11)

can then be combined to yield the following expression for the initial condition vector which corresponds to the periodic state

$$\mathbf{x}^P(0) - \mathbf{x}_{N_p+1} = [\mathcal{Q}(\tau) - \mathcal{Q}^{-1}(t')]^{-1} [\mathcal{Q}(\tau) - \mathcal{I}][\mathbf{x}_0 - \mathbf{x}_{N_p+1}]$$

(4.12)
D. Solution of the Column Equations

The matrix function $\mathfrak{C}(t)$ in Equation (4.4), which describes the column during the time when only vapor is transported, can be derived with the aid of the Laplace transform. After considerable algebraic manipulation, Equations (1.3) and (1.8) yield the following recurrence relation

$$-rac{x_1(s)}{x_0} = \frac{x_1(0) - x_0}{s + \gamma \varepsilon \tau/\tau}$$  \hspace{1cm} (4.13a)

and

$$-rac{x_{\nu+1}(s) - x_0}{x_0} = \frac{(1 - \varepsilon)s + \gamma \varepsilon \tau/\tau}{s + \gamma \varepsilon \tau/\tau} \cdot \left[ x_\nu(s) - x_0 \right]$$

$$+ \frac{\gamma \left[ x_{\nu+1}(0) - x_0 \right] - (1 - \varepsilon) \left[ x_\nu(0) - x_0 \right]}{s + \gamma \varepsilon \tau/\tau}$$  \hspace{1cm} (4.13b)

Here $\mathfrak{x}_\nu(s)$ denotes the Laplace transform of $x_\nu(t)$. An inductive argument can be used to show that Equation (4.13b) can be written in the form

$$-rac{x_\nu(s)}{x_0} = \frac{\gamma \varepsilon \tau}{\tau} \sum_{\mu=1}^{\nu-1} \frac{\left[ ((1 - \varepsilon)s + \gamma \varepsilon \tau/\tau)^{\nu-(\mu+1)} \right]}{s + \gamma \varepsilon \tau/\tau} \cdot \left[ x_\mu(0) - x_0 \right]$$

$$+ \frac{x_\nu(0) - x_0}{s + \gamma \varepsilon \tau/\tau} \quad \nu = 2, \ldots, N_p$$  \hspace{1cm} (4.14)

Equations (4.13a) and (4.14) are conveniently written in vector form

$$\mathfrak{x}(s) - x_0 \mathfrak{C}(s)[x(0) - x_0]$$  \hspace{1cm} (4.15)
$C(s)$ is the matrix

$$
C(s) = \begin{bmatrix}
0 & 0 & \cdots & 0 & 0 \\
C_1(s) & 0 & \cdots & 0 & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots \\
C_k(s) & \cdots & C_2(s) & C_1(s) & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots \\
C_{N_P-1}(s) & \cdots & C_k(s) & \cdots & C_2(s) \\
C_{N_P}(s) & C_{N_P-1}(s) & \cdots & C_k(s) & \cdots
\end{bmatrix}
$$

$C(s)$, (4.16)

The scalar functions $C_k(s)$ are given by

$$C_1(s) = \frac{1}{s + \gamma \varepsilon \eta / \tau}$$

$$C_k(s) = \frac{\gamma \varepsilon^2 \eta}{\tau} \left[ \frac{(1 - s) s + \gamma \varepsilon \eta / \tau}{s + \gamma \varepsilon \eta / \tau} \right]^{k-2} \frac{1}{(k - 1 - j)!} \left( \frac{\gamma \varepsilon^2 \eta}{\tau} \right)^{k-1-j} \frac{(k - 1 - j)!}{(s + \gamma \varepsilon \eta / \tau)^{k-j}}$$

Inversion of $C(s)$ or equivalently the $N_P$ scalar functions $C_k(s)$ yields the matrix function $C(t)$ in Equation (4.4). $C_1(s)$ can be inverted by inspection to give

$$C_1(t) = \exp^{-\gamma \varepsilon \eta t / \tau}$$

The inversion of $C_k(s)$ for $k \geq 2$ is easily accomplished by first expanding the numerator of Equation (4.17b) in powers of $(s + \gamma \varepsilon \eta / \tau)$.

This gives

$$C_k(s) = \sum_{j=0}^{k-2} \binom{k-2}{j} \frac{(1 - s)^j}{(k - 1 - j)!} \left( \frac{\gamma \varepsilon^2 \eta}{\tau} \right)^{k-1-j} \frac{(k - 1 - j)!}{(s + \gamma \varepsilon \eta / \tau)^{k-j}}$$

Equation (4.19) can be inverted immediately to give the functions $C_k(t)$.
Finally, the matrix function $\mathcal{Q}(t)$ in equation (4.7) is obtained by combining the elements $A_k(t)$ of $\mathcal{Q}(t)$ according to Equation (4.8). The result is

$$
\mathcal{Q}(t) = \begin{bmatrix}
D_1(t) & D_2(t) & \ldots & D_k(t) & \ldots & D_{N_p-1}(t) & D_{N_p}(t) \\
0 & D_1(t) & D_2(t) & \ldots & D_k(t) & \ldots & D_{N_p-1}(t) \\
\vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\
0 & \ldots & 0 & D_1(t) & D_2(t) & \ldots & D_k(t) \\
\vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\
0 & \ldots & 0 & \ldots & 0 & \ldots & D_1(t) \\
0 & \ldots & \ldots & 0 & \ldots & 0 & D_1(t)
\end{bmatrix}
$$

(4.25)

The functions $D_k(t)$ are given in terms of the functions $A_k(t)$ by the rather complicated looking relations

$$
D_1(t) = \sum_{j=1}^{m} \frac{(m+1-i)}{m} A_j(t) \quad (4.26a)
$$

$$
D_k(t) = A_{(k-1)m+1} + \sum_{j=1}^{m-1} \frac{m-j}{m} [A_{(k-1)m+1+j} + A_{(k-1)m+1-j}] \quad (4.26b)
$$

E. The Performance of a Periodic Column

The initial composition given by Equation (4.12) can be used to calculate the composition $\xi_{1M}$ of the liquid leaving the bottom of the column and consequently the quantity $G$ in Equation (4.2) from which the relative overall stage efficiency is determined. The composition of the liquid leaving the bottom of the column is given by (see Equation (4.5))
\[
\xi_{1m}(t) - x_{N_p+1} = \sum_{\nu=1}^{N_p} [x_{\nu}(\tau) - x_{N_p+1}] \sum_{\mu=1}^{m} A(t) \quad \text{(4.27)}
\]

(since \(\xi_{\nu\mu}(0) = x_{\nu}(\tau)\) \(\mu = 1, 2, \ldots, m\))

But Equations (4.9), (4.10) and (4.12) can be combined to give

\[
x(\tau) - x_{N_p+1} = \left[ [A(\tau) - A(t')]^{-1} - I \right] [x_0 - x_{N_p+1}]
\]

from which it follows that

\[
x_{\nu}(\tau) - x_{N_p+1} = T_{\nu}(\gamma, \varepsilon, \eta, m) \cdot (x_0 - x_{N_p+1}) \quad \text{(4.29)}
\]

where \(T_{\nu}\) is the sum of the elements of the \(\nu\)th row of the matrix which multiplies \((x_0 - x_{N_p+1})\) on the right hand side of Equation (4.28). Thus

\[
\xi_{1m} - x_{N_p+1} = [x_0 - x_{N_p+1}] \sum_{\nu=1}^{N_p} T_{\nu} \sum_{\mu=1}^{m} A(t) \quad \text{(4.30)}
\]

The average composition of the liquid leaving the bottom of the column, \(x_1\), is given by

\[
x_1 = \frac{\int_0^{t'} \xi_{1m}(t) \, dt}{t'}
\]

so that

\[
(x_1 - x_{N_p+1}) = (x_0 - x_{N_p+1}) \cdot G \quad \text{(4.32)}
\]
Using the definition of $A_k(t)$ (Equation (4.24)) $G$ is given by

$$G = \sum_{\nu=1}^{N_P} \sum_{\mu=1}^{\nu} \frac{1}{t^2} \int_0^{\eta_m} \exp^{-\eta_m t} \cdot (\eta_m t')^{\nu-1} m + (\mu-1) \, dt$$

and by a change of variables

$$G = \frac{1}{\eta_m} \sum_{\nu=1}^{N_P} \sum_{\mu=1}^{\nu} \int_0^{\eta_m} \exp^{-t} \cdot (t)^{\nu-1} m + (\mu-1) \, dt$$

The integrals in Equation (4.34) can be calculated successively by the formulas

$$\int_0^{\eta_m} \exp^{-t} \, dt = 1 - \exp^{-\eta_m}$$

$$\int_0^{\eta_m} \exp^{-t} (t)^n \, dt = n \int_0^{\eta_m} \exp^{-t} \cdot (t)^{n-1} \, dt - (\eta_m)^n \exp^{-\eta_m}$$

F. **Comments Concerning Columns with a Finite Number of Stages**

It is evident from the discussion already given in this chapter that a digital computer is required in order to calculate the value of the overall stage efficiency for a periodically operated column with a finite number of stages by directly integrating the differential equations which describe the column. The efficiency can be calculated with a computer either by simulating the column or by the method outlined above, which determines the periodic state directly.
To calculate the efficiency by simulating the column, values of the two inputs, $x_0$ and $x_{N_p+1}$, are specified and the simulation is carried out with arbitrary initial conditions until the periodic state is reached. The average value of the composition of the liquid leaving the column, $x_1$, is then determined by numerical integration. Once $x_1$ has been determined the values $x_0$, $x_1$ and $x_{N_p+1}$ are used in Equation (4.2) to determine the quantity $G$, which in turn is used in Equation (4.3) to calculate the value of the overall stage efficiency. The direct determination of the stage efficiency requires the calculation of the three matrices $Q(t'), C(\tau)$ and $\hat{A}(t')$ as well as the two inverse matrices indicated in Equation (4.28). Once these matrices have been found, the value of the stage efficiency is computed as described in section (IV-E).

The method used to find the stage efficiency is determined by the computer time required by the two methods. Several cases were calculated in order to compare the methods. In all cases it was found that the direct method was much faster than simulation. The approach to the periodic state is generally very slow and this more than offsets the time required to compute the inverse matrices in the direct method. Fortunately, it is seldom necessary to consider columns with more than about ten stages and thus the matrix inversions do not consume excessive computer time. Values of the stage efficiency calculated by the direct method have already been presented in Figures (14) through (17).
G. **Comparison of Exact and Eigenfunction Solutions**

According to the theory presented in Chapter III, the solution of the linear column equations is of the form

\[ x_\nu(t) = \sum_{j=0}^{\infty} c_j f_j(t) a_j^\nu \]  \hspace{1cm} (4.36)

Furthermore, except for stages near the ends of the column, the behavior is almost completely governed by the first two eigenfunctions \( f_0 \) and \( f_1 \) corresponding to the real eigenvalues \( a_0 \) and \( a_1 \). The other infinitely many eigenfunctions which correspond to the complex eigenvalues, are important only for stages near the ends of the column. The asymptotic value of the stage efficiency for difficult separation was determined for some cases in the preceding chapter by calculating \( a_0 \) (which always equals unity) and \( a_1 \), but \( c_0 \) and \( c_1 \) were not calculated. Here, values of the constants \( c_0 \) and \( c_1 \) are estimated for the case of complete mixing from results obtained by simulating the column and the two solutions compared.

Consider a periodically operated column with complete mixing during the down transport period. During the time when only vapor is transported the column is described by Equations (1.3) and (1.8). During the time of down transport the column is described by

\[ \frac{d\xi_\nu}{dt} = \frac{1}{t^1} (\xi_{\nu+1} - \xi_\nu) \]  \hspace{1cm} (4.37)
Equations (1.3), (1.8) and (4.37) together with Equation (3.10) and the periodicity condition give the eigenvalue equation and the eigenfunctions. The eigenvalue equation for this case is given by Equation (3.20), i.e.

\[
\exp \left[ \frac{\gamma \sigma \eta (a-1)}{a - (1-\varepsilon)} \right] = \exp \left[ \eta (a - 1) \right] \tag{4.38}
\]

The two real eigenvalues are \( a_0 = 1 \) and \( a_1 = 1 + (\gamma-1)\varepsilon \). The eigenfunctions can be written as

\[
f_i = \exp \left[ \frac{\gamma \sigma \eta (1 - a_i)}{a_i - (1 - \varepsilon) \tau} \right] \tag{4.39a}
\]

\[
h_i = \exp \left[ \eta (a_i - 1) \frac{(t - t')}{t'} \right] \tag{4.39b}
\]

Thus the solution of the linear column equations is of the form

\[
x_v(t) = \sum_{i=0}^{\infty} c_i a_i^v \cdot \exp \left[ \frac{\gamma \sigma \eta (1 - a_i)}{a_i - (1 - \varepsilon) \tau} \right] \tag{4.40a}
\]

\[
y_v(t) = \sum_{i=0}^{\infty} c_i a_i^v \cdot \frac{\varepsilon \sigma a_i}{a_i - (1 - \varepsilon)} \exp \left[ \frac{\gamma \sigma \eta (1 - a_i)}{a_i - (1 - \varepsilon) \tau} \right] \tag{4.40b}
\]

\[
\xi_v(t) = \sum_{i=0}^{\infty} c_i a_i^v \cdot \exp \left[ \eta (a_i - 1) \frac{(t - t')}{t'} \right] \tag{4.40c}
\]

Now consider a material balance on the reference component around the first \( v \) stages over a complete cycle. This gives

\[
\gamma \chi_0 - \chi_1 = \frac{\gamma}{K} \int_0^{\tau} y_v(t) \, dt - \int_0^{t'} \xi_{v+1} \, dt \tag{4.41}
\]

where \( \chi_1 \) denotes the average component of the liquid leaving the
column. This equation together with Equations (4.40a) and (4.40b) for \( y_0 \) and \( \xi_{N+1} \) and the eigenvalue equation gives the constant \( c_0 \) in terms of \( x_0 \) and \( x_1 \). The result is

\[
c_0 = \frac{\gamma x_0 - x_1}{\gamma - 1}
\]  
(4.42)

For a given value of \( x_0 \) and \( x_{N+1} \) the column can be simulated by integrating the differential equations and the value of \( x_1 \) determined. Thus \( c_0 \) can be determined for a particular case from the result of the simulation.

\( c_1 \) is determined in a much more crude manner. For a stage away from the ends of the column the composition is given approximately by the first two eigenfunctions. Thus

\[
x_0(t) = c_0 + c_1 \left[ 1 + \varepsilon(\gamma-1) \right]^\gamma \exp\left[-\varepsilon(\gamma-1)t/\tau\right] \quad (4.43a)
\]

and \( \xi_0(t) = c_0 + c_1 \left[ 1 + \varepsilon(\gamma-1) \right]^\gamma \exp\left[-\varepsilon(\gamma-1)(t'-t)/t'\right] \quad (4.43b)\)

Simulation of the column gives \( c_0 \) according to Equation (4.42).

Also for any time \( t_1 \) the quantity \( x_0(t_1) \) or \( \xi_0(t_1) \) is known from the simulation. Only the quantity \( c_1 \) in Equation (4.43) is unknown and may be solved for.

In order to compare the exact and eigenfunction solutions, a twenty stage column was simulated for the case \( \gamma = .85, \eta = .8, \varepsilon = 1.0, x_0 = .4, x_{N+1} = .1, \) and \( K = 1.5 \). From the results of the simulation it was found that \( c_0 = 0.0939 \). \( c_1 \) was calculated from the Equation (4.43) for several different times based on the composition in the tenth stage. The value of \( c_1 \) corresponding
FIGURE 18.-COMPARISON OF EXACT AND EIGENFUNCTION SOLUTIONS FOR A 20 STAGE COLUMN WITH COMPLETE MIXING DURING THE DOWN TRANSPORT PERIOD.
to the different times was very nearly constant and the average value was \( c_1 = .2245 \).

The exact and eigenfunction solutions are compared in Figure (18) where the compositions in the stages at a particular time are plotted against the stage number. From the figure it is seen that the shape of the two solutions is very similar. The two solutions have been forced to agree at \( v = 10 \) because of the method used to calculate \( c_1 \). Nevertheless, except for the first few stages the solutions agree quite well even with the crude method used to calculate \( c_1 \).
TABLE OF NOMENCLATURE

<table>
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<th>Roman Letter</th>
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<tr>
<td>A</td>
<td>defined by Equation 2.6 or Equation 4.22</td>
</tr>
<tr>
<td>a_j</td>
<td>root of transcendental eigenvalue equation,</td>
</tr>
<tr>
<td></td>
<td>Equation 3.18</td>
</tr>
<tr>
<td>B</td>
<td>parameter in asymptotic expression for</td>
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<tr>
<td></td>
<td>stage efficiency (see Equations 2.10 and 3.1)</td>
</tr>
<tr>
<td>B'</td>
<td>defined by Equation 2.13</td>
</tr>
<tr>
<td>b_j</td>
<td>constant defined by Equation 2.14</td>
</tr>
<tr>
<td>C</td>
<td>contour in the complex number plane</td>
</tr>
<tr>
<td>C_k</td>
<td>defined by Equation 4.16</td>
</tr>
<tr>
<td>c_j</td>
<td>constant defined by Equation 2.15 or 3.2</td>
</tr>
<tr>
<td>D</td>
<td>defined by Equation 3.31</td>
</tr>
<tr>
<td>D_k</td>
<td>defined by Equation 3.32, 3.33 or 4.25</td>
</tr>
<tr>
<td>Exp.</td>
<td>denotes terms which decrease exponentially</td>
</tr>
<tr>
<td></td>
<td>with increasing number of stages</td>
</tr>
<tr>
<td>F</td>
<td>defined by Equation 2.30, 2.31 or 3.49</td>
</tr>
<tr>
<td>f</td>
<td>defined by Equation 2.3</td>
</tr>
<tr>
<td>f_j</td>
<td>eigenfunction corresponding to the eigenvalue</td>
</tr>
<tr>
<td></td>
<td>a_j. See Equation 3.2, 3.10 and 3.17</td>
</tr>
<tr>
<td>G</td>
<td>defined by Equation 4.2</td>
</tr>
<tr>
<td>g</td>
<td>defined by Equation 3.10</td>
</tr>
<tr>
<td>H_j</td>
<td>denotes Laplace transform of h_j</td>
</tr>
<tr>
<td>h_j</td>
<td>defined by Equation 3.10</td>
</tr>
<tr>
<td>K</td>
<td>equilibrium constant, defined by Equation 1.1</td>
</tr>
<tr>
<td>L</td>
<td>constant occurring in linearized form of</td>
</tr>
<tr>
<td></td>
<td>nonlinear equilibrium relations (see Equation 1.1)</td>
</tr>
<tr>
<td>M</td>
<td>defined by Equation 2.20</td>
</tr>
</tbody>
</table>
**Greek Letter**

- $\alpha$: defined by Equation 2.12
- $\gamma$: separation factor, equals equilibrium constant times ratio of vapor transported per cycle to liquid transported per cycle

- $t'$: time required to carry out liquid transport
- $U$: defined by Equation 2.33b
- $u$: z-transform of $x$
- $V$: liquid holdup of a stage or defined by Equation 2.33c
- $v$: z-transform of $y$
- $w$: defined by Equation 2.3
- $X$: real part of the complex variable $Z$
- $X^*$: defined by Equation 2.37
- $X^{**}$: defined by Equation 2.38
- $x$: mole or mass fraction of reference substance in liquid phase; may also denote real part of complex variable $z$
- $x_e$: respective fraction in liquid phase entering column
- $x_0$: defined by Equation 1.5
- $x^p(0)$: initial composition vector corresponding to periodic state
- $Y$: imaginary part of complex variable $Z$
- $y$: mole or mass fraction of reference substance in vapor phase; may also denote imaginary part of complex variable $Z$
- $Z$: defined by Equation 2.11
- $Z_1$: for $\gamma \neq 1$, real root of Equation 2.12a which differs from 1; for $\gamma = 1$, $Z_1 = 1$. 
\( \Delta \) represents change in argument of a complex valued function as the contour \( C \) is transversed in the counterclockwise direction (see Equation 2.35)

\( \delta \) small positive quantity, defined by Equation 2.41

\( \varepsilon \) Murphree efficiency

\( \zeta \) for \( \gamma \neq 1 \), real zero of \( \psi(z) \) which differs from 1; for \( \gamma = 1 \), \( \zeta = 1 \).

\( \eta \) transport number. Ratio of liquid transported per cycle to the liquid holdup of a stage

\( \theta \) defined by Equation 2.41

\( \Lambda \) defined by Equation 3.53

\( \mu, \nu \) stage number

\( \Xi \) vector defined by Equation 4.7

\( \xi \) composition of liquid during down transport period

\( \rho_m \) defined by Equation 3.53

\( \sigma \) defined by Equation 2.39

\( \tau \) interval of time during which no liquid transport takes place

\( \bar{\psi} \) defined by Equation 3.14

\( \phi \) defined by Equation 2.8

\( \Psi \) transformed eigenvalue equation, defined by Equation 2.25

\( \psi \) eigenvalue equation, defined by Equation 2.8

\( \Omega_m \) defined by Equation 3.56

\( \mathcal{C} \) matrix which describes a periodic column during the time of liquid transport (see Equation 4.5)
\( C \) matrix which describes a periodic column during the time when only vapor is transported (see Equation 4.4)

\( \mathcal{L} \) matrix defined by Equation 4.7

\( \mathcal{L}(f) \) denotes Laplace transform of function \( f \)
BIBLIOGRAPHY


APPENDIX I

Relation Between the Murphree Efficiency and Mass Transfer Coefficient

The relationship between the Murphree stage efficiency and the more basic concept of an overall mass transfer coefficient is investigated here. In particular the applicability of such efficiencies to unsteady state processes is studied.

Consider a single stage of a stagewise separation apparatus as represented in Figure (19). The molar (mass) holdup of the light phase in the stage is denoted by $V_l$ and that of the heavy phase by $V$. The molar (mass) flow rates of the light and heavy phases through the stage are denoted by $q$ and $p$ respectively. In the actual case, the phases will be dispersed in one another but it is assumed that the total interfacial area is constant.

If the holdup of both the light and heavy phases can be assumed constant then an unsteady state material balance on the reference component yields, for the light phase

$$\frac{dy}{dt} = q(y_{y-1} - y) + N(y, y) \quad (A.I.1a)$$

and for the heavy phase

$$\frac{dx}{dt} = p(x_{y+1} - x) - N(y, y) \quad (A.I.1b)$$

In these equations, the quantities $y$ and $x$ denote the bulk compositions of the reference component in the light and heavy phases, $y$ and $x$ stand for the composition of the reference
FIGURE 19 - SCHEMATIC REPRESENTATION OF ONE STAGE OF A COUNTERCURRENT STAGEWISE SEPARATION PROCESS
component at the interface between the two phases and are related to each other by the equilibrium relationship. The function $N(y^1_v, y_v)$ represents the rate of mass transfer of the reference component across the total interfacial area.

For many systems the rate of mass transfer of a component across the interface can be assumed to be proportional to the difference between the bulk concentration of the component and the concentration at the interface. Such a situation is shown in Figure (20) for the case in which the reference component is being transferred from the heavy phase to the light phase. The function $N(y^1_v, y_v)$ can be written in the form

$$N(y^1_v, y_v) = \lambda_L (y^1_v - y_v) = \lambda_H (x_v - x^*_v) \quad (A1.2)$$

In this equation $\lambda_L$ and $\lambda_H$ are overall mass transfer coefficients based on the light and heavy phases respectively. If the equilibrium relation for the system is linear, the interfacial compositions can be eliminated from Equation (A1.2) to yield

$$N(y^1_v, y_v) = \Lambda_L (y^*_v - y_v) = \Lambda_H (x_v - x^*_v) \quad (A1.3)$$

where $y^*_v$ is the vapor composition in equilibrium with $x_v$, and $x^*_v$ is the liquid composition in equilibrium with $y_v$.

Equation (A1.3) has a limited theoretical basis for steady state but can also be used for unsteady state if the holdup of the transferred component in the region near the interface is negligible with respect to the amount transferred [22]. This is equivalent to the statement that the amount of material leaving
FIGURE 20 - CONCENTRATION PROFILES NEAR AN INTERFACE
one phase is equal to the amount entering the other phase.

Using the overall mass transfer coefficient based on the light phase in Equation (AI.1), the following equations are obtained

\[
V' \frac{dy^*}{dt} = q\left(y_{N-1} - y_v^*\right) + \Lambda_L \left(y_v^* - y_v\right) \quad (AI.4a)
\]

\[
V \frac{dx}{dt} = p\left(x_{N+1} - x_v^*\right) - \Lambda_L \left(y_v^* - y_v\right) \quad (AI.4b)
\]

If the process is steady state or if the holdup of the light phase is negligible, Equation (AI.4a) becomes an algebraic equation and may be rearranged to give

\[
y_v = \frac{\Lambda_L}{q} y_v^* + \frac{1}{1 + \frac{\Lambda_L}{q}} y_{v-1} \quad (AI.5)
\]

In many systems the quantity \(\frac{\Lambda_L}{q}\) is very nearly constant [17] and Equation (AI.5) can be written

\[
y_v = \varepsilon K_v + (1 - \varepsilon) y_{v-1} \quad (AI.6)
\]

where \(\varepsilon\) is the Murphree efficiency.

If the process is steady state or if the mass holdup of either of the phases is negligible, a Murphree efficiency can be defined in terms of the appropriate mass transfer coefficient. If the process is unsteady state and the mass holdup of neither of the phases is negligible the Murphree efficiency is not valid.
APPENDIX II

Taylor's Series Expansion of $\exp f(z)$

Let

$$r(z) = \exp f(z)$$ \hspace{1cm} (AII.1)

Then it can be established by induction that the $n$th derivative of $r(z)$ is given by

$$r^{(n)} = \sum_{k=0}^{n-1} \binom{n-1}{k} r^{(k)} f^{(n-k)}$$ \hspace{1cm} (AII.2)

Here superscripts indicate differentiation with respect to $z$ and the quantities $\binom{n-1}{k}$ are binomial coefficients.

Equation (2.16) follows directly from Equation (AII.2) and the definitions

$$b_j = \frac{1}{j!} f^{(j)}(0)$$ \hspace{1cm} (AII.3a)

$$c_j = \frac{1}{j!} r^{(j)}(0)$$ \hspace{1cm} (AII.3b)

Thus, only the validity of Equation (AII.2) need be discussed. The equation is obviously true for $n = 1$. Assuming the truth for $n$ and taking the derivative yields

$$r^{(n+1)} = \sum_{k=0}^{n-1} \binom{n-1}{k} r^{(k)} f^{(n+1-k)} + \sum_{k=0}^{n-1} \binom{n-1}{k} r^{(k+1)} f^{(n-k)}$$ \hspace{1cm} (AII.4)

By shifting the index in the second summation and making use of the relation
\[ \binom{n-1}{k-1} + \binom{n-1}{k} = \binom{n}{k} \]  \hspace{1cm} \text{(AII.5)}

It follows that

\[ r^{(n+1)} = \sum_{k=0}^{n} \binom{n}{k} r^{(k)} f^{(n+1-k)} \]  \hspace{1cm} \text{(AII.6)}

which is Equation (AII.2) with \( n \) replaced by \( n + 1 \). Induction then establishes the validity of Equation (AII.2) and consequently of Equation (2.16).
APPENDIX III

Behavior of the Coefficients $A_\nu$ for Large $\nu$

The power series expansion of $w(z)$ may be written

$$w(z) = \lim_{k \to \infty} \sum_{\nu=1}^{k} A_\nu z^\nu$$  \hspace{1cm} (AIII.1)

while

$$w(z)/z - A_1 = \lim_{k \to \infty} \sum_{\nu=1}^{k} (A_{\nu+1} - A_\nu) z^\nu$$  \hspace{1cm} (AIII.2)

Subtracting Equation (AIII.1) from Equation (AIII.2) yields

$$\frac{(1 - z)}{z} \cdot w(z) - A_1 = \lim_{k \to \infty} \sum_{\nu=1}^{k} (A_{\nu+1} - A_\nu) z^\nu$$  \hspace{1cm} (AIII.3)

Now let $z = 1$, assuming that the order of taking the limits may be interchanged

$$\lim_{z \to 1} \left[ \frac{(1 - z)}{z} \cdot w(z) \right] - A_1 = \lim_{k \to \infty} \sum_{\nu=1}^{k} (A_{\nu+1} - A_\nu)$$  \hspace{1cm} (AIII.4)

$$= \lim_{k \to \infty} [(A_2 - A_1) + (A_3 - A_2) + \ldots + (A_k - A_{k-1}) + (A_{k+1} - A_k)]$$

$$\lim_{k \to \infty} [A_{k+1} - A_1]$$

So finally we obtain

$$\lim_{\nu \to \infty} A_\nu = \lim_{z \to 1} \left[ \frac{(1 - z)}{z} \cdot w(z) \right]$$  \hspace{1cm} (AIII.5)
provided this limit exists.

Strictly speaking, the power series representation of $w(z)$ (Equation (AIII.1)) and consequently Equation (AIII.5) is valid only in a circular region about the origin which extends up to the nearest singularity of $w(z)$. For $\gamma < 1$ the singularity of $w(z)$ nearest the origin is at $z = 1$ and therefore the limit in Equation (AIII.5) may be valid. The indicated limit yields Equation (2.17). For $\gamma > 1$ the singularity nearest the origin is less than unity and Equation (AIII.5) is not valid.
APPENDIX IV

Some Relations Concerning the Principle of the Argument

Along the part of the contour $C_n$ from point (2) to point (3)

$$X = X^{**} = 1 + \frac{1}{\alpha \gamma} \ln(1 + \alpha) + \sigma / \alpha \gamma$$  \hspace{1cm} (AIV.1)

and the equations for $U$ and $V$ are

$$U = \exp \sigma (1 + \alpha) \cos \alpha \gamma Y - (1 + \alpha) + \frac{\sigma X^{**}}{(X^{**})^2 + Y^2}$$  \hspace{1cm} (AIV.2)

$$V = \exp \sigma (1 + \alpha) \sin \alpha \gamma Y - \frac{\sigma Y}{(X^{**})^2 + Y^2}$$  \hspace{1cm} (AIV.3)

It is trivial to observe that

$$\exp \sigma (1 + \alpha) \sin \alpha \gamma Y > \alpha \sin \alpha \gamma Y$$  \hspace{1cm} (AIV.4)

for $\sigma \geq 0$ and values of $Y$ on this part of the contour. Now let

$$R(X^{**}, Y) = \frac{\sigma Y}{(X^{**})^2 + Y^2}$$  \hspace{1cm} (AIV.5)

Then $R(X^{**}, Y)$ takes on its maximum value as a function of $Y$ at $Y = X^{**}$ so that

$$R(X^{**}, Y) \leq \frac{\alpha}{2X^{**}} < \frac{\alpha}{2}$$  \hspace{1cm} (AIV.6)

since $X^{**} > 1$. It follows from Equations (AIV.4) and (AIV.6) that if

$$Y \geq \frac{\pi}{\alpha \gamma} (2n + 1/6)$$  \hspace{1cm} (AIV.7)
$V > 0$ for any $\sigma > 0$. In other words, along the part of the contour from point (2) to point (3) any zeroes of $V$ must occur between

$$\frac{\pi}{\alpha Y} 2n < Y < \frac{\pi}{\alpha Y} (2n + 1/6) \quad (AIV.8)$$

Now choose

$$\sigma = \ln(2/\sqrt{3}) \quad (AIV.9)$$

Then

$$U = (2/\sqrt{3} \cos \alpha Y 0 1)(1 + \sigma) + \frac{\alpha X**}{(X**)^2 + \gamma^2} \quad (AIV.10)$$

Thus $U > 0$ for $Y$ satisfying Equation (AIV.8). This means that $U > 0$ for any $Y$ such that $V = 0$ and conversely $V > 0$ for any $Y$ such that $U = 0$. 
APPENDIX V

The Equation for \( \frac{d^2 \hat{F}}{da^2} \bigg|_{a=1} \)

\[ \frac{d^2 \hat{F}}{da^2} \bigg|_{a=1} = \frac{2}{m} \cdot L^{-1} \{F(s)\} \bigg|_{t=\tau_m} \]  

(AV.1a)

\[ F(s) = \frac{1}{s^2} \cdot \frac{1}{(s+1)^m - 1} \]  

(AV.1b)

\( F(s) \) has a third order pole at \( s = 0 \) and first order poles at \( s_k = -1 + \exp(i2\pi k/m) \) \( k = 1, 2, \ldots, (m-1) \) (AV.2)

Thus, the partial fraction expansion of \( F(s) \) is of the form

\[ \frac{1}{s^2} \cdot \frac{1}{(s+1)^m - 1} = \frac{M_{01}}{s} + \frac{M_{02}}{s^2} + \frac{M_{03}}{s^3} + \sum_{k=1}^{m-1} \frac{M_k}{s - s_k} \]  

(AV.3)

The coefficients \( M_k \) are easy to calculate. Multiplying both sides of Equation (AV.3) by \( (s - s_j) \)

\[ \frac{1}{s^2} \cdot \frac{s - s_j}{(s+1)^m - 1} = M_j + (s - s_j) \left[ \frac{M_{01}}{s} + \frac{M_{02}}{s^2} + \frac{M_{03}}{s^3} + \sum_{\substack{k=1 \\text{to} \ m-1} \ k\neq j} \frac{M_k}{s - s_k} \right] \]  

(AV.4)

Taking the limit as \( s \to s_j \) yields

\[ M_j = \lim_{s \to s_j} \left[ \frac{1}{s^2} \cdot \frac{(s - s_j)}{(s+1)^m - 1} \right] \]  

(AV.5)

Expanding the second term in the denominator in a Taylor's series about \( s = s_j \) gives
\[ M_j = \lim_{s \to s_j} \frac{\frac{1}{2} (s - s_j)^{\frac{1}{2}}}{m(s_j + 1)^{m-1} (s - s_j)^2} \]  
(AV.6)

and taking the indicated limit yields \( M_j \)

\[ M_j = \frac{1}{m(s_j + 1)^{m-1} \cdot s_j^2} \]  
(AV.7)

Combining Equations (AV.2) and (AV.7) gives

\[ M_k = -\frac{1}{2m} \cdot \frac{1}{1 - \cos(2km/m)} \quad k = 1, 2, \ldots, (m-1) \]  
(AV.8)

The coefficients \( M_{0k} \) are a little more difficult to obtain.

Multiplying both sides of Equation (AV.3) by \( s^3 \) gives

\[ \frac{s}{(s + 1)^m - 1} = M_{01} s^2 + M_{02} s + M_{03} + s^3 \sum_{k=1}^{m-1} \frac{M_k}{s - s_k} \]  
(AV.9)

And from this equation it follows that

\[ M_{03} = \lim_{s \to 0} \left\{ \frac{s}{(s+1)^m - 1} \right\} \]  
(AV.10a)

\[ M_{02} = \lim_{s \to 0} \left\{ \frac{d}{ds} \left\{ \frac{s}{(s+1)^m - 1} \right\} \right\} \]  
(AV.10b)

\[ M_{01} = \lim_{s \to 0} \left\{ \frac{d^2}{ds^2} \left\{ \frac{s}{(s+1)^m - 1} \right\} \right\} \]  
(AV.10c)

Taking the indicated limit in Equation (AV.10a) yields \( M_{03} \)

\[ M_{03} = 1/m \]  
(AV.11)

Performing the indicated differentiation in Equation (AV.10b) gives

\[ M_{02} = \lim_{s \to 0} \left\{ \frac{(s + 1)^m - ms(s + 1)^{m-1} - 1}{[(s + 1)^m - 1]^2} \right\} \]  
(AV.12)
Expansion of the denominator and numerator of Equation (AV.12) in powers of \( s \) results in

\[
M_{02} = \lim_{s \to 0} \left[ -\frac{m(m-1)s^2 + 0(s^3)}{2m^2 s^2 + 0(s^3)} \right]
\]  \hspace{1cm} (AV.13)

Taking the limit yields \( M_{02} \)

\[
M_{02} = -\frac{(m-1)}{2m}
\]  \hspace{1cm} (AV.14)

The coefficient \( M_{01} \) is calculated from Equation (AV.10c) in a manner very similar to that used to calculate \( M_{02} \). The calculation is quite lengthy and tedious; the result is

\[
M_{01} = \frac{m^2 - 1}{12m}
\]  \hspace{1cm} (AV.15)

Combining Equation (AV.1) with the partial fraction expansion of \( F(s) \) gives

\[
\frac{d^2 \tilde{F}}{da^2} \bigg|_{a=1} = \mathcal{L}^{-1} \left\{ \frac{m^2 - 1}{m^2} \cdot \frac{1}{s} - \frac{(m-1)}{m^2} \cdot \frac{1}{s} + \frac{1}{s} \cdot \frac{2}{3} - \rho_m(\eta, s) \right\}
\]  \hspace{1cm} (AV.16a)

\[
\rho_m(\eta, s) = \frac{1}{m} \sum_{k=1}^{m-1} \frac{1}{1 - \cos(2kn/m)} \cdot \frac{1}{s - s_k}
\]  \hspace{1cm} (AV.16b)

Inversion of this equation gives

\[
\frac{d^2 \tilde{F}}{da^2} \bigg|_{a=1} = \frac{m^2 - 1}{6m^2} \cdot \frac{(m-1)}{m} \cdot \eta + \eta^2 - \rho_m(\eta)
\]  \hspace{1cm} (AV.17a)

\[
\rho_m(\eta) = \frac{1}{m} \sum_{k=1}^{m-1} \frac{\exp(\eta s_k)}{1 - \cos(2kn/m)}
\]  \hspace{1cm} (AV.17b)

For uneven \( m \), all the roots \( s_k \) are complex and occur in
conjugate pairs. Thus, by combining terms corresponding to conjugate pairs, $\rho_m(\eta)$ may be written in the form

$$
\rho_m(\eta) = \frac{1}{m^2} \sum_{k=1}^{(m-1)/2} \left[ \exp(\eta m s_k) + \exp(\eta m s_k^-) \right] \frac{1}{1 - \cos(2k\eta/m)}
$$

(AV.18)

Combination of Equation (AV.18) with the definition of $s_k$ (Equation (AV.2)) gives Equation (3.53d).

For even $m$, $s_{m/2} = -2$ is one root; the other $(m-2)$ roots are complex. The terms corresponding to the complex roots can be combined as in the case of uneven $m$ to write $\rho_m$ in the form

$$
\rho_m(\eta) = \frac{1}{2m^2} \exp(-2\eta m) + \frac{1}{2} \sum_{k=1}^{(m-2)/2} \left[ \exp(\eta m s_k) + \exp(\eta m s_k^-) \right] \frac{1}{1 - \cos(2k\eta/m)}
$$

(AV.19)

The first term on the right hand side of this equation corresponds to the real root. Combination of Equation (AV.19) with the definition of $s_k$ gives Equation (3.53c).