SIMULTANEOUS GAS ABSORPTION AND
SUCCESSIVE STEP CHEMICAL REACTION

by

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Dear Sir:

In accordance with the regulations of the Faculty, we herewith submit a thesis, entitled "Simultaneous Gas Absorption and Successive Step Chemical Reaction", in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering from the Massachusetts Institute of Technology.

Respectfully submitted,

Robert N. Gurnitz

Gerald K. Litton
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I. SUMMARY

The object of this thesis was to theoretically investigate the increase in the rate of absorption of a species in the gas phase into the liquid phase when the absorption was accompanied by a two-step chemical reaction.

Employing Hatta's (4, 2) theory of "stagnant films" to describe the fluid dynamics of the system, mathematical equations describing the system, in terms of three dimensionless groups encompassing reaction rate constants, diffusivities, gas and liquid concentrations and physical absorption coefficients, were formulated.

The resulting set of non-linear, second order, boundary-value differential equations was solved by a finite difference technique, employing the use of an IBM-704 digital computer. Solutions were obtained for various values of the aforementioned dimensionless groups.

Results indicated that the increase in the rate of absorption due to a successive step chemical reaction was within the range of limiting cases previously analyzed by Van Krevelen and Hoftijzer (2).

A program, included in this thesis, for solution of the problem on an IBM-704 computer can be used for further study where different ranges of the parameters may be of interest.
II. INTRODUCTION

The kinetic theory of simultaneous gas diffusion and chemical reaction within the liquid phase has been of significant interest to the chemical engineer in his study of commercial absorption equipment such as packed or plate towers. The theory was developed by Hatta\(^2\), based on the assumption that resistance to diffusion is concentrated within a thin film adjacent to the gas liquid interface. This film is assumed to have negligible capacity for holding the solute compared with the main body of the liquid, which is so thoroughly mixed that no concentration gradients exist within it.

The theory has been applied by Hatta\(^2\) for the case of an infinitely rapid, second-order, irreversible chemical reaction and also for a slow, first-order, irreversible chemical reaction with analytical solutions being derived.

Van Krevelen and Hoftijzer \(^2\) studied the case of a second-order, irreversible, chemical reaction of finite rate and derived an approximate analytical solution for that case.

Brian \(^1\), from experimental investigation, has suggested the possibility of simultaneous gas diffusion and successive-step chemical reaction.

This investigation applied Hatta's theory of stagnant films to that of a successive-step reaction mechanism. The particular mechanism studied was that of a species A absorbing from the gas phase into the liquid phase and reacting with a species B in the liquid phase in a second order, irreversible, reaction of finite rate to form an intermediate C.

\[
A + B \rightarrow \text{C}
\]

The intermediate C then reacts with the species B in the liquid phase in a second order, irreversible reaction of finite rate to form the product P.
(2) \[ B + C \rightarrow P \]

The result obtained was the effect of these reactions on the rate of absorption of species A into the liquid phase, more specifically, the increase in the rate of absorption due to successive-step chemical reaction over and above that due to just physical absorption.

To obtain this result, the kinetics were first expressed mathematically. Then, employing a simplified model to describe the fluid dynamics of the system, mathematical equations describing the model were derived. Employing a finite difference technique, these equations were solved with the aid of an IBM-704 digital computer. Results were obtained for a wide variety of system parameters expressed as three dimensionless groups.
III. PROCEDURE

A. The Kinetics

The kinetics representing the system are:

\[ r_a = k_1 ab \]

\[ r_b = k_1 ab + k_2 bc \]

\[ r_c = k_2 bc - k_1 ab \]

where:

- \( a \) = conc. of species A
- \( b \) = conc. of species B
- \( c \) = conc. of species C
- \( k_1 \) = reaction rate constant of reaction (1)
- \( k_2 \) = reaction rate constant of reaction (2)
- \( r_a \) = rate of reaction of species A
- \( r_b \) = rate of reaction of species B
- \( r_c \) = rate of reaction of species C

B. The Model

The physical model employed to describe the system of absorption and successive step chemical reaction was that of Hatta (4, 5), namely the "film theory" or "stagnant film model." In this model a thin, stagnant liquid film is assumed to be at the boundary between the gas and the liquid. The resistance to diffusion is concentrated within this film, and the film is assumed to have negligible capacity for holding the solute compared with that of the main body of the liquid, which is in turbulent motion and in which no concentration gradients exist. Figure I, (2), shows a diagram of this model together with typical concentration profiles of the species A, B, and C. The concentration of A at the interface is \( a_1 \). This interfacial concentration is assumed to be in equilibrium with the concentration of the species A in the gas phase. The concentration of B in the bulk is assumed to be constant.
throughout the bulk and equal to \( b_0 \). Components B and C are assumed to be non-volatile and hence non-existent in the gas phase, with concentration gradients \( \frac{db}{dx} \) and \( \frac{dc}{dx} \) at the interface equal to zero. Finally it is assumed that neither species A nor C exists in the bulk.

C. Mathematical Description of the System

A mathematical description of the system was obtained through use of a material balance around a volume element of thickness \( \Delta x \) and of unit cross section.

\[
\begin{array}{c}
\text{x} \\
\longrightarrow \\
\text{x+\Delta x}
\end{array}
\]

For species A:

Moles A in per unit time at \( x=x \):

\[ N_{a1} = -D_a \left( \frac{da}{dx} \right)_x \]  
\[ D_a = \text{Diffusivity of species A} \]

Moles A out per unit time at \( x = x+\Delta x \):

\[ N_{a2} = -D_a \left( \frac{da}{dx} \right)_{x+\Delta x} \]

Moles A reacted in volume element per unit time:

\[ N_{a3} = k_{ab} \Delta x \]

By assumption, the concentration of A in this volume element does not vary with respect to time. Therefore:

\[ N_{a1} - N_{a2} = N_{a3} \text{ or,} \]

\[ D_a \left[ \left( \frac{da}{dx} \right)_{x+\Delta x} - \left( \frac{da}{dx} \right)_x \right] \frac{\Delta x}{\Delta x} = k_{ab} \]

In the limit as \( x \to 0 \),

\[ D_a \frac{d^2a}{dx^2} = k_{ab} \]  \( (1) \)

By similar balances on species B and C, the following two equations are obtained.
Figure 1
CONCENTRATION PROFILES,
FILM THEORY MODEL

\[ x = \text{distance into liquid phase} \]
\[ D_b d^2 b/dx^2 = k_1 a b + k_2 b c \]  
\[ D_c d^2 c/dx^2 = k_2 b c - k_1 a b \]  

(2)  
(3)

Under the assumptions made in the physical description of the system denoted above, the following boundary conditions prevail:

At \( x = 0 \):

\[
\begin{align*}
    a &= a_1 \\
    db/dx &= 0 \\
    dc/dx &= 0
\end{align*}
\]

(b.c. 1)

At \( x = x_f \):

\[
\begin{align*}
    b &= b_0 \\
    a &= 0 \\
    c &= 0
\end{align*}
\]

(x_f = film thickness)  
(b.c. 2)

The following variable transformations are convenient: \( Z = x/x_f \);

\[
\begin{align*}
    A &= a/a_1 \\
    B &= b/b_0 \\
    C &= c/b_0
\end{align*}
\]

The following definitions are also made: \( E = k_1 b_0 x_f^2 / D_a \)

\[
G = D_b b_0 / D_a a_1 \\
P' = D_b / D_c \\
R = k_2 D_a / k_1 D_c
\]

In terms of these new variables, equations (1), (2), and (3) become:

\[
d^2 A/dZ^2 = E A B \]  
(1A)

\[
d^2 B/dZ^2 = (E/G)A B + (E/R)B C' \]  
(2A)

\[
d^2 C'/dZ^2 = (E/R)B C' - (E/F)A B \]  
(3A)

and the boundary conditions become:

At \( Z = 0 \):

\[
\begin{align*}
    A &= 1 \\
    dB/dZ &= 0 \\
    dC'/dZ &= 0
\end{align*}
\]

(b.c. 1a)

At \( Z = 1 \):

\[
\begin{align*}
    A &= 0 \\
    B &= 1 \\
    C' &= 0
\end{align*}
\]

(b.c. 2a)

The three equations (1A), (2A), and (3A) can be reduced to two by the following method.

Adding \((-2)(Eq. \ 1A) + (G)(Eq. \ 2A) - (G/P')(Eq. \ 3A)\) yields

\[
d^2 (G B - G C'/P' - 2 A)/dZ^2 = 0.
\]
Integrating,
\[ d(2A - GB + GC'/P')/dz = F_1. \]

Using the first of the two sets of boundary conditions,
\[ F_1 = 2(dA/dZ)Z = 0 = -2\phi, \]
defining \( \phi \) to be identical with \(-dA/dZ\) \(Z = 0\).

Therefore,
\[ d(2A - GB + GC'/P')/dz = -2\phi. \]

Integrating once more,
\[ 2A - GB + GC'/P' = -2\phi Z + F_2. \]

Using the second of the two sets of boundary conditions,
\[ F_2 = 2\phi - G. \]

Therefore,
\[ 2A - GB + GC'/P' = -2\phi Z + 2\phi - G. \]

Solving for \( C' \):
\[ C' = P'(B-1) + 2P'/G \phi(1-Z) - A. \quad (3b) \]

Since \( C' \) is not an independent variable but, in fact, depends on \( B \) and \( A \), only two of the three equations \((1A), (2A), \) and \((3A)\) are necessary to describe the system. Choosing the first two of these, and substituting for \( C' \) in \((2A)\), the following equations result.

\[ d^2A/dz^2 = EAB \quad (1b) \]
\[ d^2B/dz^2 = (E/G)AB + ERB \left\{ (B-1)+(2/G) \left[ \phi(1-Z) - A \right] \right\} \quad (2b) \]

The mathematical description of the problem is now reduced to two equations, \((1b)\) and \((2b)\), subject to the following boundary conditions:

At \( Z = 0 \)
\[ A = 1 \]
\[ dA/dZ = 0 \]

(b.c. 1b)

At \( Z = 1 \)
\[ A = 0 \]
\[ B = 1 \]

(b.c. 2b)
III. PROCEDURE (Cont.)

D. Determination Of The Absorption Ratio

The answer desired in this investigation is that of the effect of chemical reaction on the rate of absorption. The following treatment shows how this effect may be conveniently expressed.

The rate of absorption, $N_a$, of the species A into the liquid phase is:

$$ N_a = -D_a \frac{da}{dx} x=0 \quad (3) $$

The absorption coefficient, $K_L$, is defined as

$$ K_L = \frac{N_a}{a_i - a_o} \quad (4) \quad \text{where: } a_o = \text{concentration of the species A at the film - turbulent bulk liquid interface.} $$

Combining equations (3) and (4),

$$ K_L = -D_a \frac{da}{dx} x=0 = \frac{-D_a (da/dz) z=0}{a_i - a_o} \quad (5) $$

Note that $a_o$ equals zero in equation (5). This is due to the previous assumption that all of species A is consumed by reaction in the film, so that at $x = x_f$, no A is present.

If species A were to be absorbing into the liquid phase in the absence of chemical reaction, the absorption coefficient, $K_L^*$, would be

$$ K_L^* = \frac{N_a^*}{a_i - a_o} \quad (6) $$

Since

$$ N_a^* = D_a \frac{a_i - a_o}{x_f} \quad (5), $$

$$ K_L^* = D_a / x_f $$

The effect of chemical reaction can be expressed as the ratio of the absorption rate with chemical reaction to that without:

$$ \frac{K_L}{K_L^*} = - \frac{(da/dz) z=0}{a_o} \quad (7) $$

or

$$ \frac{K_L}{K_L^*} = \phi $$

This absorption ratio, $\phi$, is the answer desired.
Thus, in essence, the problem now entails finding φ from solution of equation (1b) and (2b), as functions of $K_1$, $K_2$, $a_1$, $b_0$, $D_a$, $D_b$, and $x_f$. The first six quantities are readily available constants for many systems, and the last quantity, $x_f$, can be obtained from equation (6):

$$x_f = \frac{D_a}{K_L^*} \quad (6)$$

In summary, then, a solution of Equations (1b) and (2b) will yield φ in terms of various constants, listed above. If $K_L^*$ is known for a particular physical system, then the increase in absorption rate may be calculated from Equation (7).

E. The Numerical Solution

An analytical solution of Equations (1b) and (2b) for φ as a function of the three dimensionless groups $E$, $G$, and $R$ is beyond the power of present mathematical methods. That being the case, a numerical method was chosen for solution of the problem. This method was that of expressing the derivatives appearing in the equations by finite difference, so that the differential equations were replaced by a set of difference equations. These difference equations were then solved by simple algebraic procedures.

In order for a numerical procedure to be satisfactory it must satisfy a stability criterion. This stability criterion deals with the growth or decay of errors which may be introduced into the numerical calculation. In practice, a finite number of increments must be used and only a finite number of significant figures can be carried in the computation. Both of these factors necessarily introduce errors into the calculations, and it is the fate of these errors which is of interest. A system in which these errors decay, rather than grow, is said to be stable. (5).
It can be shown (see VII, APPENDIX, Section A) that Equations (1b) and (2b) when expressed directly in finite difference form, do not meet this stability criterion.

Therefore, the method of solution used was the construction of a time variant stable system of equations whose solution in the limit approached the steady state solution, that is, the solution of equations (1b) and (2b) subject to boundary conditions b.c. (1b) and b.c. (2b).

The time variant differential equations (see VII, APPENDIX, Section F) generated were:

\[
\frac{\partial^2 A}{\partial Z^2} - \frac{\partial A}{\partial \vartheta} = EAB
\]

\[
\frac{\partial^2 B}{\partial Z^2} - \frac{\partial B}{\partial \vartheta} = \frac{E_{AB} + E_{RB}}{G} \left\{ (B-1) + \frac{2}{G} \left[ \vartheta(1-Z)-A \right] \right\}
\]

These equations were then expressed in finite difference form.

The following notation is employed. The values of A and B at the interface are represented by A(1) and B(1), respectively. The values of A and B at Z = 1 are represented by A(N) and B(N), respectively where N is equal to:

\[ N = \frac{1}{\Delta Z} + 1 \]

\( \Delta Z \) being equal to the increment of Z between successive A's and B's along the "Z-axis."

The increment of the modified time variable, \( \vartheta \), is denoted by \( \Delta \vartheta \).
Writing equations (8) and (9) in finite difference form:

\[
\frac{\text{ALTR}(I+1) - 2\text{ALTR}(I) + \text{ALTR}(I-1)}{\Delta Z^2} - \frac{\text{ALTR}(I) - A(I)}{\Delta \Theta} = \text{BALTR}(I)B(I)
\]

\[
\frac{\text{BLTR}(I+1) - 2\text{BLTR}(I) + \text{BLTR}(I-1)}{\Delta Z^2} - \frac{\text{BLTR}(I) - B(I)}{\Delta \Theta} = \frac{E}{G^A(I)\text{BLTR}(I) + \text{ERBLTR}(I)} \left\{ [B(I) - 1] + \frac{2}{G} \left[ \varphi(1-Z) - A(I) \right] \right\}
\]

where: \( A(I) \) denotes the value of \( A \) at \( Z = (I-1) \Delta Z \); \( \text{ALTR}(I) \) denotes the values of \( A \) at \( Z = (I-1) \Delta Z \), but at a value of \( \Theta \) which is \( \Delta \Theta \) greater than that at which \( A(I) \) is evaluated.

A special set of equations is required at a value of \( I = 1 \):

\[
2 \frac{\text{ALTR}(2) - 1}{\Delta Z^2} + 2\varphi \Delta Z = \text{EB}(1)
\]

\[
2 \frac{\text{BLTR}(2) - \text{BLTR}(1)}{\Delta Z^2} - \frac{\text{BLTR}(1) - B(1)}{\Delta \Theta} = \frac{E}{G} \text{BLTR}(1) + \text{ERBLTR}(1) \left\{ B(1) - 1 + \frac{2}{G} \left[ \varphi - 1 \right] \right\}
\]

where it is noted that use is made of boundary conditions b.c. (1b)

At \( Z = 0 \)

\[
A = 1, \quad \frac{\partial A}{\partial Z} = 0
\]

and the definition,

\[
\varphi \equiv - \left( \frac{\partial A}{\partial Z} \right)_Z = 0
\]

together with the approximations:

\[
\frac{\partial^2 A}{\partial Z^2} \left. \right|_{Z = 4} \approx \frac{\partial}{\partial Z} \left( \frac{\partial^2 A}{\partial Z^2} \right) \left. \right|_{Z = 0}
\]
\[
\left( \frac{\partial^2 B}{\partial Z^2} \right)_{Z=0} = \frac{z}{4} \\
\left( \frac{\partial B}{\partial \Theta} \right)_{\Theta=0} = \frac{e}{2}
\]

The following method of solution of the resulting set of difference equations was employed.

Initial values of A and B at \( \Theta = 0 \) for the interval \( 0 \leq Z \leq 1 \) are arbitrarily chosen:

\[
A^e = (1-Z)^2 \\
B^e = Z^2
\]

where it is noted that at \( Z=0 \):

\[
A = 1 \quad \frac{\partial B}{\partial Z} = 0 \quad -\frac{\partial A}{\partial Z} = 2 \neq \phi
\]

and at \( Z=1 \):

\[
A = 0 \quad B = 1
\]

Equation (12) and the set of equations (10) are a set of \( N - 1 \) equations in \( N - 1 \) unknowns, the unknowns being \( ALTR(1) \) to \( ALTR(N) \), and \( \phi \). All of the values of \( A(I) \), together with the value of \( \phi \) for \( \Theta = 0 \) have been specified by equation (14). Therefore all of the values of \( ALTR(1) \) together with the value of \( \phi \) can be calculated. Similarly, all of the values of \( B(I) \) at \( \Theta = 0 \) are specified by equation (14b), and therefore all values of \( BLTR(I) \) can be calculated.

Once the values of \( ALTR(I), BLTR(I), \) and \( \phi \) are calculated, the procedure is to replace the terms \( A(I) \) and \( B(I) \) with the numerical values of \( ALTR(I) \) and \( BLTR(I) \), respectively, in equations (10) through (13). The terms \( ALTR(I), BLTR(I), \) and \( \phi \) are again considered unknowns.
and their values may again be solved for.

This process is continued until two successively calculated values of $\phi$ satisfy convergence criteria (see V. RESULTS, Section C).
IV. RESULTS

In this section, the variations of \( \varnothing \) with respect to the dimensionless groups \( R \), \( G \), and \( E \) are tabulated and presented graphically.

Table I

\( \varnothing \) Versus \( R \) at Constant \( G \) at Various Values of \( E \)

<table>
<thead>
<tr>
<th>( R )</th>
<th>( \varnothing )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 0.0000001 )</td>
<td>16.099</td>
</tr>
<tr>
<td>( 0.0000010 )</td>
<td>16.098</td>
</tr>
<tr>
<td>( 0.0000100 )</td>
<td>16.086</td>
</tr>
<tr>
<td>( 0.0010000 )</td>
<td>15.969</td>
</tr>
<tr>
<td>( 0.0100000 )</td>
<td>15.100</td>
</tr>
<tr>
<td>( 0.1000000 )</td>
<td>12.660</td>
</tr>
<tr>
<td>( 1.0000000 )</td>
<td>10.252</td>
</tr>
<tr>
<td>( 5.0000000 )</td>
<td>10.050</td>
</tr>
</tbody>
</table>

| \( 0.000001 \) | 1.309  | \( E = 1.0 \) |
| \( 0.00100 \)  | 1.309  | \( G = 20 \)  |
| \( 0.10000 \)  | 1.302  |

| \( 0.000001 \) | 2.885  | \( E = 9.0 \) |
| \( 0.00100 \)  | 2.885  | \( G = 20 \)  |
| \( 0.01000 \)  | 2.866  |
| \( 0.10000 \)  | 2.85   |

| \( 0.000001 \) | 8.106  | \( E = 100 \) |
| \( 0.01000 \)  | 7.793  | \( G = 20 \)  |
| \( 0.10000 \)  | 7.141  |

| \( 0.000001 \) | 20.18   | \( E = 10,000 \) |
| \( 0.01000 \)  | 12.772  | \( G = 20 \)  |

These results are illustrated in Figure II.
Figure 11

ϕ versus R at constant G at various values of E

\[ R = \frac{k_2 D_a}{k_1 D_c} \]
Table II

$\phi$ Versus $G$ at Constant $R$ at Various Values of $E$

<table>
<thead>
<tr>
<th>$G$</th>
<th>$\phi$</th>
<th>$E$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.247</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>1.311</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1.312</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$E = 1$</td>
<td>$R = 0.01$</td>
</tr>
</tbody>
</table>

|      |              | $E = 9$ | $R = 0.01$ |
| 1    | 1.760        |      |       |
| 20   | 2.866        |      |       |
| 50   | 2.960        |      |       |
| 100  | 2.987        |      |       |

|      |              | $E = 100$ | $R = 0.01$ |
| 1    | 1.956        |      |       |
| 20   | 7.793        |      |       |
| 50   | 9.018        |      |       |
| 100  | 9.509        |      |       |

|      |              | $E = 1000$ | $R = 0.01$ |
| 1    | 1.866        |      |       |
| 20   | 12.66        |      |       |
| 50   | 20.295       |      |       |
| 100  | 25.320       |      |       |

|      |              | $E = 10,000$ | $R = 0.01$ |
| 1    | 1.69         |      |       |
| 20   | 12.772       |      |       |
| 50   | 27.684       |      |       |
| 100  | 46.391       |      |       |

These results are presented in Figure III.
Figure III
φ versus G at constant R at various values of E

\[ \phi = \frac{E_b b_c}{D_{a_1}} \]

\[ G = \frac{D_{b b_c}}{D_{a_1}} \]
Table III

\( \phi \) versus \( E \) for constant \( R \) at various values of \( G \)

<table>
<thead>
<tr>
<th>( E )</th>
<th>( \phi )</th>
<th>( G = 1 )</th>
<th>( R = 0.01 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.247</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1.760</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>1.956</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,000</td>
<td>1.866</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td>1.690</td>
<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>( E )</th>
<th>( \phi )</th>
<th>( G = 20 )</th>
<th>( R = 0.01 )</th>
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</thead>
<tbody>
<tr>
<td>4</td>
<td>2.022</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>2.866</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>7.793</td>
<td></td>
<td></td>
</tr>
<tr>
<td>225</td>
<td>9.929</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,000</td>
<td>12.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td>12.772</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,000,000</td>
<td>11.5</td>
<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>( E )</th>
<th>( \phi )</th>
<th>( G = 50 )</th>
<th>( R = 0.01 )</th>
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<tbody>
<tr>
<td>1</td>
<td>1.311</td>
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<tr>
<td>9</td>
<td>2.960</td>
<td></td>
<td></td>
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<tr>
<td>100</td>
<td>9.018</td>
<td></td>
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<tr>
<td>1,000</td>
<td>20.295</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td>27.684</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100,000</td>
<td>27.856</td>
<td></td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>( E )</th>
<th>( \phi )</th>
<th>( G = 100 )</th>
<th>( R = 0.01 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.312</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>2.987</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>9.509</td>
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</tr>
<tr>
<td>1,000</td>
<td>25.320</td>
<td></td>
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</tr>
<tr>
<td>10,000</td>
<td>46.391</td>
<td></td>
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</tr>
<tr>
<td>100,000</td>
<td>53.229</td>
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<td>1,000,000</td>
<td>52.745</td>
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</tbody>
</table>

These results are presented in Figure IV.
Figure IV
Φ VERSUS √E AT CONSTANT R
AT VARIOUS VALUES OF G

\[ \sqrt{E} = \sqrt{\frac{k_1 b x_f^2}{D_a}} = \frac{\sqrt{k_1 b D_a}}{K_L} \]
Table IV

$\phi$ Versus $E$ at Constant $G$ at Various Values of $R$

<table>
<thead>
<tr>
<th>$E$</th>
<th>$\phi$</th>
<th>$G$</th>
<th>$R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.302</td>
<td>20</td>
<td>0.1</td>
</tr>
<tr>
<td>9</td>
<td>2.885</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>7.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>225</td>
<td>9.929</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,000</td>
<td>12.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td>12.772</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,000,000</td>
<td>11.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| 1    | 1.309   | 20   | 0.01 |
| 9    | 2.885   |      |      |
| 1,000| 15.1    |      |      |

| 1    | 1.309   | 20   | 0.001|
| 9    | 2.885   |      |      |
| 100  | 8.106   |      |      |
| 1,000| 16.086  |      |      |
| 10,000| 20.18  |      |      |
| 100,000| 20.8  |      |      |

These results are depicted in Figure V.
Figure V
Φ VERSUS $\sqrt{E}$ AT CONSTANT G
AT VARIOUS VALUES OF R

$\sqrt{E} = \sqrt{\frac{k_b x^2}{D_a}} = \sqrt{\frac{k_b D_a}{K_L^*}}$
<table>
<thead>
<tr>
<th>$E$</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>1.0003</td>
</tr>
<tr>
<td>0.010</td>
<td>1.003</td>
</tr>
<tr>
<td>0.100</td>
<td>1.033</td>
</tr>
<tr>
<td>1.00</td>
<td>1.313</td>
</tr>
<tr>
<td>9.00</td>
<td>3.016</td>
</tr>
<tr>
<td>100.0</td>
<td>10.04</td>
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<tr>
<td>1,000.0</td>
<td>33.104</td>
</tr>
</tbody>
</table>

$G = 10,000$  
$R = 0.00001$
V. DISCUSSION OF RESULTS

A. Theoretical Limits of Results

If \( k_2/k_1 \) were to approach zero, chemical reaction (2) would not affect the absorption rate. In this case, the reaction in the film would be

\[
(1) \quad A + B \rightarrow C
\]

with the rate represented by

\[
r = k_1 AB
\]

Thus, the entire reaction in the film would be a second order, finite rate, irreversible chemical reaction. The approximate analytical solution has been given by Van Krevelen and Hoftijzer (7) for the film theory model of a second order irreversible chemical reaction.

\[
\phi = \frac{\sqrt{E \cdot \sqrt{1 - (\phi - 1)/G}}}{\tanh[\sqrt{E \cdot \sqrt{1 - (\phi - 1)/G}}]}
\]

This equation is plotted on Figure VI (2) which is a log-log plot of \( \phi \) versus \( E \) at various values of the parameter \( G \).

If \( k_2/k_1 \) were to approach infinity, chemical reaction (1) and (2) would be equivalent to chemical reaction (3)

\[
A + 2B \rightarrow P
\]

with the rate represented by

\[
r = k_1 AB
\]

It can be shown that Figure VI represents the graphic solution of this system, provided that \((D_B/D_a)(b_0/a_0)\) is interpreted as \( 2G \).

In other words, for a values of \( k_2/k_1 \) approaching infinity, the value of \( \phi \) at a particular value of \( E \) is that corresponding to \( G/2 \), where \( G \) is the value of \( G \) corresponding to \( \phi \) at \( k_2/k_1 = 0 \).

For the case studied, the value of \( k_2/k_1 \) was between the two limiting cases, namely between zero and infinity. It is therefore expected that
Figure VI
FILM THEORY SOLUTION FOR A
SECOND ORDER IRREVERSIBLE REACTION
(Equation 15)

\[ \phi = \frac{K_L}{K_L^*} \]

\[ \sqrt{E} = \sqrt{\frac{k_b \cdot x_f}{D_a}} = \sqrt{\frac{k_b \cdot D_a}{K_L^*}} \]
for given values of \( E \) and \( G \), the value of \( \phi \) will range between those values on Figure VI corresponding to \( G \) and \( G/2 \) at the particular value of \( E \).

For example, at values of \( E \) and \( G \) of 1000 and 20, respectively, \( \phi \) should vary from approximately 16 to 10 as \( R \) varies from zero to infinity.

### B. Interpretation of Data

Table 1 lists the variation of \( \phi \) with \( R \) for constant values of \( G \) at various values of \( E \). These data are presented in Figure II.

Considering the variations of \( R \) to be due solely to the ratio \( k_2/k_1 \), very small values of \( R \) correspond to a gas absorption controlled only by the first reaction. Thus, as the ratio \( k_2/k_1 \) becomes small, the effect of reaction (2) on absorption becomes negligible. Since the absolute value of \( k_1 \) may be interpreted as being dictated by the value of \( E \) (which is constant for this case), it follows that as \( R \) becomes very small, \( \phi \) approaches a limiting value corresponding to an overall reaction expressed by reaction (1).

For large values of \( R \), or \( k_2/k_1 \), the rate of the second reaction becomes much larger than that of the first, and the first therefore becomes the controlling reaction, with respect to absorption. Thus, as \( R \) increases, the effect of the second reaction becomes negligible, and using the same argument as above, \( \phi \) again approaches an asymptotic value. For this case, however, the asymptotic value corresponds to an overall reaction expressed by reaction (3). For small values of \( E \), the variation of \( \phi \) with \( R \) becomes small, and, in fact, as \( E \to 0 \), \( \phi \) must approach 1.0. This is due to the fact that small values of \( E \) can be interpreted as corresponding to small values of either \( K_1 \), \( B_0 \), or \( X_p \).
leading to the conclusion that the amount of chemical reaction in the film is small.

It is instructive to note that the asymptotic values of Figure II correspond to those predicted by Figure VI. For example, at $E = 1000$ and $G = 20$, the asymptotic values are approximately 10.05 and 16.1. By reference to figure 1, the values of $\varphi$ at $G = 20$ and $G = 10$ are approximately 16 and 10, respectively.

This correspondence is discussed in V. RESULTS, Section A.

Table 2 lists the variation of $\varphi$ with $G$ at constant values of $R$ at various values of $E$. These results are presented in Figure III.

At low values of $G$, all of the curves approach a value of $\varphi$ equal to 1.0. This is a consequence of the fact that as $G$ approaches zero, either $D_B$ or $B_0$ approaches zero, or $D_A$ or $A_1$ approaches infinity. If the first interpretation is chosen, so little $B$ diffuses into the liquid film that there is essentially no chemical reaction, and $\varphi$ consequently approaches 1.0.

In the second interpretation, species $A$ diffuses so rapidly that the effect of the chemical reaction on absorption is negligible, and $\varphi$ again approaches 1.0.

The lower curves of Figure III indicate that as $G$ grows large, $\varphi$ approaches an asymptotic value. If $D_B/D_A$ is taken to be the increasing quantity, the interpretation is that diffusion of $B$ into the film is so fast that the chemical reaction is limited only by the values of the rate-reaction constants. In other words, up to a certain value of $D_B/D_A$ diffusion has some control on the amount of chemical reaction occurring, since it takes a finite amount of time for a molecule of $B$ to reach one molecule of $A$. Beyond this value, however, diffusion ceases to play a
significant role, and hence $G$ ceases to have any effect on $\phi$.

From this discussion, it seems reasonable to assume that all of the curves in Figure III must eventually reach asymptotic values, with respect to $\phi$.

All of the values listed in Table 2 correspond with the values predicted by Figure VI. That is, for any given values of $G$, $E$, and $R$ in Table 2, the value of $\phi$ lies between those values of $\phi$ in Figure VI corresponding to the same $E$ and to $G$ and $G/2$.

For example, Table 2 lists a value of $\phi$ of 12.772 for $G = 20$, $E = 10,000$, and $R = 0.01$. From Figure VI, the values of $\phi$ at $G = 20$, and $G = 10$, and at $E = 10,000$ are 20 and 11, respectively.

Tables 3, 4 and 5 list $\phi$ as a function of $E$ for constant values of $R$ and $G$. In Table 3, the value of $R$ is 0.01 throughout, and in Table 4, the value of $G$ is consistently 20.

Tables 3 and 4 are plotted in Figures IV and V.

Several features associated with Figures IV and V are worth discussing. First, as $E$ approaches zero, $\phi$ approaches 1.0 in all cases. This is to be expected, since as any of the parameters $K_1$, $B_0$, or $X_f$ approach zero, the amount of reaction in the film approaches zero. Similarly, as $D_A$ approaches infinity, the rate of absorption without chemical reaction is so large that the reaction itself has a negligible effect on the rate of absorption.

For any particular set of values of $G$ and $R$, as $E$ assumes large values, $\phi$ approaches a maximum value. At still larger values of $E$, $\phi$ starts to decrease. It can, in fact, be argued that for any given $G$, the value of $\phi$ at very large values of $E$ must drop down to that $\phi$ corresponding to an overall reaction (3), irrespective of $R$. Assuming the variation of $E$ to
be due only to $k_1$, small values of $E$ correspond to small values of $k_1$, and hence the first reaction is controlling. As $k_1$ increases, however, the point is reached where the diffusion of $A$ becomes the controlling process. As $k_1$ is increased still further, however, another point is reached where the first reaction is practically instantaneous. At this point, as far as gas absorption is concerned, the controlling reaction is given by

$$A + 2B \longrightarrow P$$

As discussed in V. RESULTS, Section A, the value of $\varphi$ at this point should correspond to a value of $G/2$ rather than $G$, and hence the drop in $\varphi$ at very large values of $E$.

Table 5 lists the variation of $\varphi$ with respect to $E$ at a value of $G = 10,000$. As explained earlier, for a given value of $G$, the curve of $\varphi$ versus $E$ lies between the two curves, on Figure VI, of $\varphi$ versus $E$ at $G$ and at $G/2$. Both of these limiting curves approach the same asymptotic curve as $G$ approaches infinity, namely the curve on Figure VI labelled "pseudo first-order reaction".

It therefore follows that at large values of $G$, the curve of $\varphi$ versus $E$, for any value of $E$, must also approach this asymptotic curve. Consequently, the figures in Table 5 should, and in fact do, lie on the curve of Figure VI corresponding to a value of $G$ approaching infinity.

C. Reliability of Results

An integral part of the computer solution was the comparison of successive values of $\varphi$. That is, each time a value of $\varphi$ was calculated, it was compared with the previously calculated value. If these two values differed by less than a certain increment, the computation
ceased, and the last value of $\phi$ calculated was taken to be the final result.

The above-mentioned increment was an arbitrary quantity; the program was so set up that any desired value for this increment could be employed in making the comparisons between values of $\phi$.

In all of the results quoted in this thesis, the value of the increment used was less than 0.005.

This criterion for convergence is a necessary one, but it is not sufficient. For example, if the change between successive values of $\phi$ is 0.001, and if this change does not vary over one hundred values of $\phi$, then the solution obviously is not a convergent one, since the first and hundredth values of $\phi$ differ by 0.1. Therefore, the rate of change of the difference between successive values of $\phi$ must be continuously negative if the values of $\phi$ are to converge.

The above-stated criteria are those which must be satisfied if any function is to approach an asymptotic value.

The results obtained from the computer solutions were analyzed with regard to both criteria, and a solution was considered a convergent one only if both criteria were satisfied.

On the basis of the study made of the data obtained from the computer solutions, it is strongly felt that the results presented in this thesis are within an accuracy of 5% of the true solution of the differential equations. This cannot, however, be fully substantiated with the available data. To test the actual accuracy, it would be necessary to rerun several of the solutions using an extremely small value of $\Delta Z$, and comparing these results with those obtained in this thesis. (see VIII. APPENDIX, Section E). Unfortunately, computer time was not available to carry out fully this test.
VI. CONCLUSIONS

1. A successful numerical method for the solution of a set of non-linear, second-order, boundary value differential equations arising out of a description of simultaneous gas absorption with successive step chemical reaction has been formulated.

2. A successful computer program for an IBM-704 digital computer has been written and verified for solution of the aforementioned differential equations.

3. The effect of a two-step reaction mechanism as a function of three dimensionless parameters, on the rate of gas absorption has been studied for a limited number of cases. Over the range of parameters investigated, correlations were made with results obtained by previous workers.
VII. RECOMMENDATIONS

1. It is recommended that the computer program be used to obtain data from which empirical quantitative relationships can be developed to correlate the optimum values of the modified time variable, $\Delta t$, for maximum rate of convergence, with the physical parameters (see VIII. APPENDIX, Section D).

2. A study of the effect of the three dimensionless groups, $E$, $G$, $R$, on $\phi$ should be taken over a wider range of these parameters than was possible during this study.

3. The results obtained from this study may be used as an aid in correlating gas absorption data, previously not possible, for the reactions of the type studied herein.

4. Finally, it is recommended that correlations between experimental data and the results predicted in this work be used to infer orders and mechanisms of chemical reactions.
VIII. APPENDIX

A. The Originally Proposed Solution of Equations (1b) and (2b)

The original differential equations were of the form

\[ \frac{\partial^2 a}{\partial z^2} = Eab \]  

(16)

It was originally proposed to solve these equations using a system of finite difference equations derived directly from them. However, before attempting to solve the system of difference equations, it was decided to perform a stability analysis to determine whether or not the system was capable of producing stable solutions.

If a system is stable, random errors introduced during the course of solution of the system will die out. If the system is not stable, random errors introduced will not die out, but will in fact increase in magnitude as the solution progresses. The following analysis will prove that a system of difference equations derived directly from equation (16) is inherently unstable.

The difference equations associated with equation (16) are of the form

\[ \frac{a(I+1) - 2a(I) + a(I-1)}{\Delta z^2} = Ea(I)b(I) \]  

(17)

Generally, if a system of linear difference equations is unstable, then a corresponding system of non-linear difference equations is sure to be unstable. Therefore, the stability analysis will be performed on equation (18).

\[ \frac{\partial^2 a}{\partial z^2} = Ea \]  

(18)

The corresponding set of difference equations are of the form
\[
\frac{a(I-1) - 2a(I) + a(I+1)}{A Z^2} = E a(I)
\] (19)

Let \(a(I)\) represent the true solution to equation (19) at the \(I^{th}\) point on the \(a\) versus \(z\) curve, and let \(a'(I)\) represent the actual solution, as obtained from the difference equation scheme, at the same point. Now, both \(a(I)\) and \(a'(I)\) must satisfy equation (19). Therefore, their difference must also satisfy equation (19). This difference, denoted by \(\varepsilon\) is the error associated with the solution at the \(i^{th}\) point.

Assuming solution of equation (19) to be of the form
\[
\varepsilon = \sigma^I
\] (20)

where: \(\sigma\) is a constant, and substituting equation (20) into equation (19), the following equation results:
\[
\frac{\sigma^{I-1} - 2\sigma^I + \sigma^{I+1}}{A Z^2} = E \sigma^I
\] (21)

Dividing equation (21) by \(\sigma^I\) and solving for \(\sigma\),
\[
\sigma = 1 + \frac{E A Z^2}{2} \pm \sqrt{\frac{(E A Z^2)^2 - 4 E A Z^2}{4}}
\] (22)

Since there are two roots for \(\sigma\), \(\varepsilon\) is of the form:
\[
\varepsilon = C_o \sigma_o^I + C_1 \sigma_1^I
\] (23)

where \(C_o\) and \(C_1\) are constants, and \(\sigma_o\) and \(\sigma_1\) are the two values given by equation (22).

It is obvious from equation (23) that since one of the values of \(\sigma\) is greater than 1.0, any errors introduced into the solution of equation (18) will grow as the solution proceeds. Hence, the set of difference equations of the form (19) are unstable, and almost certainly the equations of the form (17) are also unstable.

A stability analysis performed on the set of linear difference equations corresponding to the non-linear ones actually used in
obtaining solutions in this thesis indicated that the system of linear equations was stable (8). This was a good indication that the non-linear equations would be stable, and it has turned out that the equations are, at least for the proper choice of variables.
VIII. APPENDIX (Cont.)

B. Solution of the "A Net" and "B Net"

Equation (10) states:

\[ \frac{\Delta Z^2}{\Delta \theta} \left( -2 \text{ALTR}(I+1) + \text{ALTR}(I-1) \right) - \frac{\Delta Z^2}{\Delta \theta} \text{ALTR}(I) - A(I) = \varepsilon \text{ALTR}(I)B(I) \]

where:

\[ 2 \leq I \leq N-1 \]

Multiplying equation (10) by \( \Delta Z^2 \), and combining terms, one obtains:

\[ -\text{ALTR}(I+1) + \text{ALTR}(I) \left[ 2(I+C) + E\Delta Z^2B(I) \right] - \text{ALTR}(I-1) = A(I)(2C) \]

where:

\[ C = \frac{\Delta Z^2}{2\Delta \theta} \]

Defining:

\[ W(I) \equiv 2(I+C) + E\Delta Z^2B(I) \quad 2 \leq I \leq N-1 \]

\[ P(I) \equiv A(I)2C \quad 2 \leq I \leq N-1 \]

one obtains:

\[ -\text{ALTR}(I-1) + \text{ALTR}(I) \left[ W(I) \right] - \text{ALTR}(I+1) = P(I) \quad (10') \]

Writing equation (10) with \( I = 2, 3, 4, \) respectively, and noting that \( \text{ALTR}(1) = 1 \), one obtains the following set of equations:

\[ \text{ALTR}(2)W(2) - \text{ALTR}(3) = P(2) + 1 \quad (d_1) \]

\[-\text{ALTR}(2) + \text{ALTR}(3)W(3) - \text{ALTR}(4) = P(3) \quad (d_2) \]

\[-\text{ALTR}(3) + \text{ALTR}(4)W(4) - \text{ALTR}(5) = P(4) \quad (d_3) \]

Defining:

\[ V(2) \equiv W(2) \]

\[ Y(2) \equiv P(2) + 1 \]

one obtains:

\[ \text{ALTR}(2)V(2) - \text{ALTR}(3) = Y(2) \quad (B_1) \]
Adding \( \frac{\text{Eq. (B_1)}}{\text{V(2)}} + \text{Eq. (d_2)} \), one obtains:

\[
\text{ALTR}(3) \left[ \text{W(3)} - \frac{1}{\text{V(2)}} \right] - \text{ALTR}(4) = \frac{\text{V(2)}}{\text{V(2)}} + P(3)
\]

Defining:

\[
\text{V}(3) \equiv \text{W(3)} - \frac{1}{\text{V(2)}}
\]

\[
\text{Y}(3) \equiv \frac{\text{V(2)}}{\text{V(2)}} + P(3)
\]

one obtains:

\[
\text{ALTR}(3)\text{V}(3) - \text{ALTR}(4) = \text{Y}(3) \tag{B_2}
\]

Adding \( \frac{\text{Eq. (B_2)}}{\text{V(3)}} + \text{Eq. (d_3)} \), one obtains

\[
\text{ALTR}(4) \left[ \text{W(4)} - \frac{1}{\text{V(3)}} \right] - \text{ALTR}(5) = \frac{\text{V(2)}}{\text{V(3)}} + P(4)
\]

Defining:

\[
\text{V}(4) \equiv \text{W(4)} - \frac{1}{\text{V(3)}}
\]

\[
\text{Y}(4) \equiv \frac{\text{V(3)}}{\text{V(3)}} + P(4)
\]

one obtains:

\[
\text{ALTR}(4)\text{V}(4) - \text{ALTR}(5) = \text{Y}(4) \tag{B_3}
\]

The final equation yields:

\[
\text{ALTR}(N-1)\text{V}(N-1) - \text{ALTR}(N) = \text{Y}(N-1) \tag{B_n}
\]

and it is noted that \( \text{ALTR}(N) = 0 \).

The complete set of equations is then

\[
\text{ALTR}(1) = 1 \tag{P_1}
\]

\[
\text{ALTR}(I) = \frac{\text{Y}(I) + \text{ALTR}(I+1)}{\text{V}(I)} \quad 2 \leq I \leq N-2 \tag{P_I}
\]
\[ \text{ALTR}(N-1) = \frac{Y(N-1)}{V(N-1)} \]  

\[ \text{ALTR}(N) = 0 \]

with the following definitions applicable:

\[ W(I) = 2(I + C) + E \Delta Z^2 B(I) \quad 2 \leq I \leq N-1 \]

\[ P(I) = \Delta(I)C \quad 2 \leq I \leq N-1 \]

\[ Y(2) = P(2) + 1.0 \]

\[ V(2) = W(2) \]

\[ V(I) = W(I) - \frac{1}{V(I-1)} \quad 3 \leq I \leq N-2 \]

\[ Y(I) = \frac{Y(I-1)}{V(I-1)} + P(I) \quad 3 \leq I \leq N-2 \]

From equation (12), one calculates \( \phi \):

\[ \phi = \frac{ER(1) \Delta Z^2 - 2 \left[ \text{ALTR}(2) - 1 \right]}{2 \Delta Z} \]  

\[ (P\phi) \]

The procedure for solving is then first to calculate the values of \( W(I), P(I), Y(I), \) and \( V(I) \). The values of \( \text{ALTR}(I) \) are then found from Equations (P1) through (Pn). \( \phi \) is then calculated from (P\phi).

Equation (13) states:

\[ 2 \left[ \text{BLTR}(2) - \text{BLTR}(1) \right] - \frac{\text{BLTR}(1) - B(1)}{\Delta \phi} = \frac{E}{G} \text{BLTR}(1) + \]

\[ \text{ERBLTR}(1) \left\{ B(1) - 1 + \frac{2}{G} \left[ \phi - 1 \right] \right\} \]

\[ (13) \]

Multiplying equation (13) by \( \Delta Z^2 \), and combining terms, one obtains:

\[ \text{BLTR}(2) - \text{BLTR}(1) \left[ 1 + C + \frac{E}{2G} \Delta Z^2 + \frac{ER \Delta Z^2}{2} U(1) \right] = -B(1)C \]

where,

\[ U(1) = B(1) - 1 + \frac{2}{G} \left[ \phi - 1 \right] \]
Defining:

\[ X(1) \equiv 1 + C + \frac{E}{2G} \Delta Z^2 + \frac{ER \Delta Z^2}{2} U(1) \]

\[ Q(1) \equiv -B(1)C \]

one obtains

\[ BLTR(2) - BLTR(1) \left[ X(1) \right] = Q(1) \quad (Y_1) \]

Equation (11) states:

\[ \frac{BLTR(I+1) - 2BLTR(I) + BLTR(I-1)}{\Delta Z^2} \cdot \frac{EA(I)BLTR(I) + ERBLTR(I)}{G} \cdot \left\{ B(I) - 1 + \frac{2}{G} \left[ \phi(1-Z) - A(I) \right] \right\} \]

\[ (11) \]

where

\[ 2 \leq I \leq N-1 \]

Multiplying Equation (11) by \( \Delta Z^2 \), and combining terms, one obtains:

\[ BLTR(I+1) - BLTR(I) \left[ 2(1+C) + \frac{E}{G} \Delta Z^2 A(I) + ER \Delta Z^2 U(I) \right] + \]

\[ BLTR(I-1) = -B(I)2C \]

where

\[ U(I) \equiv B(I) - 1 + \frac{2}{G} \left[ \phi(1-Z) - A(I) \right] \quad 2 \leq I \leq N-1 \]

Defining:

\[ X(I) \equiv 2(1+C) + \frac{E}{G} \Delta Z^2 A(I) + ER \Delta Z^2 U(I) \quad 2 \leq I \leq N-1 \]

\[ Q(I) \equiv -B(I)2C \quad 2 \leq I \leq N-1 \]

one obtains:

\[ BLTR(I+1) - BLTR(I) \cdot X(I) + BLTR(I-1) = Q(I) \quad (11a) \]

Writing Equation (11a) with \( I=2,3,4 \), one obtains:

\[ BLTR(3) - BLTR(2) \cdot X(2) + BLTR(1) = Q(2) \quad (Y_2) \]
\[
\text{BLTR}(4) - \text{BLTR}(3) X(3) + \text{BLTR}(2) = Q(3) \quad (Y_3)
\]
\[
\text{BLTR}(5) - \text{BLTR}(4) X(4) + \text{BLTR}(3) = Q(4) \quad (Y_4)
\]

Adding Eq. \((Y_3)\) - Eq. \((Y_2)\), one obtains:

\[-\text{BLTR}(2) \left( \frac{1}{X(1)} + X(2) \right) + \text{BLTR}(3) = \frac{Q(1)}{X(1)} + Q(2)\]

Defining:

\[T(1) \equiv Q(2) + \frac{Q(1)}{X(1)}\]

\[S(1) \equiv X(2) - \frac{1}{X(1)}\]

one obtains,

\[-\text{BLTR}(2)S(1) + \text{BLTR}(3) = T(1) \quad (S_1)\]

Adding Eq. \((S_1)\) + Eq. \((Y_3)\), one obtains:

\[-\text{BLTR}(3) \left( X(3) - \frac{1}{S(1)} \right) + \text{BLTR}(4) = \frac{T(1)}{S(1)} + Q(3)\]

Defining:

\[S(2) \equiv X(3) - \frac{1}{S(1)}\]

\[T(2) \equiv \frac{T(1)}{S(1)} + Q(3)\]

one obtains:

\[-\text{BLTR}(3)S(2) + \text{BLTR}(4) = T(2) \quad (S_2)\]

Adding Eq. \((S_2)\) + Eq. \((Y_4)\), one obtains:

\[-\text{BLTR}(4) \left( X(4) - \frac{1}{S(2)} \right) + \text{BLTR}(5) = \frac{T(2)}{S(2)} + Q(4)\]
Defining:

\[ S(3) \equiv X(4) - \frac{1}{S(2)} \]

\[ T(3) \equiv \frac{T(2)}{S(2)} + Q(4) \]

one obtains:

\[-BLTR(4)S(3) - BLTR(5) = T(3)\]

The final equation yields:

\[-BLTR(N-1)S(N-2) + BLTR(N) = T(N-2)\]

where it is noted that \(BLTR(1) = 1\).

The complete set of equations is then:

\[ BLTR(1) = \frac{BLTR(2) - Q(1)}{X(1)} \quad (P_1) \]

\[ BLTR(I) = \frac{BLTR(I+1) - T(I-1)}{S(I-1)} \quad 2 \leq I \leq N-2 \quad (P_I) \]

\[ BLTR(N-1) = \frac{1 - T(N-2)}{S(N-2)} \quad (P_{N-1}) \]

\[ BLTR(N) = 1 \quad (P_N) \]

with the following definition applicable:

\[ Q(1) \equiv -B(1)C \]

\[ Q(I) \equiv -B(I)2C \quad 2 \leq I \leq N-1 \]

\[ U(1) \equiv B(1) - 1 + \frac{2}{G} \left[ \phi - 1 \right] \]

\[ U(I) \equiv B(I) - 1 + \frac{2}{G} \left[ \phi(I-2) - A(I) \right] \quad 2 \leq I \leq N-1 \]

\[ X(1) \equiv 1 + C + \frac{E}{2G} Z^2 + \frac{K}{2} U(1) \]

\[ X(I) \equiv 2(1+C) + \frac{E}{G} Z^2A(I) + K Z^2 U(I) \quad 2 \leq I \leq N-1 \]
\[ S(1) = \frac{X(1)X(2)}{X(1)} - 1 \]

\[ T(1) = Q(2) + \frac{S(1)}{X(1)} \]

\[ S(I) = \frac{X(I+1)S(I-1) - 1}{S(I-1)} \quad 2 \leq I \leq N-2 \]

\[ T(I) = Q(I+1) + \frac{T(I-1)}{S(I-1)} \quad 2 \leq I \leq N-2 \]

The procedure for calculating the values of BLTR(I) is first to calculate the values of Q(I), V(I), X(I), S(I) and T(I). BLTR(I) are then calculated by means of equations \( \rho_1 \) through \( \rho_N \).

VIII. APPENDIX (Cont.). C. The Computer Solution

The system of difference equations derived in Appendix B are in a form readily adaptable to computer solution. Such a solution was programmed for the IBM-704 digital computer, employing the FORTAN system. The program used is included at the end of this section.

Basically, the program is divided into four sections: (1) the main program, (2) the A Net solution (Subroutine Robert), (3) the B Net solution, (Subroutine Litton), and (4) a section including a provision for the variation of \( \Delta \Theta \) during the solution (Subroutine Brian).

The main program acts as coordinator for the entire solution. It accomplishes seven functions. It (1) provides for an input routine to read in data, (2) establishes an initial set of values for A and B, (3) employs Subroutine Robert for calculation of the A Net and \( \varnothing \), (4) employs Subroutine Litton for calculation of the B Net, (5) employs Subroutine Brian for changing the value of \( \Delta \Theta \) during the solution according to a pre-programmed scheme, (6) deter-
mines convergence, and (7) provides for an output routine to print out the desired answers.

Subroutine Robert, employing the input data together with the previously calculated values of A, B, and \( \theta \), calculates values of ALTR and the corresponding new value of \( \theta \).

Subroutine Litton, employing the input data together with the previously calculated values of A, B, and \( \theta \), calculates values of ELTR.

Subroutine Brian, employing input data, supplies the main program with a value of \( \Delta \theta \), as a function of the cycle of the program.

The data is input on standard eighty column IBM cards, punched in decimal form. The following data is required:

\[
E \ldots \ldots \ldots k_1 b_0 \frac{Z}{D_a} \\
G \ldots \ldots \ldots D_b \frac{a}{D_a} \\
R \ldots \ldots \ldots k_2 \frac{D_a}{k_1 D_c} \\
Z \ldots \ldots \ldots \text{distance increment} \\
C \ldots \ldots \ldots Z^2/2\Delta \theta
\]

DELTA......a criteria for convergence. If a value of \( \theta \) for the previous cycle differs from the newly calculated value of \( \theta \) by a quantity less than DELTA, then the program will print its presently stored values of A, B, and \( \theta \), together with the number of the cycle at which this convergence has taken place. The computer will then complete one more cycle, and print the newly calculated values of A, B, and \( \theta \) and will then end the run or read in a new set of data if such data are present.

CONE......a constant used in Subroutine Brian. If the number of cycles has reached a value equal to CONE, a value of C
equal to CFOUR will be supplied to the main program.

CTWO......a constant used in Subroutine Brian. If the number of
cycles has reached a value equal to CTWO, a value of C
equal to CFIVE will be supplied to the main program.

CTHREE.....a constant used in Subroutine Brian. If the number of
cycles has reached a value equal to CTHREE, a value of C
equal to CSIX will be supplied to the main program.

CFOUR......as explained under CONE above.

CFIVE......as explained under CTWO above.

CSIX.......as explained under CTHREE above.

CNO.......a feature of the program providing for culmination of
the run if the number of cycles exceeds CNO. Such
would be the case if the solution did not converge.

Included in the output are the following:

(1) Identification code
(2) A statement indicating that convergence has taken place.
(3) The cycle at which convergence has occurred together with the
values of A, B, and $\phi$ calculated.
(4) The next set of A's, B's, and $\phi$ calculated together with all
data input for the particular run.

If convergence has not taken place, i.e. the number of cycles has
exceeded CNO before the DELTA criterion had been satisfied, items (2)
and (3) in the above listing are omitted. Such an output is accomplished
with all sense switches in the down position.

Optional print-out included the following:

(1) Sense Switch 3 up: $\phi$ at all cycles will be printed together
with the corresponding cycle number.
(2) Sense Switch 2 up: All intermediate data will be printed.
This includes all values of A, B, and $\phi$, together with the
intermediate variables, P, Q, S, T, U, V, W, and Y.

VIII. APPENDIX (Cont.). D. Convergence and Stability

Since the differential equations to be solved contain a theta
derivative, it is to be expected that the intermediate calculated values
of $\phi$ will be "theta-varying." Furthermore, it is expected that at large
values of theta, the value of $\phi$ becomes independent of theta. This must
be so if the solution of the partial differential equations is to con-
 verge to the solution of the original, total differential equations.

Figure VIII shows a typical curves of $\phi$ converging as a function
of machine cycles.

The effect of $\Delta \theta$ on convergence is illustrated by these curves.
For all of the curves, the values of E, G, R, and $\Delta Z$ are the same,
but each curve represents a different value of $\Delta \theta$.

Several points may be noted from this graph. First, increasing
$\Delta \theta$ from 0.0005 to 0.0010 almost doubles the rate of convergence, the
two solutions converging at approximately 29 and 15 cycles, respectively.

Again doubling $\Delta \theta$ to a value of .002, however, does not double the
rate of convergence. In fact, the values of $\phi$ initially oscillate
markedly before it begins to approach a convergent value.

Increasing $\Delta \theta$ beyond .002 yields a non-convergent solution.

Another conclusion to be drawn from Figure 7 is the convergent
values of $\phi$ do not depend on $\Delta \theta$. Thus, curves 1, 2, 3 are all
approaching the convergent solutions of 10.25.

The independence of the solution of $\Delta \theta$ is to be expected. The
original physical system from which the equations were derived is a steady
C PROJECT M 969

DIMENSION A(999), B(999), ALTR(999), BLTR(999), U(999), X(999), W(999),
XS(999), T(999), H(999), V(999), P(999), Y(999)
COMMON A, B, ALTR, BLTR, U, W, S, T, H, V, P, Y

1 FORMAT (F15.7)
2 FORMAT (55H1K, GURNITZ AND G. LITTON, COMPUTER RESULTS, PROJ. NO.
XM969)
3 FORMAT (7H CYCLE=F15.7)
4 FORMAT (15H VALUES OF A(K))
5 FORMAT (15H VALUES OF B(I))
6 FORMAT (6H PHI= F15.7)
7 FORMAT (3H OEV=F15.7, 3H G=F15.7, 3H K=F15.7)
8 FORMAT (3H Z=F15.7)
9 FORMAT (3H C=F15.7)
10 FORMAT (8H DELTA=F15.7)
11 FORMAT (6H CONE=F15.7, 6H CTWO=F15.7, 8H CTHREE=F15.7)
12 FORMAT (7H CFOUR=F15.7, 7H CFIVE=F15.7, 6H CSIX=F15.7)
13 FORMAT (5H CNO=F15.7)

WRITE OUTPUT TAPE 2, 2

49 READ 1,E
50 READ 1,G
51 READ 1,R
52 READ 1,Z
53 READ 1,C
54 READ 1, DELTA
55 READ 1, CONE
56 READ 1, CTWO
57 READ 1, CTHREE
58 READ 1, CFOUR
READ 1, CFIVE
READ 1, CSIX
READ 1, CNO
CYCLE = 0.0
ZTWO = Z*Z
DD = E*ZTWO/G
EE = DD*G*K
HH = E*ZTWO
N = XINTF (1.0/Z + 1.0)
NN = N-1
DIFF = -1.0
DO 50 I=1,NN
DIFF = DIFF + 1.0
50 A(I) = (DIFF*Z-1.0)*(DIFF*Z-1.0)
A(N) = 0.0
PHI = 2.0
B(1) = 0.0
DIFF = 0.0
DO 51 I=2,NN
DIFF = DIFF + 1.0
51 B(I) = (DIFF*Z)*(DIFF*Z)
B(N) = 1.0
IF (SENSE SWITCH 2) 52, 910
510 WRITE OUTPUT TAPE 2,4
WRITE OUTPUT TAPE 2,1, (A(I), I=1, N)
WRITE OUTPUT TAPE 2,3
WRITE OUTPUT TAPE 2,1, (O(I), I=1, N)
52 CYCLE = CYCLE + 1.0
CC = 2.0 * (1.0 + C)
CCC=C
PROD = -2.0 * C

CALL ROBERT (A,D,C,E,Z,PHI,PHITWO,N,NN,ALTR,BLTR,PROD,ZTWO,CC,MM)

CHANGE = ABSF(PHI - PHITWO)

PHI = PHITWO

CALL LITTON(A,B,C,PHI,E,G,R,Z,N,NN,ALTR,BLTR,ZTWO,CC,DU,EE,PROD)

DO 53 I=1,N
A(I) = ALTR(I)
53 B(I) = BLTR(I)

IF (SENSE SWITCH 3) 55, 54

54 WRITE OUTPUT TAPE 2,3 ,CYCLE
WRITE OUTPUT TAPE 2,6,PHI

55 IF (CYCLE = CNO) 550, 59, 59

550 IF (DELTA - CHANGE) 56, 57, 572

56 C = BRIAN (CHANGE,CYCLE,CONE,CTWO,CTHREE,CFOUR,CFIVE,CSIX,CCC)
GO TO 52

57 FORMAT(1/H IT HAS CONVERGED)

571 FORMAT(10H AT CYCLE F10.1,2H PHI=F10.6)

572 WRITE OUTPUT TAPE 2,57
WRITE OUTPUT TAPE 2,571,(CYCLE,PHI)
WRITE OUTPUT TAPE 2,4
WRITE OUTPUT TAPE 2,1,(A(I), I=1,N)
WRITE OUTPUT TAPE 2,5
WRITE OUTPUT TAPE 2,1,(B(I), I=1,N)

CYCLE = CNO+1.0
GO TO 52

59 WRITE OUTPUT TAPE 2,4
WRITE OUTPUT TAPE 2,1,(A(I), I=1,N)
WRITE OUTPUT TAPE 2,5
WRITE OUTPUT TAPE 2,1,(B(I), I=1,N)
WRITE OUTPUT TAPE 2,6,PHI
WRITE OUTPUT TAPE 2,7, (E, G, K)
WRITE OUTPUT TAPE 2,8, (Z)
WRITE OUTPUT TAPE 2,9, (C)
WRITE OUTPUT TAPE 2,10, (DELTA)
WRITE OUTPUT TAPE 2,11, (CONE, CTWO, CTREE)
WRITE OUTPUT TAPE 2,12, (CFOUR, CFIVE, CSIX)
WRITE OUTPUT TAPE 2,13, (CNO)
GO TO 49
END (0,1,0,0,0)

C
SUBROUTINE ROBERT
SUBROUTINE ROBERT (A,B,C,E,Z,PHI,PHI2,MIN,NN,ALTR, BLTR, PROD, CTWO,
XCC, HH)
DIMENSION A(999), B(999), ALTR(999), BLTR(999), U(999), X(999),
XQ(999), S(999), T(999), W(999), V(999), P(999), Y(999)
COMMON A, B, ALTR, BLTR, U, S, T, W, V, P, Y
1 FORMAT (23H SUBROUTINE ROBERT DATA)
2 FORMAT (E15.7)
3 FORMAT (12H VALUES OF W)
4 FORMAT (12H VALUES OF V)
5 FORMAT (12H VALUES OF P)
6 FORMAT (12H VALUES OF Y)
7 FORMAT (15H VALUES OF ALTR)
CALL EFM
DO 11 I=2,NN
11 W(I) = CC + HHREB(I)
IF (SENSE SWITCH 2) 12, 110
110 WRITE OUTPUT TAPE 2,1
      WRITE OUTPUT TAPE 2,3
      WRITE OUTPUT TAPE 2,2,(W(I), I=2,NN)
12    DO 13 I=2,NN
13    P(I) = -A(I)*PROD
      Y(2) = P(2) + 1.0
      V(2) = W(2)
      DO 14 I=3,NN
14    V(I) = W(I) - 1.0/V(I-1)
      DO 15 I=3,NN
15    Y(I) = Y(I-1)/V(I-1) + P(I)
      IF (SENSE SWITCH 2) 16,150
150   WRITE OUTPUT TAPE 2,4
      WRITE OUTPUT TAPE 2,2,(V(I), I=3,NN)
      WRITE OUTPUT TAPE 2,5
      WRITE OUTPUT TAPE 2,2,(P(I), I=2,NN)
      WRITE OUTPUT TAPE 2,6
      WRITE OUTPUT TAPE 2,2,(Y(I), I=3,NN)
16    ALTR (N) = 0.0
      ALTR (N-1)=Y(N-1)/V(N-1)
      K=N-2
      DO 18 J=2,K
      I=N-J
18    ALTR (I) = (Y(I) + ALTR (I+1))/V(I)
      ALTR (1) = 1.0
      IF (SENSE SWITCH 2) 19,180
180   WRITE OUTPUT TAPE 2,7
      WRITE OUTPUT TAPE 2,2,(ALTR (I), I=1,N)
19    PHITWO = (E*Z*B(I))/2.0 - (ALTR(2) - 1.0)/Z
C SUBROUTINE LITTON

SUBROUTINE LITTON (A,B,C,PHI,E,G,K,Z,N,N1,ALTR,BLTR,ZTWO,CC,DD,EE,
XPROD)

DIMENSION A(999),B(999),ALTR(999),BLTR(999),U(999),X(999),W(999),
XS(999),T(999),W(999),V(999),P(999),Y(999),

1 FORMAT (23H SUBROUTINE LITTON DATA)

2 FORMAT (E15.7)

3 FORMAT (12H VALUES OF U)

4 FORMAT (12H VALUES OF U)

5 FORMAT (12H VALUES OF X)

6 FORMAT (12H VALUES OF S)

7 FORMAT (12H VALUES OF T)

8 FORMAT (15H VALUES OF BLTR)

Q(1) = PROD*B(1)/2.0

DO 11 I=2,N

11 Q(I) = PROD * B(I)

U(I) = B(I) - 1.0 + (2.0/G)*(PHI - 1.0)

DO 12 I = 2,NN

PP = FLOAT(I-1)

12 U(I) = B(I) - 1.0 + (2.0/G)*(PHI*(1.0-PP*Z) -A(I))

IF (SENSE SWITCH 2) 13,120

120 WRITE OUTPUT TAPE 2,1

WRITE OUTPUT TAPE 2,3

WRITE OUTPUT TAPE 2,2, (Q(I), I = 1,N)

WRITE OUTPUT TAPE 2,4
WRITE OUTPUT TAPE 2,2, (U(I), I = 1,NN )

13  X(I) = EE*U(I)/2.0 + DD/2.0 + 1.0 + C

DO 14 I = 2,NN

14  X(I) = CC + DD*A(I) + EE*U(I)

IF (SENSE SWITCH 2) 15,140

140 WRITE OUTPUT TAPE 2,5

WRITE OUTPUT TAPE 2,2, (X(I), I = 1,NN)

15  S(I) = (X(I)*X(2) - 1.0)/X(I)

T(I) = Q(2) + (Q(1))/X(I)

NNN = N-2

DO 16 I = 2,NNN

S(I) = (S(I-1)*X(I+1) - 1.0)/S(I-1)

16  T(I) = Q(I+1) + (T(I-1)/S(I-1))

IF (SENSE SWITCH 2) 17,160

160 WRITE OUTPUT TAPE 2,6

WRITE OUTPUT TAPE 2,2, (S(I), I = 1,NNN)

WRITE OUTPUT TAPE 2,7

WRITE OUTPUT TAPE 2,2, (T(I), I = 1,NNN)

17  BLTR(N-1) = (1.0 - T(N-2))/S(N-2)

BLTR(N) = 1.0

DO 18 J = 2,NNN

1  = N-J

18  BLTR(I) = (BLTR(I+1) - T(I-1))/S(I-1)

BLTR(1) = (BLTR(2) - Q(1))/X(1)

IF (SENSE SWITCH 2) 19,180

180 WRITE OUTPUT TAPE 2,6

WRITE OUTPUT TAPE 2,2, (BLTR(I), I = 1,N)

19 RETURN

END (0,1,0,0,0)
C FUNCTION BRIAN

FUNCTION BRIAN(CCHANGE, CYCLE, CONE, CTWO, CTHREE, CFOUR, CFIVE, CSIX, CCC)

1 IF(CYCLE = CONE) 4,0,4
2 IF(CYCLE = CTWO) 6,0,3
3 IF(CYCLE = CTHREE) 8,10,10
4 BRIAN = CCC
5 GO TO 15
6 BRIAN = CFOUR
7 GO TO 15
8 BRIAN = CFIVE
9 GO TO 15
10 BRIAN = CSIX
15 RETURN

END (0,1,0,0,0)
**Figure VIII**

EFFECT OF $\varphi$ ON CONVERGENCE

\[ \varphi = \frac{V_L}{V_I} \]

**Curve 1**
- $E = 1000$
- $G = 20$
- $R = 1$
- $Z = 0.01$
- $\varphi = 0.002$

**Curve 2**
- $E = 1000$
- $G = 20$
- $R = 1$
- $Z = 0.01$
- $\varphi = 0.001$

**Curve 3**
- $E = 1000$
- $G = 20$
- $R = 1$
- $Z = 0.01$
- $\varphi = 0.0005$
state one, and in fact, the original equations did represent the steady-state system. The introduction of theta-derivatives into the equations was only an artifice by which a stable system of difference equations could be obtained, and consequently, any convergent solution must be independent of $\Delta \theta$.

The effect of the parameters $E$, $R$, and $G$, on stability is complex, and it has not been possible to formulate quantitative criteria with regard to stability versus parameter values.

Several useful statements can, however, be made concerning stability, the most general being that for a given set of values of $E$, $R$, and $G$, there is a certain value of $\Delta \theta$ above which the solution does not converge. Below this value, the solution does converge, the rate of convergence decreasing as $\Delta \theta$ decreases.

For the sake of the following discussion, the maximum allowable value of $\Delta \theta$ which yields a convergent solution will be referred to as "convergent-theta."

For a given set of values of $E$ and $G$, the value of convergent-theta decreases as $R$ increases. Values of convergent-theta as large as 1000 and as small as $10^{-5}$ were employed, corresponding to a very "small" and very "large" values of $R$, respectively. Small values of $R$ were in the range of $10^{-4}$ to $10^{-6}$, and large values were in the range of 1.0 to 5.0.

For a given value of $R$ and $G$, convergent-theta decreases as $E$ increases, and for a given value of $E$ and $R$ convergent-theta increases as $G$ increases.

With the data obtained, it has not been possible to obtain more precise formulations than the ones stated above.

Table 6 is a compilation of many of the results, both convergent
and non-convergent, obtained. Listed for each run are E, R, G, Δ Z, Δ θ, the value of \( \theta \) obtained, and a general comment about the result.

The various symbols listed under the column labelled "Comments" have the following significance.

C: The run had produced a convergent value of \( \theta \).

S: The solution was converging, but at too slow a rate. This corresponds to too small a value of Δ θ.

D: The solution was non-convergent, corresponding to too large a value of Δ θ.

G: The solution was close enough to a convergent result that it was possible to extrapolate the \( \theta \) versus machine cycle curve to obtain a convergent value of \( \theta \).

Table 6 may be used as a guide in future work for choosing optimum values of Δ θ for a new set of parameters.
### Table VI

**Summary of Computer Results**

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E. The Effect of $\Delta Z$ on the Convergent Value of $\phi$

It was necessary to ascertain which value of $\Delta Z$ to use in solving the difference equations. As $\Delta Z$ is made smaller, the solution of the difference equations will more closely approximate the true solution of the differential equations. However, the number of difference equations to be solved is inversely proportional to $\Delta Z$, and hence the amount of computer time necessary to obtain a particular solution is almost inversely proportional to the value of $\Delta Z$.

The following table lists the convergent values of $\phi$ obtained using different values of $\Delta Z$ for a given set of values for $E$, $R$, and $G$.

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Although the effect of $\Delta Z$ on $\phi$ seems to be random, it is nevertheless small. A variation in $\Delta Z$ over an eight-fold range gave less than an 0.55% change in $\phi$.

A value of $\Delta Z$ of .02 was used for most of the solutions obtained. The choice of this value was dictated by the following reasoning. First of all, the machine time requirement for a $\Delta Z$ of .02 is roughly one-quarter of that for a $\Delta Z$ of .005. Second, the value of $\phi$ at $\Delta Z = .02$ differs from that at .005 by less than one quarter of a percent, consequently justifying the use of .02 for the value of $\Delta Z$. 
VIII. APPENDIX (Cont.)

F. Justification of Time Variant System

The time variant differential equations are constructed in the following manner.

Considering, again, a volume element of thickness $\Delta x$ and of unit cross section, a material balance is taken.

For species $A$:

Moles in per unit time at $x = x$:

$$N_{a1} = -D_a \frac{\partial a}{\partial x}$$

Moles out per unit time at $x = x + \Delta x$:

$$N_{a2} = -D_a \frac{\partial a}{\partial x} x + \Delta x$$

Moles reacted in volume element per unit time:

$$N_{a3} = k_{ab} \Delta x$$

Moles accumulated in volume element per unit time:

$$N_{a4} = \frac{\partial a}{\partial t} \Delta x \quad t = \text{time}$$

(Note that in the steady state, $N_{a4}$ will be equal to zero.)

By a material balance:

$$N_{a1} = N_{a2} + N_{a3} + N_{a4}, \quad \text{or}$$

$$D_a \left[ \frac{\partial a}{\partial x} \right]_{x + \Delta x} - \left[ \frac{\partial a}{\partial x} \right]_x - \Delta x \frac{\partial a}{\partial t} \Delta x = k_{ab}$$
In the limit, as $\Delta X \to 0$,

$$D_a \frac{\partial^2 a}{\partial x^2} - \frac{\partial a}{\partial t} = k_{1ab}$$

A similar balance on species $B$ yields:

$$D_b \frac{\partial^2 b}{\partial x^2} - \frac{\partial b}{\partial t} = k_{1ab} + k_{2bc}$$

The following variable transformations are again convenient:

$$Z = x/x_f \quad A = a/a_i \quad B = b/b_o \quad C' = c/b_o$$

and the following definitions again are made:

$$E = k_{1b} x_f^2 / D_a \quad G = D_b b_o / D_a a_i \quad P' = D_b / D_c$$

$$R = k_{2D} / k_{1D}$$

In terms of these new variables, equations (8) and (9) become:

$$\frac{\partial^2 A}{\partial Z^2} - \frac{x_f^2}{D_a} \left( \frac{\partial A}{\partial t} \right) = EAB$$  \hspace{1cm} (8a)

$$\frac{\partial^2 B}{\partial Z^2} - \frac{x_f^2}{D_b} \left( \frac{\partial B}{\partial t} \right) = \frac{E}{G} AB + \frac{FR}{P'} BC'$$  \hspace{1cm} (9a)

Defining:

$$\varphi = t \frac{D_b}{x_f}$$, therefore:

$$d\varphi = \frac{D_b}{x_f} dt$$

Substituting into equations (8a) and (9a):

$$\frac{\partial^2 A}{\partial Z^2} - \frac{D_b}{D_a} \frac{\partial A}{\partial \varphi} = EAB$$ \hspace{1cm} (8b)
\[
\frac{\partial^2 \theta}{\partial Z^2} - \frac{\partial \theta}{\partial Z} = \frac{A}{G} \frac{\partial^2}{\partial Z^2} - \frac{\partial \theta}{\partial Z} = \frac{E}{G} AB + \frac{FR}{P} BC
\]

(9b)

The variable \( C' \) in equation (9b) is eliminated by substituting the steady-state value of \( C' \), given by equation (9b), leading to the following equations.

\[
\frac{\partial^2 A}{\partial Z^2} - \frac{D_b A}{D_a} \frac{\partial \theta}{\partial Z} = EAB
\]

(8c)

\[
\frac{\partial^2 B}{\partial Z^2} - \frac{D_b B}{D_a} \frac{\partial \theta}{\partial Z} = EAB + \frac{2}{G} \left\{(B-1) + \frac{2}{G} \left(\theta(1-Z) - A\right)\right\}
\]

(9c)

This rather arbitrary procedure is justified by the following argument. The solution of equations (8b) and (9b) approaches the steady-state solution, that is, the system described by equations (8) and (9), as a limit. The effect of introducing the steady-state value of \( C' \) into equation (b) therefore helps "pull" the solution to steady-state.

A further simplification of equation (8c) is made by setting the ratio \( D_b/D_a \) equal to unity. This is justified by the fact that in the steady-state solution, the derivative \( \partial A/\partial \theta \) is equal to zero. Therefore, any constant multiplying this derivative will have no effect on the steady-state solution. Setting \( D_b/D_a \) equal to unity leads to equation (8) and (9).

\[
\frac{\partial^2 A}{\partial Z^2} - \frac{\partial A}{\partial Z} = EAB
\]

(8)

\[
\frac{\partial^2 A}{\partial Z^2} - \frac{\partial B}{\partial Z} = \frac{E}{G} AB + \frac{2}{G} \left\{(B-1) + \frac{2}{G} \left(\theta(1-Z) - A\right)\right\}
\]

(9)
VIII. APPENDIX (Cont.)

G. Location of Original Data

All data obtained from the IBM-704 Computer is located in the files of Professor P.L.T. Brian, Dept. of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.
VIII. APPENDIX (Cont.)

H. Literature Citations


(9) Van Krevelen, D. W., and P. J. Hoftijzer, Rec. trav. chim., 67, 563 (1948)
## VIII. APPENDIX (Cont.)

### I. List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>normalized concentration of species $A$, $a/a_1$</td>
</tr>
<tr>
<td>ALTR</td>
<td>normalized concentration of species $A$, at a &quot;time&quot; $\Delta \theta$ greater than that at which $A$ is evaluated</td>
</tr>
<tr>
<td>a</td>
<td>concentration of species $A$</td>
</tr>
<tr>
<td>B</td>
<td>normalized concentration of species $B$, $b/b_0$</td>
</tr>
<tr>
<td>BLTR</td>
<td>normalized concentration of species $B$, at a &quot;time&quot; $\Delta \theta$ greater than that at which $B$ is evaluated</td>
</tr>
<tr>
<td>b</td>
<td>concentration of species $B$</td>
</tr>
<tr>
<td>C</td>
<td>$\Delta Z^2/2\Delta \theta$</td>
</tr>
<tr>
<td>C'</td>
<td>normalized concentration of species $C$, $c/b_0$</td>
</tr>
<tr>
<td>c</td>
<td>concentration of species $C$</td>
</tr>
<tr>
<td>D</td>
<td>liquid phase diffusivity</td>
</tr>
<tr>
<td>DELTA</td>
<td>convergence criterion</td>
</tr>
<tr>
<td>E</td>
<td>$k_1 b_0 N^2/D_a$</td>
</tr>
<tr>
<td>G</td>
<td>$D_b b_0/D_a a_1$</td>
</tr>
<tr>
<td>K_L</td>
<td>liquid phase absorption coefficient</td>
</tr>
<tr>
<td>k</td>
<td>reaction phase rate constant</td>
</tr>
<tr>
<td>N</td>
<td>$1/\Delta Z + 1$</td>
</tr>
<tr>
<td>P'</td>
<td>$D_b/D_c$</td>
</tr>
<tr>
<td>P(I)</td>
<td>$A(I)2C$</td>
</tr>
<tr>
<td>Q(I)</td>
<td>$-B(I)C$ if $I = 1$ [ -B(I)2C \text{ if } 2 \leq I \leq N-1 ]</td>
</tr>
<tr>
<td>R</td>
<td>$k_2 D_a/k_1 D_c$</td>
</tr>
</tbody>
</table>
\[ S(I) \quad \frac{X(I)X(I+1)-1}{X(I)} \quad I = 1 \]
\[ \frac{X(I+1)S(I-1)-1}{S(I-1)} \quad 2 \leq I \leq N-1 \]

\[ T(I) \quad Q(I+1) + \frac{Q(I)}{X(I)} \quad I = 1 \]
\[ Q(I+1) + T(I-1)/S(I-1) \quad 2 \leq I \leq N-1 \]

\[ t \quad \text{time} \]

\[ U(I) \quad B(I) - 1 + \frac{2}{G} (\phi-1) \quad I = 1 \]
\[ B(I) - 1 + \frac{2}{G} \left[ \phi(1-Z) - A(I) \right] \quad 2 \leq I \leq N-1 \]

\[ V(I) \quad W(I) \quad I = 2 \]
\[ W(I) = 1/V(I-1) \quad 3 \leq I \leq N-2 \]

\[ W(I) \quad 2(I+C) + E \Delta Z^2 B(I) \]

\[ X(I) \quad 1 + C + \frac{E}{2G} \Delta Z^2 + \frac{ER \Delta Z^2}{2} U(1) \quad I = 1 \]
\[ 2(I+C) + E \Delta Z^2 A(I) + ER \Delta Z^2 U(I) \quad 2 \leq I \leq N-1 \]

\[ x \quad \text{distance into liquid phase} \]

\[ x_f \quad \text{film thickness} \]

\[ Y(I) \quad P(I) + 1 \quad I = 2 \]
\[ \frac{Y(I-1)}{V(I-1)} + P(I) \quad 3 \leq I \leq N-1 \]

\[ Z \quad \text{normalized distance into liquid phase, } x/x_f \]

**GREEK LETTERS**

\[ \varepsilon \quad \text{error associated with solution of difference equation} \]

\[ \phi \quad \text{modified time increment, } D_t/x_f^2 \]

\[ \Gamma \quad \text{as defined in equation (20)} \]

\[ \phi \quad \frac{K_L^z}{K_L} \]
**SUBSCRIPTS**

a  referring to species A  
b  referring to species B  
c  referring to species C  
i  referring to gas-liquid interface  
o  referring to liquid bulk  
l  referring to reaction (1)  
2  referring to reaction (2)  

**SUPERSCRIPTS**

*  referring to absorption without chemical reaction