ture. A theoretical mechanism for the adsorption-based cohesive-energy-density differences is suggested.

## NOTATION

$A$ = liquid component $A$, the more highly adsorbed component (benzene in this case)
$A_A$ = effective area occupied by a mole of component $A$ in a monolayer (sq. m./g.)
$A_B$ = effective area occupied by a mole of $B$ in a monolayer (sq. m./g.)
$a_o$ = attractive force constant between components and adsorbent surface
$a_x$ = attractive force constant between binary solution and components
$a_y$ = attractive force constant between binary solution and pore
$B$ = liquid component $B$, component (cyclohexane in this case)
$C$ = Stuart slope of $\ln y/1-y$ vs. $\ln x/1-x$
$D$ = adsorbent pore diameter, Å.
$d$ = constant in Stuart equation
$G$ = selective adsorption capacity (g. of component $A$ adsorbed/g. of adsorbent)
$G'$ = moles of component $A$ adsorbed /g. of adsorbent
$k$ = constant in Stuart equation
$M$ = Stuart intercept of plot $\ln y/1-y$ vs. $\ln x/1-x$
$M_{(m)}$ = average molecular weight of binary solution in monolayer
$M_{(x)}$ = average molecular weight of equilibrium solution
$n$ = moles of total original solution
$n_A$ = moles of component $A$ adsorbed /g. of adsorbent
$n_B$ = moles of component $B$ adsorbed/g. of adsorbent
$R$ = universal gas constant
$r$ = pore radius, Å.
$S_T$ = adsorbent surface area, sq. m./g.
$T$ = temperature, °K.
$V_p$ = adsorbent pore volume cc./g.
$W_s$ = weight of original solution, g.
$W_a$ = adsorbent weight, g.
$X$ = equilibrium weight fraction of adsorbed component (bulk solution)
$X_o$ = weight fraction of stronger adsorbed component in original solution
$x$ = equilibrium mole fraction of adsorbed component (bulk solution)
$x_o$ = mole fraction of more highly adsorbed component in original solution
$Y$ = weight fraction of component $A$ in equilibrium solution
$y_{(m)}$ = mole fraction of component $A$ in monolayer calculated by the use of Williams equation
$y'_{(m)}$ = equilibrium mole fraction of component $A$ in the pore as calculated by the Williams equation

### Greek Letters

$\xi$ = constant in Stuart equation
$\rho_b$ = density of benzene, g./cc.
$\rho_{x(m)}$ = density of binary mixture in monolayer, g./cc.
$\rho_x$ = density of equilibrium solution, g./cc.
$\Delta\rho_x$ = density differences between the equilibrium liquid components, g./cc.
$\Delta\rho_y$ = density difference between adsorbate components, g./cc.
$\Psi$ = constant in Stuart equation

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*Manuscript received September 22, 1958; revision received September 30, 1959; paper accepted October 12, 1959.*


# Calculation Procedures for Binary Batch Rectification


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**A rigorous mathematical description, consisting of differential-difference equations, is presented for binary batch rectification in the plate type of column. Two approaches are taken to solving these equations for the condition of constant reflux ratio: an integration by numerical means employing an IBM 650 computer, and a hand calculation procedure that involves trial-and-error computation of batch-rectification curves, which is of interest primarily where high-speed computing equipment is not available.**

**Enthalpy balances are used to avoid assumption of equal rate of overflow in the tower; weight units are used instead of mole units; means for accounting for holdup in the condenser-accumulator system are described. Criteria of convergence and stability of the numerical solution are presented. The validity of the results of the proposed calculation procedures is substantiated by the close agreement of experimental and calculated batch-rectification curves.**


Interest in batch-rectification calculations has grown during recent years, as evidenced by the contributions which have appeared in the technical literature. For a review of most of this work it is recommended that the reader consult the work of Rose and Rose (*1*) and Rose and Johnson (*2*). Rose, Johnson, and Williams (*3*) also give a brief historical outline of many of the accomplishments in the field.

The mathematical model describing batch rectification is inherently very complex even for the case of a binary mixture. Batch-rectification calculation procedures, comparable in rigor to methods for continuous steady state distillation calculations, have therefore led to long and tedious procedures. Simplification for convenience, on the other hand, has tended to restrict applicability of the results to the conditions embodied within the simplifying assumptions. For instance, the use of


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some of the traditional assumptions frequently employed in continuous steady state distillation has in most cases not met with great success in batch-rectification computations. It should be generally recognized now that because of the assumptions required the McCabe-Thiele (4) method can lead to gross errors in batch-rectification calculations where appreciable holdup is present in the tower. This was pointed out by Colburn and Stearns (5) and has been discussed by Van der Hoeven (6) and Rose *et al.* (7). Huckaba and Tour (8) presented further confirmation of the wide divergence which can exist by comparing experimentally determined batch-rectification operating lines with the corresponding lines calculated by both the McCabe-Thiele and Ponchon-Savarit (9, 10) methods.

Rose and Johnson (2) made a very comprehensive study of the various nonidealities which might have to be considered in batch-rectification calculations. They suggested approaches for handling variable relative volatility, plate efficiency less than 100%, nonadiabatic operation, condenser holdup, and variation of column holdup with time. Huckaba and Tour (8) pointed out the advantages of using weight units in batch-rectification computations and showed that equality of plate-to-plate overflow in batch rectification would not usually occur on either a mole or weight basis.

The investigation reported in this paper represents a continuation of the work of Huckaba and Tour (8), who, emphasizing rigor rather than convenience, presented design procedures that were tedious and time consuming.

The work has proceeded along two lines of approach. The hand-calculation method of Huckaba and Tour was simplified in order to be of more practicable value for those workers who do not have access to a high-speed computing machine. The other portion of the work was devoted to the adaptation of the solution of the basic equations to a medium-speed digital computer. Confirmation of the hand and machine procedures was obtained through direct comparison of calculated and experimental curves.

## THEORETICAL ANALYSIS

To select the proper operating conditions and number of plates required in designing a batch-rectification column to perform a given separation, it is necessary to predict the composition of the distillate and kettle liquid as a function of the fraction of the batch distilled. This can be accomplished by solving a series of simultaneous differential-difference equations, based on enthalpy and material balances around the individual plates. These balances consist of merely an extension of the work of Sorel (11) to transient conditions. Most of the previous work has involved material balances, but only Rose and Johnson (2) and Huckaba and Tour (8) have written the enthalpy balances.

For a column having $N$-plates $N+1$ differential material balances of the more volatile component can be written, one around each plate and one around the kettle. A corresponding number of enthalpy balances can also be made. Several authors (2, 5, 7, 12) have discussed the possible assumptions upon which these balances can be written. The basic assumptions made in setting up the differential equations in this paper are (1) the holdup of vapor in the column is small compared with that of the liquid; (2) heat losses from the column are negligible; (3) holdup per plate is constant; (4) liquid composition on a tray is uniform.

Under these conditions a differential material balance for the more volatile component and a differential enthalpy balance around plate $n$ (section $A$ in Figure 1), written as suggested by Pigford *et al.* (13) in terms of fraction distilled, give respectively

$$\frac{V_{n+1}\,y_{n+1}}{D} - \frac{L_n x_n}{D} + \frac{L_{n-1}\,x_{n-1}}{D} - \frac{V_n y_n}{D} = \frac{H_n}{S_o}\frac{dx_n}{d\phi} \qquad (1)$$

$$\frac{V_{n+1}\,I_{n+1}}{D} - \frac{L_n i_n}{D} + \frac{L_{n-1}\,i_{n-1}}{D} - \frac{V_n I_n}{D} = \frac{H_n}{S_o}\frac{di_n}{d\phi} \qquad (2)$$

Similar material and enthalpy balances around the kettle (section $B$ in Figure 1) yield

$$\frac{L_N x_N}{D} - \frac{V_S y_S}{D} = \frac{d(x_S S/S_o)}{d\phi} = \frac{d(x_S(1-\phi))}{d\phi} \qquad (3)$$

$$\frac{L_N i_N}{D} - \frac{V_S I_S}{D} = \frac{d(i_S S/S_o)}{d\phi} - \frac{Q_B}{D} \qquad (4)$$

It is the solution of this group of differential equations which is sought, given the boundary conditions for $\phi = 0$, that is the steady state conditions at the end of the warmup period. In addition to the initial steady state conditions, it is also necessary to prescribe the value of one of the variables as a function of $\phi$. This may be the specification of $L_R/D$, for operation of constant reflux ratio, or, alternately, a constant or prescribed variation of $y_1$ with $\phi$ might be the given condition. These two alternatives are the ones most commonly met in industrial applications, but a number of other possibilities exist. However care must be taken to set up a boundary condition which will lead to a physically significant solution.

The solutions developed in this investigation are for constant reflux ratio. If the reflux to the column is below its boiling point, $i_R$ is not only a function of $x_R$ but also of the degree of subcooling, which must be known.

It should be noted that in developing the basic equations it was not necessary to stipulate constancy of $D$, $(V_S - L_N)$, $Q_B$, or, in fact, any mass or heat flow rates. Thus a varying boilup rate throughout a batch-rectification run would result in the same curve of overhead composition vs. fraction distilled as a constant boilup rate, providing the plate-efficiency relationships were not affected.

To make the solution as general as possible the equilibrium and plate-efficiency relationships are taken as

$$y^*_n = f(x_n) \qquad (5)$$

and

$$y_n = E_{MVn}y^*_n + (1-E_{MVn})y_{n+1} \qquad (6)$$

or

$$x^*_n = f(y_n) \qquad (7)$$

$$x_n = E_{MLn}x^*_n + (1-E_{MLn})x_{n-1} \qquad (8)$$

With a functional relationship between $E_{MVn}$ (or $E_{MLn}$) and $x_n$ there are a sufficient number of equations available to solve the set of differential equations. If $H_n$ cannot be assumed constant, there are $N$ additional variables, $H_1, H_2, \ldots H_N$, but since each of these is a function only of the corresponding compositions, $x_1, x_2, \ldots x_N$, the solution of the differential equations can still be accomplished.

### Consideration of Condenser and Accumulator Holdup

In most actual batch-rectification systems the holdup of material in the condenser-accumulator system cannot be neglected. Consideration of this holdup was omitted from the previous section on derivation of the basic equations, since there is some question as to the manner in which this holdup should be treated.

As pointed out by Rose *et al.* (14), the overhead holdup can be broken down as follows: holdup of vapor in the line between the top of the column and the condenser, holdup of vapor and condensate in the condenser, liquid holdup in the lines between the condenser and accumulator and between the accumulator and reflux inlet of the column, and accumulator holdup. For the first three types of holdup

listed, the assumption of slug flow with no back mixing definitely seems to be better than that of complete mixing; however, the degree of mixing in the accumulator can be expected to vary widely from one installation to the next depending on the shape of the vessel, the position of the inlet and outlet nozzles, and the liquid flow rate.

One of the following assumptions could be made concerning condenser-accumulator holdup: (1) the entire holdup of the condenser-accumulator system is completely mixed, or (2) all flow through the overhead system is free of back mixing. Based on what little information is available on the applicability of these alternate assumptions, the assumption of no back mixing appears to be the better founded of the two. If an analytical solution of the design equations were to be attempted, material- and enthalpy-balance equations written around section C of Figure 1 would have to be used to relate $x_R$ with $y_1$. However in solving the equations by numerical methods, as will be shown later, the value of $x_R$ when $\phi = k\Delta\phi$ can readily be determined, since it is equal to the value of $y_1$ when $\phi = k\Delta\phi - (\Delta\phi)_c$ where $(\Delta\phi)_c$ is the time lag expressed in terms of $\phi$ for a small increment of material to pass through the condenser-accumulator system.

Since $C$ is the mass of the overhead holdup and $(R+1)D$ is the mass rate of flow, the time lag between entering and leaving the condenser-accumulator system is $C/(R+1)D$. To express this lag in terms of $\phi$ it must be multiplied by $D/S_o$:

$$(\Delta\phi)_c = \frac{C}{S_o}\frac{1}{(R+1)} \qquad (9)$$

From $\phi = 0$ to $\phi = C/S_o(R+1)$, that is the time required to displace completely the original contents of the overhead system, the composition of the reflux is equal to the composition of the vapor leaving the top plate at steady state. For larger values of $\phi$ the appropriate value of $x_R$ can be determined from the portion of the $y_1$ vs. $\phi$ curve already developed in the calculation.

The assumption of no back mixing was verified experimentally by taking samples simultaneously from each end of the condenser-accumulator system during the batch-rectification runs described below and establishing that the difference in compositions of the two samples did, in fact, correspond to a lag between entering and leaving the system of $C/S_o(R+1)$.

### Derivation of the Over-all Material-Balance Equation

When it is assumed that the amount of holdup on each tray is equal and

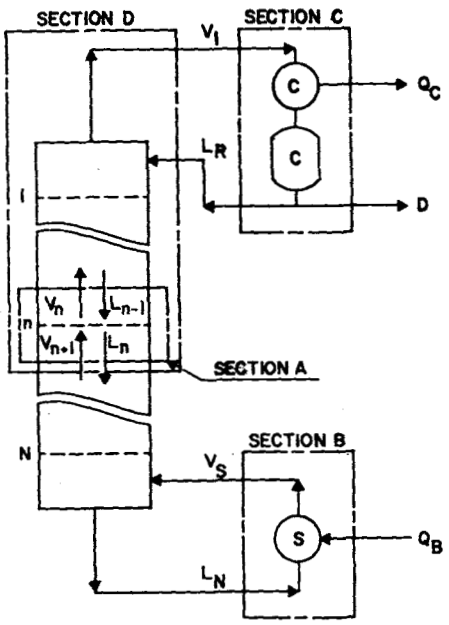


Fig. 1. Sections of the batch-rectification system about which material and enthalpy balances are made.

constant, a material balance of the more volatile component around the entire system shown in Figure 1 leads to

$$\frac{d(S/S_o)}{dx_S} - \frac{S/S_o}{x_D - x_S} = \frac{1}{x_D - x_S}\left(\frac{H_T}{S_o}\frac{dx_{HT}}{dx_S} + \frac{C}{S_o}\frac{d\bar{x}_C}{dx_S}\right) \qquad (10)$$

This equation is a linear, first order differential equation in the variable $S/S_o$, and so its solution can be expressed as

$$\frac{S}{S_o} = e^{-M}\left[1 + \int_{x_{S_o}}^{x_S} \frac{e^M}{x_D - x_S}\left[\frac{H_T}{S_o}\frac{dx_{HT}}{dx_S} + \frac{C}{S_o}\frac{d\bar{x}_C}{dx_S}\right]dx_S\right] \qquad (11)$$

where $M = \int_{x_{S_o}}^{x_S} -\frac{dx_S}{x_D - x_S}$

This equation is very similar to the one obtained by Rose (15).

If $dx_{HT}/dx_S$, $d\bar{x}_C/dx_S$, and $x_D$ are known as a function of $x_S$, the value of $S/S_o$ corresponding to any given value of $x_S$ can be found by a double graphical integration. First, $e^M$ is determined graphically as a function of $x_S$, and then the integral of Equation (11) can be evaluated graphically. For $H_T$ and $C$ equal to zero the integral term vanishes and the conventional Rayleigh type of equation results.

### Simplification of the Basic Equations

Plate-to-plate calculations based on the use of both material and heat balances around a plate normally involve a trial-and-error procedure. In calculating down a column, $y_{n+1}$ must be determined from $x_n$. However this requires a knowledge of $V_{n+1}$, which in turn depends on $y_{n+1}$.

For a number of systems, however, the enthalpy-composition relationships are essentially linear, and simplified equations can be derived expressing $y_{n+1}$ directly as a function of $x_n$, the rates and composition of the streams entering and leaving the top of the column, and the rate of change of holdup of the more volatile component on plates 1 through $n$.

In this paper the enthalpies of the saturated vapor and saturated liquid are expressed by

$$I_n = A + By_n \qquad (12)$$

$$i_n = a + bx_n \qquad (13)$$

A material balance for the more volatile component and an enthalpy balance around section D shown in Figure 1 gives

$$V_{n+1}y_{n+1} - L_nx_n + L_Rx_R - V_1y_1 = \sum_{j=1}^{n}\frac{H_j dx_j}{d\theta} \qquad (14)$$

$$V_{n+1}I_{n+1} - L_ni_n + L_Ri_R - V_1I_1 = \sum_{j=1}^{n}\frac{H_j di_j}{d\theta} \qquad (15)$$

The degree of subcooling of the reflux below its boiling point is given by

$$\Delta T = (a + bx_R - i_R)/C_p \qquad (16)$$

Substitution of the above together with the linear expressions for $I_n$ and $i_n$ into Equation (15) and combining with Equation (14) gives

$$y_{n+1} = \frac{\beta x_n + [(x_R - x_n) + (R+1)(y_1 - x_R) + \sum_{j=1}^{n}(H_j/S_o)dx_j/d\phi]}{\beta - g[(x_R - x_n) + (R+1)(y_1 - x_R) + \sum_{j=1}^{n}(H_j/S_o)dx_j/d\phi]} \qquad (17)$$

where $\beta = (R+1)(1+gy_1) + RC_p\Delta T/(A-a)$, $g = (B-b)/(A-a)$, and $R = L_R/D$.

The above equation relates $y_{n+1}$ to $x_n$ and thus represents the operating-line

equation. At steady state $dx_1/d\theta = 0$ and $y_1 = x_R$, and so for use in steady state warm-up calculations the equation becomes

$$y_{n+1} = \frac{\beta x_n + (x_R - x_n)}{\beta - g\ (x_R - x_n)} \qquad (18)$$

Use of either the unsteady state or steady state forms of the above equation eliminates the trial-and-error procedure normally required in plate-to-plate calculations employing enthalpy balances. It should be restated, however, that the applicability of these simplified equations is limited to systems having essentially linear enthalpy-composition relationships.

## CALCULATION PROCEDURES

Two approaches to the solution of the basic differential-difference equations were taken. The first involved a numerical integration of the differential equations in the direction of increasing $\phi$ with the conditions at the end of the steady state start-up period used as the boundary conditions. The second approach was based on the method of Huckaba and Tour (8), in which the finite-difference equations are integrated step by step in the direction of increasing $n$ and in which it is necessary to establish the relationship between $x_D$ and $\phi$ by trial and error.

### Selection of Units

Distillation calculations are generally carried out with compositions and flow rates expressed in mole units, since for many binary systems it is possible to assume constant molal liquid overflow from tray to tray. Since this assumption is rather restrictive, it was obviated in the derivation of the basic unsteady state equations by inclusion of enthalpy balances around the individual plates. If it is not necessary to assume constant molal overflow, there is no particular advantage in the use of molar units; in fact there is a definite disadvantage in their use, since flowmeters and level gauges cannot be used to measure molar rates and quantities directly.

The reason for using weight units is that the pounds of holdup per plate is generally much less dependent on composition of the plate liquid than is the moles of holdup. Strictly speaking, it is probably the volume of holdup that is least dependent upon composition, but since volumetric flow rates of liquid mixtures are not necessarily additive, the use of weight units appears preferable. As the range of liquid densities normally encountered is much narrower than the range of molecular volumes, the assumption of constant weight of holdup would seem for most cases to be better than that of constant moles holdup. However for those cases in which the moles of holdup do not vary greatly with time, if it should be desired to work in mole units, the calculation procedures described in this paper can be employed without alteration except for conversion of units.

### Solution by Numerical Methods

Solution of the $N+1$ differential equations relating the dependent variables $x_1, x_2, \ldots x_N$, and $x_S$ with the independent variable $\phi$ can be accomplished by conventional techniques for numerical integration. The simplest of these, known as the Euler method, assumes that $dx_n/d\phi$ is constant over the increment from $\phi_k$ to $\phi_{k+1}$, so that

$$x_{n:k+1} = x_{n:k} + (dx_n/d\phi)_k\, \Delta\phi \qquad (19)$$

A considerably better assumption is that $dx_n/d\phi$ is linear between $\phi_k$ and $\phi_{k+1}$. This corresponds to the assumption that the curve of $x_n$ vs. $\phi$ can be fitted by a second-degree polynomial in $\phi$ over a single $\Delta\phi$ increment. In this case the numerical formula is

$$x_{n:k+1} = x_{n:k} + \frac{\Delta\phi}{2} [(dx_n/d\phi)_k + (dx_n/d\phi)_{k+1}] \qquad (20)$$

Since the derivative $(dx_n/d\phi)_{k+1}$ cannot be determined until $x_{n:k+1}$ is known, an iterative process is necessary to satisfy the above equation.

This method, known as the modified Euler method, was the one selected for use in starting the solution of the unsteady state distillation equations, since is could be applied beginning with the very first increment in $\phi$. Methods based on a past history are obviously not applicable over the first few increments, where no past history yet exists.

The great disadvantage in the modified Euler method is that under certain circumstances many iterations may be necessary for the prescribed degree of satisfaction of Equation (20). This is undesirable from the standpoint of the calculating time required.

Consequently in most of the calculations the modified Euler method was used over only the first few increments, and the simple Euler method was employed thenceforth for numerical integration of Equations (1) and (3).

### Convergence and Stability of the Numerical Formulas

Rose *et al.* (7) and Rosenbrock (17) have pointed out the necessity of ensuring convergence and stability in calculations of this type. In the application of the numerical formulas the size of the increment in $\phi$ that could be employed in the solution was found to be limited by one or the other of two factors. When the modified Euler method was used, there was an increment size above which the iterative process, common to all numerical formulas of the closed type, would not converge. On the other hand, the increment size used in the simple Euler method was limited by the stability of the solution; that is, the use of too large an increment size caused successive values of $x_n$ to oscillate about the true curve with ever increasing amplitude, resulting ultimately in completely absurd values of $x_n$.

By a derivation similar to that given by Hildebrand (18) for the case of a single dependent variable, it can be shown that the limiting increment size for convergence of the modified Euler method is defined by

$$\Delta\phi < \frac{H_n/S_n}{(R_n + 1)\, m + R_n} \qquad (21)$$

In the derivation of the limiting value of $\Delta\phi$ it is necessary to assume that $R_n$ and $m$ are constant over a range of two plates. Under these conditions it can further be shown that the limiting condition for stability of the simple and modified Euler methods is also given by Equation (21).

Equation (21) was not derived until most of the computer runs had been completed, and consequently this equation was not used in the work described in the following sections. However the need for a relationship by which a satisfactory increment size could be estimated became increasingly apparent as the work progressed, and more and more hours of computer time were wasted because an increment size was used which ultimately led to divergence or instability.

The validity of Equation (21) for convergence of the modified Euler method was demonstrated by a series of calculations over the first increment in $\phi$. The values of $x_{n:1}$ were punched out by the computer for $n$ from one to $N$ following each of eight to ten iterations, and from these data it was possible to determine whether the iterative process was converging or diverging. The enthalpy data used in the program for this calculation was chosen such that $R_n$ was constant, since this was assumed in the derivation of the limiting increment size for convergence. In addition, the operating conditions and equilibrium data were chosen to minimize the variation of $m$.

In one series of runs, in which $H/S_n$ was taken as 0.012, $R$ was 2.0 and $m$ varied from 0.520 at the bottom of a twelve-plate column to 0.500 at the top; $\phi = 0.0035$ was found to give convergence, whereas $\phi = 0.0040$ gave divergence. When the maximum value of $m$ is used, the limiting $\Delta\phi$ predicted

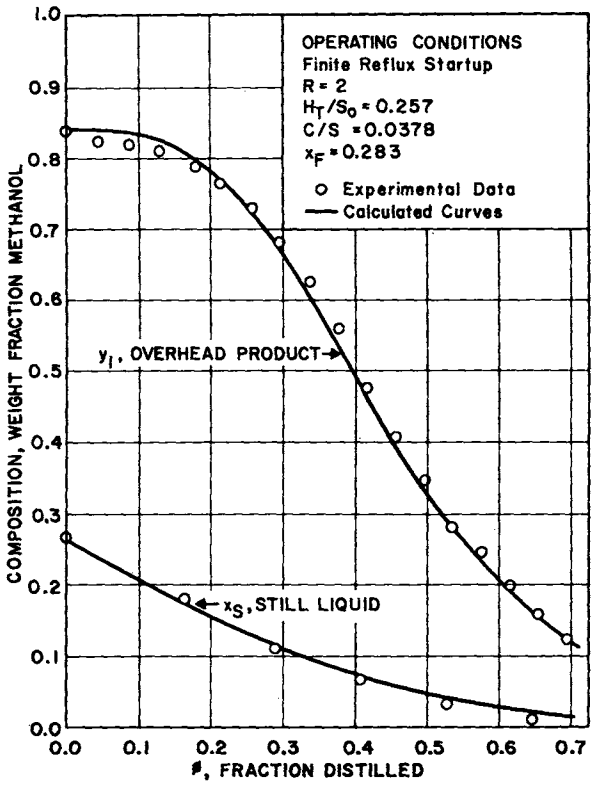


Fig. 2. Comparison of calculated and experimental data—run B-1.

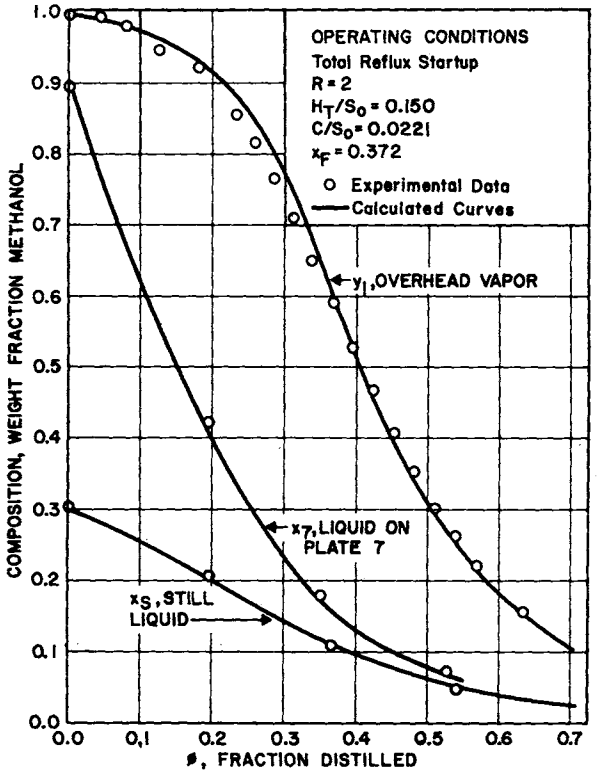


Fig. 3. Comparison of calculated and experimental data—run B-4.

by Equation (21) is $\phi < 0.00343$. Thus the predicted value of $\Delta\phi$ would give convergence of the iterative process but is only slightly less than the maximum usable value, determined by trial and error to lie between 0.0035 and 0.0040.

For the general case where $R_n$ and $m$ vary from plate to plate, use of the maximum value of the term $(R_n + 1)\ m + R_n$ in Equation (21) was found, in some instances, to predict a value of $\Delta\phi$ which gave divergence, and values 20 to 30% less than the predicted maximum were found to be necessary for convergence. Thus in general Equation (21) can be used to determine only a first approximation of the maximum increment size for convergence and stability and is exact only if $R_n$ and $m$ are constant. The equation does however give the right order of magnitude for the maximum value of $\Delta\phi$ that can be used and can therefore save a large portion of the trial and error involved in establishing the increment size.

### The Computer Program

The numerical integration of the $N + 1$ differential equations was programed on an IBM 650 data-processing machine. This was desirable since the extremely small increment size required for convergence and stability made a hand-calculated solution entirely impractical. The initial, steady state calculation was also included in the program, and so a minimum number of data is needed for calculation of the complete batch-rectification curves. Danly (*19*) has presented a detailed discussion of this program.

The computing time on the IBM 650 required for the unsteady state calculation is approximately 0.5 sec./plate/$\Delta\phi$ increment when the simple Euler method is used and about two to four times as long with the modified Euler method, depending on the number of iterations necessary. In the calculations made for comparison with the experimental runs described below, the modified Euler method was used for only the first twenty increments ($\Delta\phi = 0.0005$), and the enthalpy data were assumed linear. About 2½ hr. was required to reach a value of $\phi = 0.70$.

## EXPERIMENTAL WORK

Mixtures of methanol and tertiary butyl alcohol were distilled at about atmospheric pressure in a twelve-plate, bubble-cap column. The column had an internal diameter of 10 in. and a plate spacing of 12 in. Five 2-in. O.D. bubble caps were contained on each plate. Sample outlets on each plate were positioned to allow withdrawal of samples of the liquid just prior to entry into the downcomer. The entire column was insulated to minimize heat losses.

A 40-gal. jacketed kettle served as the still pot. A rotary pump was used to circulate the contents of the kettle during runs to ensure adequate mixing.

The accumulator was designed to keep a constant liquid head on the reflux to the column to allow close control of the reflux rate. The split of condensate into reflux and product was controlled manually by means of a valve in the reflux line. The portion of the flow from the condenser that was not returned as reflux overflowed to the product receivers. An electric immersion heater in the reflux line was provided for reheating the reflux.

After passing through the product rotameter, the product stream could be directed into either one of two receivers or returned to the kettle. A bypass line was installed between the vapor line from the kettle and the condenser. This line enabled the column holdup to be determined at various operating conditions, since the column could be completely isolated from the system by directing the vapor flow from the kettle through the bypass, instead of through the column, and by closing valves in the reflux line and column-bottoms line.

### Experimental Procedure

The experimental runs were of two different types. First a preliminary set of runs was made to investigate the effects of liquid composition, vapor velocity, and reflux ratio on the plate efficiencies. The second series, the batch-rectification runs, comprised the major part of the experimental program. The purpose of these runs was to determine sets of experimental curves of product and kettle composition vs. fraction distilled for comparison with calculated curves.

Since the initial conditions for the batch runs were those of steady state, two types of batch runs were possible. One involved an initial steady state start-up at the same finite reflux ratio as that used for the unsteady state portion of the run, returning the product stream directly to the

kettle. Alternately, the column could be allowed to come to equilibrium at total reflux for the start-up condition. The latter mode of operation is the one more commonly employed in industry. All runs were made at constant reflux ratio during the unsteady state portion of the run.

In the batch runs when equilibrium had been reached, the twelve plates, kettle, and reflux were sampled. The unsteady state portion of the run was then initiated either by diverting the product stream from the kettle to a product receiver (for finite-reflux start-up) or by cutting down on the reflux rate to begin withdrawal of product to a receiver (for total-reflux start-up). At regular time intervals the product flow was switched from one product receiver to the other, and the liquid was immediately drained from the partially full receiver into a tared container.

During an entire run about fifteen to twenty samples of the overhead condensate and about half as many kettle samples were withdrawn at recorded times. In some runs samples were also taken from selected plates directly after each change in product receivers.

When about 5 gal. of liquid remained in the kettle, the run was terminated. Following shutdown the liquid drained from the accumulator and associated lines was weighed. From these weights, along with those of the intermediate product accumulations, a material balance could be made, and in turn the relationship between time and fraction distilled could be determined. From the refractive-index measurements of the liquid samples, it was then possible to make plots of composition vs. fraction distilled. The determination of these plots for a variety of operating conditions constituted the main objective of the experimental program.

### Comparison of Calculated and Experimental Results

In making the calculations for comparison with the experimental data the following empirical relationships were employed to represent the binary-system data:

*Plate-Efficiency Data*

$$E_{MLn} = 0.845 - 0.740\,x_n, \quad 0.000 < x_n < 0.224 \qquad (22)$$

$$E_{MLn} = 0.763 - 0.374\,x_n, \quad 0.224 < x_n < 1.000 \qquad (23)$$

*Equilibrium Data*

$$x^*_n = 0.6184\,y_n, \quad 0 < y_n < 0.3234 \qquad (24)$$

$$x^*_n = (y_n - 0.0355)/1.4393, \quad 0.3234 < y_n < 0.4670 \qquad (25)$$

$$x^*_n = \frac{y_n + 0.406}{4.232 - 2.826\,y_n}, \quad 0.4670 < y_n < 1 \qquad (26)$$

*Enthalpy Data*

$$i_n = 115.0 - 44.0x_n \qquad (27)$$

$$I_n = 349.8 + 194.2y_n \qquad (28)$$

*Heat-Capacity Data for Saturated Liquid*

$$C_p = 0.880 - 0.244x \qquad (29)$$

The plate-efficiency data were obtained experimentally for the desired rate of throughput as a function of liquid composition. Equilibrium data were obtained with a Fenske (*20*) still. Basic thermal data were obtained from Perry (*21*) and Parks and Anderson (*22*).

Comparisons of calculated and experimental batch-rectification curves are given in Figures 2 through 4. It is seen that in general the agreement is excellent. A number of other experimental and calculated batch-rectification plots were determined with mutual agreement comparable to the runs shown. The ranges of operating variables studied were $1 < R < 4$ and $0.119 < H_T/S_o < 0.257$.

The close agreement obtained in these comparisons substantiates the validity of the numerical calculation procedure for the ranges of variables considered. Thus it is believed that this procedure provides a generally satisfactory means for making accurate batch-rectification calculations provided that electronic computation equipment is available. Without such equipment however this method is too lengthy, and for hand computations an alternative procedure is recommended.

### Solution by the Huckaba-Tour Method

The basic difference between the numerical solution previously described and the Huckaba-Tour method (*8*) is that in the former a series of differential equations is integrated in the direction of increasing $\phi$, whereas

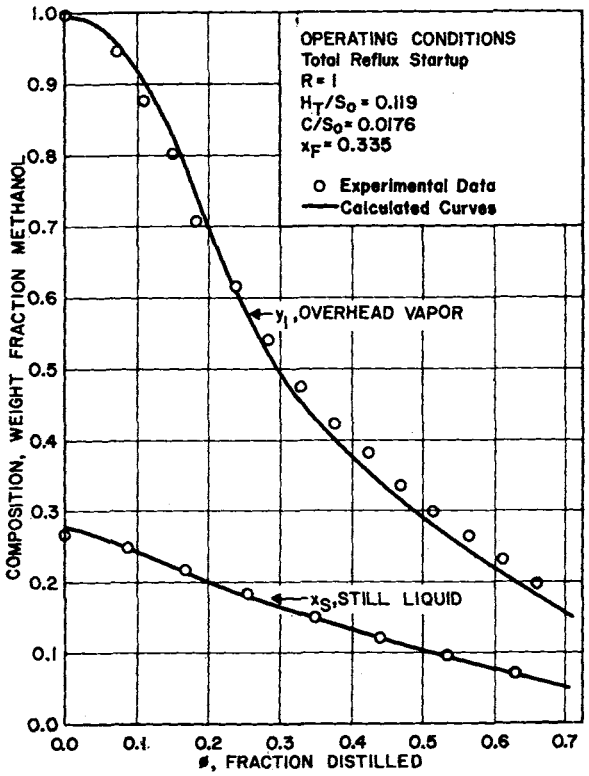


Fig. 4. Comparison of calculated and experimental data—run B-6.

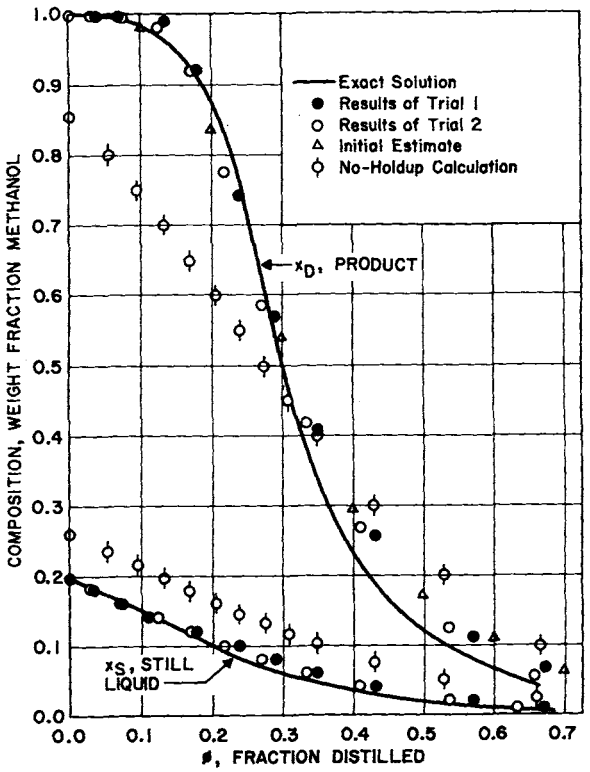


Fig. 5. Calculated batch-rectification curves illustrating the Huckaba-Tour method.

Table 1. Summary of Results of Second Trial Calculation in Illustrative Problem by the Use of the Huckaba-Tour Method

| | Composition, weight fraction methanol | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\phi$ | 0.0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 |
| $x_D$ | 0.9995 | 0.991 | 0.874 | 0.543 | 0.302 | 0.170 | 0.096 | 0.059 |
| $y_1$ | 0.9995 | 0.989 | 0.845 | 0.515 | 0.284 | 0.160 | 0.090 | 0.057 |
| $x_C$ | 0.9995 | 0.990 | 0.860 | 0.529 | 0.293 | 0.165 | 0.093 | 0.058 |
| $x_{HT}$ | 0.8370 | 0.563 | 0.268 | 0.129 | 0.067 | 0.037 | 0.021 | 0.014 |
| $x_S$ | 0.1962 | 0.154 | 0.112 | 0.076 | 0.045 | 0.027 | 0.016 | 0.011 |

| $x_S$ | $x_D$ | $e^{-M}$ | $\frac{H_T}{S_o}\frac{dx_{HT}}{dx_S}$ | $\frac{C}{S_o}\frac{dx_C}{dx_S}$ | $-f_1$ | $f_2$ | $\phi$ |
|---|---|---|---|---|---|---|---|
| 0.1962 | 0.9995 | 1.000 | 0.318 | 0.000 | 0.396 | 0.000 | 0.000 |
| 0.1800 | 0.998 | 0.980 | 0.591 | 0.005 | 0.745 | 0.009 | 0.029 |
| 0.1600 | 0.995 | 0.956 | 1.189 | 0.012 | 1.504 | 0.033 | 0.075 |
| 0.1400 | 0.981 | 0.934 | 1.062 | 0.040 | 1.403 | 0.062 | 0.125 |
| 0.1200 | 0.920 | 0.912 | 0.900 | 0.163 | 1.459 | 0.090 | 0.170 |
| 0.1000 | 0.775 | 0.888 | 0.606 | 0.282 | 1.481 | 0.119 | 0.218 |
| 0.0800 | 0.585 | 0.858 | 0.445 | 0.262 | 1.632 | 0.150 | 0.271 |
| 0.0600 | 0.417 | 0.818 | 0.298 | 0.243 | 1.852 | 0.185 | 0.334 |
| 0.0400 | 0.269 | 0.763 | 0.228 | 0.211 | 2.518 | 0.227 | 0.411 |
| 0.0200 | 0.125 | 0.666 | 0.193 | 0.211 | 5.77 | 0.303 | 0.536 |
| 0.0100 | 0.055 | 0.568 | 0.193 | 0.211 | 15.82 | 0.397 | 0.658 |

$$f_1 = \frac{e^M}{x_D - x_S}\left[\frac{H_T}{S_o}\frac{dx_{HT}}{dx_S} + \frac{C}{S_o}\frac{dx_C}{dx_S}\right]$$

$$f_2 = \int_{x_{S_o}}^{x_S} f_1\, dx_S$$

in the latter an integration of a series of finite-difference equations is performed in the direction of increasing $n$. One basic advantage of the Huckaba-Tour approach is that only $N$ increments need be taken in the $n$ direction, with $x_n$ evaluated only at as many values of $\phi$ as are necessary to draw in the curve of $x_n$ vs. $\phi$, whereas in the numerical solution as many as 2,000 to 10,000 increments may be required in the integration in the $\phi$ direction for a stable solution. Thus the Huckaba-Tour method finds applicability where high-speed computers are not available.

However this method also has one serious drawback, in that the boundary condition relating $x_D$ as a function of $\phi$ cannot be established in advance. Therefore it is necessary to assume a curve of $x_D$ vs. $\phi$, corresponding to specified values of $N$ and $R$, from which curves of $x_1$, $x_2$, . . . $x_n$, and $x_S$ vs. $\phi$ can successively be determined. Then an over-all material balance is made to give a corrected curve of $x_D$ vs. $\phi$. This iterative process is continued until the assumed and calculated curves are in satisfactory agreement.

The steps involved in the calculation procedure are

1. Assume a curve of $x_D$ vs. $\phi$ based on a knowledge of the initial value of $x_D$ (that is the steady-state value of $x_D$ existing at end of warm-up period) and the relationship between the area under the entire curve and the over-all composition of the material charged to the still.

2. At discrete values of $\phi$, for example, 0.05, 0.10, 0.15, . . ., determine the values of $y_1$ from the curve of $x_D$ vs. $\phi$ and the condenser lag $(\Delta\phi)_c$.

3. Calculate the corresponding values of $x_1$ from the equilibrium and plate-efficiency relationships. If the plate efficiency varies with $x$, trial and error will be necessary.

4. Plot $x_1$ vs. $\phi$ and evaluate the slopes $dx_1/d\phi$ at the selected values of $\phi$. Then determine the corresponding value of $di_1/d\phi$ from the composition-enthalpy relationship.

5. Calculate $y_2$ by Equation (1) with $V_1/D$ used as a first approximation of $V_2/D$.

6. Calculate $V_2/D$ by Equation (2) and compare with the value used in step 5. Repeat steps 5 and 6, if the agreement is not satisfactory.

7. Determine $x_2$ from the equilibrium and plate-efficiency relationships, as done for $x_1$ in step 3. Calculate on down the column in this manner until $y_N$ has been determined.

8. Calculate $x_S$ as the liquid in equilibrium with $y_N$.

9. Integrate Equation (11) graphically to relate $x_S$ with $S/S_o$. Since for constant holdup $S/S_o = 1 - \phi$, $x_S$ and the corresponding value of $x_D$ can then be related with $\phi$. Compare the calculated curve of $x_D$ vs. $\phi$ with that assumed in step 1 and repeat the entire calculation procedure if necessary.

If the enthalpy-composition relationships are linear, then Equation (17) can be used to calculate $y_{n+1}$ from $x_n$, avoiding the necessity for the iterative procedure described in steps 5 and 6.

### Illustrative Problem

A batch-rectification design calculation was carried out by the Huckaba-Tour method with the following data assumed:

| | | |
|---|---|---|
| 1. | Relative volatility | 2.0 |
| 2. | Reflux ratio | 2.0 |
| 3. | Number of plates | 12 |
| 4. | Enthalpy constant, $g$ | 1.0 |
| 5. | Reflux subcooling | 0 |
| 6. | Plate efficiency, $E_{ML}$ | 1.0 |
| 7. | Plate holdup $H/S_o$ | 0.012 |
| 8. | Condenser holdup $C/S_o$ | 0.030 |
| 9. | Charge composition $x_F$ | 0.295 |

Total reflux start-up was assumed; therefore the operating-line relationship for the steady state period was merely $y_{n+1} = x_n$. Although the steady state calculation for total reflux is straightforward, a trial-and-error approach was necessary in order to find the set of still, plate, and condenser compositions which has a composite value equal to that of the liquid charged to the system.

The initially assumed curve of $x_D$ vs. $\phi$ is shown in Figure 5. The value of $x_D$ at $\phi = 0$ was determined in the steady state calculation, and then a curve was drawn through this point such that the total area under the curve was approximately $x_F$ $(1 - HN/S_o - C/S_o)$. This relationship follows by equating the amount of the more volatile component initially in the system to that removed in the product when the contents of the kettle have been depleted, with the liquid on the plates and in the condenser assumed to be essentially pure high boiler at $\phi = 1.0$. Values of $y_1$, $x_1$, $y_2$, $x_2$, . . . $y_S$, $x_S$ were calculated successively at a number of values of $\phi$ as described earlier. Following the plate-to-plate calculations the values of the average plate holdup $\overline{x_{HT}}$ and the average condenser holdup $\overline{x_C}$ were determined corresponding to each value of $\phi$. Plots were then made of $\overline{x_C}$ and $\overline{x_{HT}}$ vs. $x_S$, and the slopes $d\overline{x_C}/dx_S$ and $d\overline{x_{HT}}/dx_S$ were evaluated. The relationship between $e^M$ and $x_S$ was found from the area under the curve of $(x_D - x_S)^{-1}$ vs. $x_S$, between $x_{S_o}$ and $x_S$. Then $S/S_o$ was related to $x_S$ by graphically integrating Equation (11). Since each value of $x_S$ had associated with it a value of $x_D$, the curve of $x_D$ vs. $\phi$ could be plotted for comparison with the curve assumed initially.

The entire procedure was then repeated with the results of the first trial calculation for the relationship between $x_D$ and $\phi$ used. The results of the second trial are summarized in Table 1.* The values of $x_D$ and $x_S$ determined in the first and second trial calculations are shown in Figure 5, together with the points defining the

* Tabular material showing results of the first trial has been deposited as document 6262 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

initial estimate of the $x_D$ vs. $\phi$ curve and the results of the computer solution, based on numerical integration of the basic differential equations. The increment in $\phi$ used in the numerical integration was sufficiently small ($\Delta\phi = 0.0005$) that this solution can be considered as exact for all practical purposes. Also shown in Figure 5 is the gross error resulting from completely neglecting column holdup in this batch-rectification calculation.

Ideally one would like to be able to repeat the trail calculations until the resulting curve of $x_D$ vs. $\phi$ falls directly on top of the one assumed at the beginning of the trail calculation. However in general such perseverance would probably not be justified, owing to the excessive amount of calculating time required. There can be little doubt however that some accounting of holdup is absolutely essential and that the above method does provide a possible approach to the problem where electronic computers are not available.

## SUMMARY

Two approaches to the solution of the basic batch-rectification equations have been demonstrated and verified by experimental data. The first involves integration of the basic differential equations by conventional numerical methods. The extremely small increments in fraction distilled that are required for stability of the numerical formulas requires the use of an electronic computer. A medium-speed computer gave rapid and accurate results.

For designers who do not have access to an electronic computer, the approach of Huckaba and Tour (8) as modified in this investigation is much faster than attempting a numerical integration with a desk calculator or slide rule.

Both of the approaches assume that the holdup per plate is constant, but use of these methods is not restricted to any particular set of units. In many cases the use of weight units appears to be satisfactory with respect to constancy of holdup and is preferable from the design standpoint of applying economic data directly to the results of the calculation. Methods of accounting both for enthalpy effects and for condenser-accumulator holdup in batch-rectification calculations have been demonstrated. Also an approach to the development of quantitative criteria for ensuring convergence and stability in the numerical machine computations has been presented.

It is believed that the two calculation procedures presented herein provide the designer with tools for development of batch-rectification curves, which are in general both convenient and valid and as such allow a high degree of confidence in batch-rectification designs in which they are applied.

## NOTATION

$a$ = y intercept in the linear liquid-enthalpy equation, $i_n = a + bx_n$, B.t.u./lb.

$A$ = y intercept in the linear vapor enthalpy equation $I_n = A + By_n$, B.t.u./lb.

$b$ = slope in the linear liquid-enthalpy equation B.t.u./lb.

$B$ = slope in the linear vapor enthalpy equation, B.t.u./lb.

$C$ = holdup in the condenser-accumulator system, lb.

$C_p$ = mean heat capacity of reflux between its subcooled temperature and boiling point, B.t.u./(lb. °F.)

$D$ = flow rate of distillate from the system, lb./hr.

$E_{ML}$ = Murphree liquid-plate efficiency

$E_{MV}$ = Murphree vapor-plate efficiency

$g$ = $(B - b)/(A - a)$, enthalpy constant

$H$ = total liquid and vapor holdup per plate, lb.

$i$ = enthalpy of the liquid, B.t.u./lb.

$I$ = enthalpy of the vapor, B.t.u./lb.

$k$ = number of increments in $\phi$ between $\phi = 0$ and $\phi = \phi$

$L$ = liquid flow rate down the column, lb./hr.

$m$ = slope of the curve of $y_n$ vs. $x_n$

$M$ = $\int_{x_{S_o}}^{x_S} -dx_S/(x_D - x_S)$

$N$ = number of plates in the column

$Q$ = heat flow rate, B.t.u./hr.

$R$ = reflux ratio, $L_R/D$

$R_n$ = internal reflux ratio, $L_n/D$

$S$ = quantity of liquid in the still, lb.

$\Delta T$ = temperature difference between the boiling point of the reflux and the temperature at which it is introduced into the column, °F.

$x$ = liquid composition, weight fraction more volatile component

$\bar{x}_C$ = average composition of condenser-accumulator holdup, weight fraction more volatile component

$y$ = vapor composition, weight fraction more volatile component

$\beta$ = $(R + 1)(1 + gy_1) + RC_p\Delta T/(A - a)$

$\theta$ = time, hr.

$\phi$ = fraction distilled, defined as $1 - S/S_o$

### Subscripts

1, 2, . . ., $n-1$, $n+1$, . . ., $N$ = top plate, second plate from the top, . . ., plates $n - 1$, $n$, and $n + 1$, . . ., and the bottom plate

$k - 1$, $k$, $k+1$ = integral number of increments in fraction distilled, $(k-1)\ \phi$, $(k)\ \phi$, and $(k+1)\ \phi$

$B$ = reboiler

$C$ = condenser-accumulator system

$D$ = distillate (pertains to instantaneous value)

$F$ = feed charged to the still initially

$HT$ = total holdup in the column

$o$ = original ($\phi = 0$)

$R$ = reflux stream

$S$ = still material

$T$ = total

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*Manuscript received February 10, 1959; revision received October 9, 1959; paper accepted October 12, 1959.*