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NON-IDEAL STAGE MULTICOMPONENT ABSORBER CALCULATIONS BY AUTOMATIC DIGITAL COMPUTER

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I. INTRODUCTION

A. Purpose of Investigation

The advent of high-speed, electronic computing machinery has caused a great deal of interest in the automatic computer solution of many chemical engineering problems. One of the first problems to be investigated was vapor-liquid mass transfer such as occurs on the plates of a distillation or gas absorption column. Most of the effort spent thus far has been directed to the machine adaptation of methods already developed for hand calculation, methods involving the simplifying assumption of the so-called "ideal", "theoretical", or "equilibrium" stage.

The purpose of the present investigation was fourfold: (1) to formulate a mathematical model of an actual or non-ideal vapor-liquid contact device, such as a bubble-cap plate, and to make this model suitable for use with an automatic computer; (2) to develop a computer procedure for predicting the mass transfer relations involved in the non-ideal stage; (3) to investigate the use of enthalpy, equilibrium, and physical property correlations more rigorous and accurate than those currently in use, methods too tedious for hand calculation; and (4) to demonstrate the soundness and applicability of the non-ideal stage approach by writing a computer program for its use and comparing predicted performance of actual equipment with test data.

The equipment selected for investigation was the multicomponent petroleum gas absorber. Computation was done on the IBM 650 magnetic drum data processing machine at the University of Michigan and the IBM 704 electronic data processing machine installed at the General Motors Technical Center.

B. Description of a Petroleum Gas Absorber

A petroleum gas absorber is a device for recovering certain hydrocarbons from a natural gas or refinery gas stream. The main components of the stream, methane and ethane, carry with them smaller percentages of materials in the LPG (liquefied petroleum gas) and natural gasoline ranges, propane through hexane or heptane, which we desire to recover. Small quantities of hydrogen, nitrogen, carbon dioxide, hydrogen sulfide, etc., may be present also.

Recovery of the desired hydrocarbons is effected by absorbing them in a heavy petroleum fraction called absorber oil, a material with average molecular weight equal to that of kerosene or heavy diesel oil. Transfer of material between gas and absorber oil streams occurs in a counter-current multi-stage contacting device called an absorption column. Figure 1 gives a schematic diagram. The rich gas stream, V_0, enters the bottom of the column; the lean gas, V_n, leaves at the top. Lean absorber oil, L_{n+1}, enters the top of the column; rich absorber oil, L_1, leaves at the bottom. At each stage or plate of the column, m, liquid and vapor streams are brought into intimate contact, the vapor bubbling upward through the liquid stream as it passes across the plate. Plates are numbered from the bottom up.

Absorption columns may have as many as forty or fifty plates, plate height or spacing of one to three feet, and column diameter of two to ten feet. Operating pressures range from 50 to 3000 psia, temperatures from 50 to 200°F. The absorption of material liberates heat; therefore, cooling may be provided by withdrawing a liquid stream from the column, cooling it, and returning it, or by putting cooling coils on the plates. Heat loss by radiation and convection from the column also occurs.

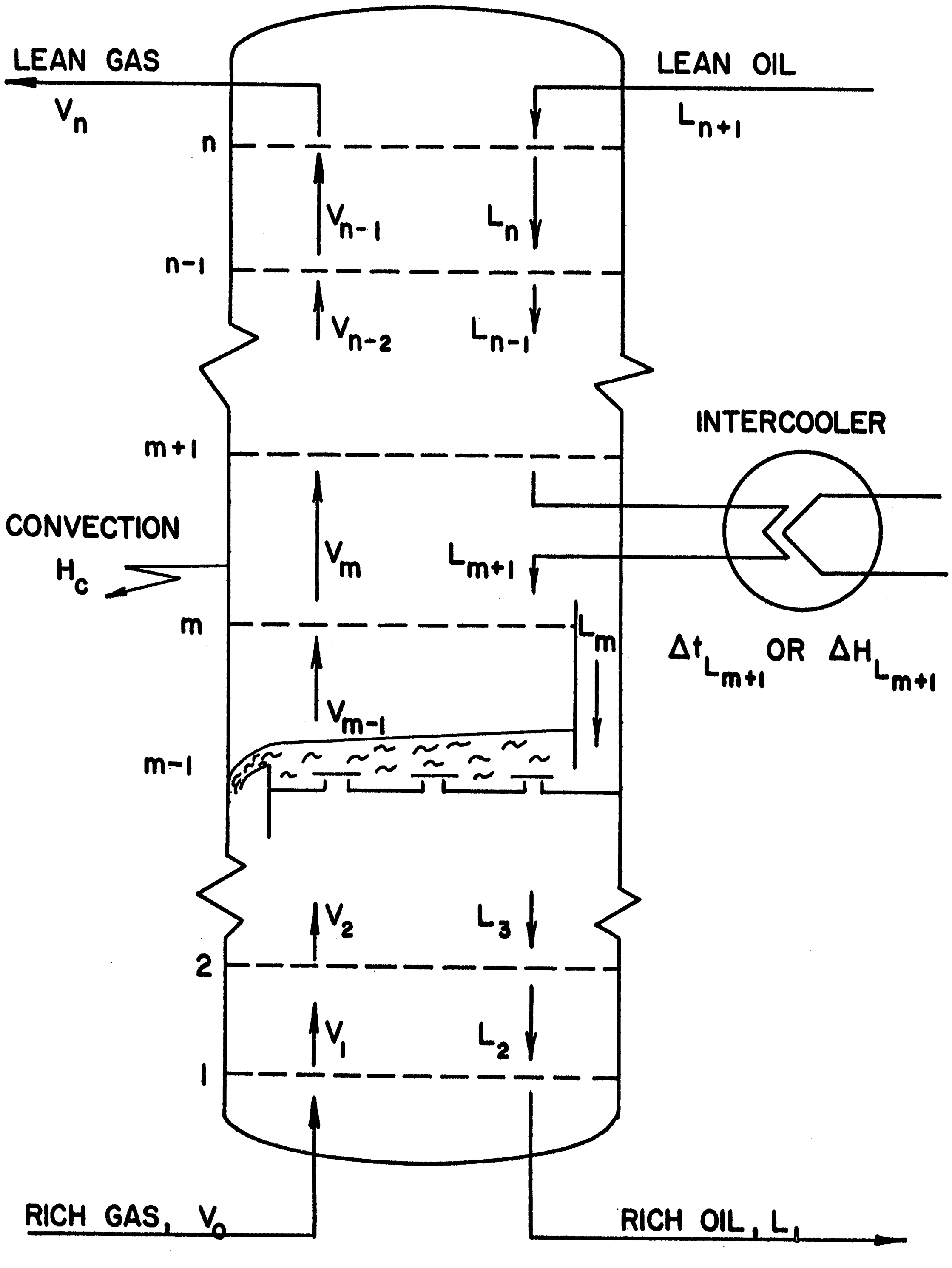


Figure 1. Schematic Diagram of an Absorber

C. Statement of the Problem

In order to demonstrate the non-ideal stage calculation, a computer program was written to solve the following problem:

Given the temperatures, compositions, and flow rates of the rich gas and the lean oil, the column pressure (assumed constant), the number, diameter, and other pertinent dimensions of the bubble-cap plates, and data on intercooling and other heat losses; compute the fractional recovery of all components and the complete properties of the lean gas, rich oil, and all internal streams of the column.

D. Summary

Following are brief statements on the purpose, content, and importance of the various sections of this dissertation.

Section II, Background, contains discussion of past and present methods for the design and performance evaluation of multicomponent distillation columns and gas absorbers. Particular emphasis is given to aspects of these methods which are of interest or utility in the development of the non-ideal stage calculation and its employment with automatic computers.

Section III, Engineering Concepts, is probably the most important section of the dissertation. It contains the theoretical engineering bases for the computational procedure employed.

Section IV, Physical Properties, contains detailed information on the ways in which the various physical and thermodynamic properties are correlated for machine use.

Section V, Problem-Solving Procedure, consists of a step-by-step account of the procedure followed in the automatic computation.

The procedure is illustrated by flow sheets which present a somewhat more machine-oriented view than the text.

Section VI, Mathematical Analysis, treats certain subjects of interest to the more mathematically inclined reader. Consideration of the whole procedure as the solution of a set of simultaneous equations is discussed here.

Section VII presents, in tabular and graphical form, the results of the investigation of an ideal stage column and four operating absorbers for which test data are available.

Section VIII, Analysis of Results, contains discussion of information and experience gained in the investigation of the various absorbers. With the exception of the treatment of the ideal stage calculation, the discussion has been outlined according to phenomenon, effect, or trend. This arrangement is considered preferable to discussion of each of the calculations in turn.

Section IX, Conclusions, consists of statements based not only on the results of computation, but on the entirety of experience gained in the research effort.

The Appendix is of importance only to the person with interest in and knowledge of automatic computation.

For the reader with limited time to devote to this dissertation and whose interest is in the general engineering (as opposed to mathematical and computational) aspects of the problem, the following sections and subsections are recommended: Introduction; Engineering Concepts; subsection A of Problem-Solving Procedure; Results; subsections A through E, I, and K of Analysis of Results; and Conclusions.

II. BACKGROUND

A. General Remarks

The inclusion of a section entitled "Background" is of only limited utility in this dissertation. The computational procedure developed here differs from previous work in one fundamental way -- it is based on the non-ideal stage. To the author's knowledge, there has been no previously published material dealing with non-ideal stage, multicomponent, plate-to-plate distillation or absorption calculations. In other particulars, e.g., the use of material and energy balances, the present method is based on previous work.

The general subject of absorption and distillation will be discussed in terms of the well-known hand computation procedures. Distillation calculation methods will be included because of their similarity or application to absorption methods. Machine procedures, which now consist mainly of adaptations of hand procedures, will then be mentioned briefly. It should be borne in mind that all the methods to be discussed are based upon the ideal stage.

B. Absorption Factor Methods

The absorption factor of component i on plate m is defined

$$A_{m,i} = \frac{L_m}{V_m\ K_{m,i}} = \frac{L_m\ x_{m,i}}{V_m\ y_{m,i}} \tag{1}$$

where

$A_{m,i}$ is the absorption factor

L_m is the liquid flow rate from plate m

V_m is the vapor flow rate from plate m

$K_{m,i}$ is the vapor-liquid equilibrium ratio of component i on plate m

$x_{m,i}$ is the mole fraction of component i in the liquid L_m

$y_{m,i}$ is the mole fraction of component i in the vapor V_m.

Considering just one component and dropping the subscript i from now on, we write the absorption factor on the next higher plate, m+1, as

$$A_{m+1} = \frac{L_{m+1}}{V_{m+1}\ K_{m+1}} \tag{1'}$$

A component material balance around plate m gives

$$L_{n+1}\ (X_m - X_{m+1}) = V_0\ (Y_{m-1} - Y_m) \tag{2}$$

where

L_{n+1} is the lean oil flow rate

X_m and X_{m+1} are the quantities of component i in L_m and L_{m+1} <u>per</u> <u>mole</u> <u>of</u> <u>L_{n+1}</u>

V_0 is the rich gas flow rate

Y_{m-1} and Y_m are the quantities of component i in V_{m-1} and V_m <u>per</u> <u>mole</u> <u>of</u> <u>V_0</u>.

Recalling the equilibrium relation

$$y_m = K_m\ x_m \tag{3}$$

we may rewrite it in the form

$$\frac{Y_m\ V_0}{V_m} = K_m \frac{X_m\ L_{n+1}}{L_m} \tag{4}$$

and solve for X_m to get

$$X_m = \frac{Y_m\ V_0\ L_m}{V_m\ L_{n+1}\ K_m} = (\frac{V_0\ A_m}{L_{n+1}})Y_m \tag{5}$$

Solving Equation (2) for Y_m, we obtain

$$Y_m = Y_{m-1} - \frac{L_{n+1}}{V_0}(X_m - X_{m+1}) \tag{6}$$

and substituting Equation (5)

$$Y_m = Y_{m-1} - A_m\, Y_m + A_{m+1}\, Y_{m+1} \tag{7}$$

Finally,

$$Y_m = \frac{Y_{m-1} + A_{m+1}\, Y_{m+1}}{1 + A_m} \tag{8}$$

If m is the bottom plate of an absorber, we may again incorporate Equation (5) and write

$$Y_1 = \frac{Y_0 + (X_2\, L_{n+1}/V_0)}{1 + A_1} \tag{9}$$

or, for a one-plate absorber

$$Y_1 = \frac{Y_0 + (X_2\, L_2/V_0)}{1 + A_1} \tag{10}$$

Equation (9) may be written for the upper plate of a two-plate absorber as

$$Y_2 = \frac{Y_1 + (X_3\, L_3/V_0)}{1 + A_2} \tag{11}$$

and Equations (10) and (11) may be combined to give

$$Y_1 = \frac{Y_0 + A_2\, Y_2}{1 + A_1} = \frac{Y_0}{1 + A_1} + \frac{A_2[Y_1 + (X_3\, L_3/V_0)]}{(1 + A_1)(1 + A_2)} \tag{12}$$

whence

$$Y_1[1 - \frac{A_2}{(1 + A_1)(1 + A_2)}] = \frac{(Y_0)(1 + A_2) + (A_2)(X_3\, L_3/V_0)}{(1 + A_1)(1 + A_2)} \tag{13}$$

and

$$Y_1 = \frac{(A_2 + 1)(Y_0) + (A_2)(X_3\, L_3/V_0)}{A_2\, A_1 + A_1 + 1} \tag{14}$$

The equation for an absorber of three plates may be developed

$$Y_1 = \frac{(A_3\, A_2 + A_2 + 1)(Y_0) + (A_3\, A_2)(X_4\, L_4/V_0)}{A_3\, A_2\, A_1 + A_2\, A_1 + A_1 + 1} \qquad (15)$$

and for one of any number of plates, n

$$Y_1 = \frac{(A_n\, A_{n-1} \cdots A_2 + A_{n-1} \cdots A_2 + \cdots + A_2 + 1)(Y_0) + (A_n\, A_{n-1} \cdots A_2)(X_{n+1}\, L_{n+1}/V_0)}{A_n\, A_{n-1} \cdots A_1 + A_{n-1} \cdots A_1 + \cdots + A_1 + 1} \qquad (16)$$

A material balance around the whole absorber may be written:

$$(L_{n+1})(X_1 - X_{n+1}) = (V_0)(Y_0 - Y_n) \qquad (17)$$

Replacing X_1 by its equivalent from Equation (5) and solving for Y_1,

$$Y_1 = \frac{Y_0 - Y_n + (L_{n+1}\, X_{n+1}/V_0)}{A_1} \qquad (18)$$

Combining Equations (16) and (18),

$$\frac{Y_0 - Y_n}{Y_0} = \left[\frac{A_n\, A_{n-1} \cdots A_1 + A_{n-1} \cdots A_1 + \cdots + A_1}{A_n\, A_{n-1} \cdots A_1 + A_{n-1} \cdots A_1 + \cdots + A_1 + 1}\right] - \frac{L_{n+1}\, X_{n+1}}{V_0\, Y_0}\left[\frac{A_{n-1}\, A_{n-2} \cdots A_1 + A_{n-2} \cdots A_1 + \cdots + A_1 + 1}{A_n\, A_{n-1} \cdots A_1 + A_{n-1} \cdots A_1 + \cdots + A_1 + 1}\right] \qquad (19)$$

and the term on the left may be designated the fractional recovery of component i from the rich gas stream.

Based upon the theoretical analysis of Kremser(63), Brown and Souders(18) developed a calculation method involving the assumption that the absorption factor of each component was constant throughout the column. A development yielded the equation

$$\frac{Y_0 - Y_n}{Y_0 - Y_{n+1}} = \frac{A^{n+1} - A}{A^{n+1} - 1} \tag{20}$$

where

A was the average absorption factor

Y_{n+1} was the number of moles of a component in equilibrium with the lean oil per mole of rich gas

n was the number of theoretical plates

Y_0 and Y_n were defined as before.

Horton and Franklin(55) assumed that an effective absorption factor might be used for each component, a factor equal to an actual absorption factor occurring a certain relative distance from the top of the column. A table was furnished, indicating that the effective factor of the light components should be evaluated quite close to the bottom of the column, that of heavy components toward the top, etc. In the short-cut procedure, the further assumptions were made that (1) a constant percentage "knock-out" occurred on each plate, i.e.,

$$\left(\frac{V_n}{V_0}\right)^{1/n} = \frac{V_m}{V_{m-1}} \tag{21}$$

and (2) the temperature difference from plate to plate was proportional to the amount of absorption occurring.

$$\frac{t_1 - t_m}{t_1 - t_{n+1}} = \frac{V_0 - V_{m-1}}{V_0 - V_n} \tag{22}$$

Edmister(28) devised an effective absorption factor method in which E_a, the absorption efficiency of each component, was evaluated by the expressions

$$A_e = \sqrt{(A_1)(A_n + 1) + 0.25} - 0.5 \qquad (23)$$

$$A' = \frac{(A_1)(A_n + 1)}{A_1 + 1} \qquad (24)$$

$$E_a = \frac{Y_0 - Y_n}{Y_0} = [1 - \frac{L_{n+1}\ X_{n+1}}{A'\ V_0\ Y_0}][\frac{A_e^{n+1} - A_e}{A_e^{n+1} - 1}] \qquad (25)$$

Harbert(46), in a manner quite similar to the rigorous absorption factor derivation given above, developed expressions for the quantity of a component leaving plate m, based on the terminal streams of the column.

$$(Lx)_m = (\frac{A_m + A_m\ A_{m+1} + \ldots + A_m\ A_{m+1} \ldots A_{n-1}\ A_n}{1 + A_1 + A_1\ A_2 + \ldots + A_1\ A_2 \ldots A_n})\ (Vy)_0 +$$

$$[\frac{(A_m\ A_{m+1} \ldots A_{n-1}\ A_n)(1 + A_1 + A_1\ A_2 + \ldots + A_1\ A_2 \ldots A_{m-1})}{1 + A_1 + A_1\ A_2 + \ldots + A_1\ A_2 \ldots A_n}](Lx)_{n+1} \qquad (26)$$

$$(Vy)_m = \frac{1}{A_m}\ (Lx)_m \qquad (27)$$

An energy balance around plate m gave the following equation:

$$V_{m-1}\ \underline{H}_{V_{m-1}} + L_{m+1}\ \underline{H}_{L_{m+1}} = V_m\ \underline{H}_{V_m} + L_m\ \underline{H}_{L_m} \qquad (28)$$

where $\underline{H}_L$ and $\underline{H}_V$ were molal enthalpies in the liquid and vapor phases. The following rigorous procedure was suggested: Given the properties of the inlet streams to the column, (1) assume L/V ratios and temperatures on each plate, (2) calculate K values and absorption factors for each component on each plate, (3) compute the quantity of each component in each liquid and vapor stream in the column using Equations (26) and (27), (4) sum the component quantities to obtain new values of L_m and V_m on each plate, (5) recalculate t_m on each plate from an energy balance around that plate, and (6) repeat steps (2) through (5) until the desired accuracy is obtained.

C. Plate-to-Plate Calculation Methods

The papers of Lewis and Matheson(68) and Thiele and Geddes(89) are usually credited with providing the groundwork for continuous, multicomponent, plate-to-plate distillation and absorption calculations. Lewis and Matheson considered a distillation column in which feed, overhead, and bottoms streams were specified, the primary unknowns being reflux ratio and the number of theoretical plates above and below the feed plate. Thiele and Geddes dealt with the case where the feed stream and the number of plates in the enriching and stripping sections were specified, the compositions and quantities of the distillate and bottoms and the reflux ratio being the primary unknowns. In both methods, the temperatures throughout the column and the pressure were secondary unknowns.

The Lewis-Matheson and Thiele-Geddes methods, being concerned with distillation columns, contain some material which has no application to absorbers. The following features, however, are of interest in both absorbers and distillation columns: (1) the use of material balances around a section of the column for relating quantities of components in adjacent or "passing" streams, (2) the use of energy or enthalpy balances for calculating the quantities or flow rates of streams and L/V ratios, (3) the use of the dew point calculation for determining the temperature of a vapor stream and the composition of a liquid stream in equilibrium with it, and (4) the use of the bubble point calculation for determining the temperature of a liquid stream and the composition of a vapor stream in equilibrium with it.

The utility of the material balance in both distillation and absorption calculations is obvious. A typical material balance applied around the reboiler and several stripping section plates in the bottom-up calculation of a distillation column (plates numbered from bottom up) might be

$$\ell_{m+1,i} = v_{m,i} + b_i \tag{29}$$

where

$\ell_{m+1,i}$ is the flow rate of component i in the liquid from plate m+1

$v_{m,i}$ is the flow rate of component i in the vapor from plate m

b_i is the flow rate of component i in the bottoms stream.

In the bottom-up calculation of an absorber, the corresponding equation would be

$$\ell_{m+1,i} + v_{0,i} = \ell_{1,i} + v_{m,i} \tag{30}$$

where $v_{0,i}$ and $\ell_{1,i}$ refer to the rich gas and rich oil streams, respectively.

The liquid and vapor rates and the L/V ratios may not change appreciably in the enriching and stripping sections of distillation columns, and it is often permissible to consider them constant. Lewis and Matheson did allow for the use of energy balances, however, and suggested that a constant change in the quantity of reflux per degree of temperature rise be used. The flow rates of vapor and liquid in an absorber do change markedly, even radically, and the use of a constant L/V ratio is usually a very gross assumption.

It is in the use or attempted use of dew point and bubble point calculations for setting temperatures that a fundamental difference between absorbers and distillation columns arises. In a distillation column, for a "sharp separation", we usually assume that no component heavier than the heavy key appears in the overhead. Even if there are one or more distributed components, as in a "sloppy separation", the heavy key is usually not a relatively heavy component; that is, its volatility relative to that of the lightest component in the column is not nearly as small as the volatility of absorber oil relative to methane or nitrogen, for example. In the enriching section, the dew point calculation, involving the equality

$$\sum \frac{y}{K} = 1 \tag{31}$$

is not especially sensitive to the presence of the heavy key, and it is not until we approach the feed plate that the heavier components of the feed appear. Even then, they are present in small concentrations and on only the bottom few plates of the enriching section, and so their effect on the stability of the temperature calculations is not serious. A similar argument holds with respect to the stripping section, the bottom-up calculation, the bubble point calculation,

$$\sum Kx = 1 \tag{32}$$

and the presence of components lighter than the light key.

When one attempts to use bubble point calculations for setting stream temperatures of absorbers, light components in liquid streams throughout the column and the sensitivity of the bubble point to light components make the temperature profile quite unstable. A similar instability in dew point calculations is caused by the presence of heavy components in the vapor. Even if one assumes that the heaviest component in the column, the absorber oil, is non-volatile, the heaviest component of the rich gas may still cause trouble.

Holcomb(54) used a plate-to-plate absorber method which exploited the advantages, but not the disadvantages, of the dew point calculation. Given the properties of input and output streams and the column pressure, he desired to calculate the number of ideal stages. The absorber oil was assumed to be non-volatile. Employing the equilibrium relation,

$$x_{m,i} = \frac{y_{m,i}}{K_{m,i}} \tag{33}$$

which is the basis of the dew point calculation, he computed the mole fraction of each component except the absorber oil in the liquid from the top plate, n. The mole fraction of the absorber oil was obtained by difference. Since x_n of the absorber oil, which we may designate as $x_{n,j}$, represented the total quantity of that component entering the column, the quantity of stream L_n was obtained by the equation

$$L_n = \frac{\ell_{n,j}}{x_{n,j}} = \frac{\ell_{n+1,j}}{x_{n,j}} \tag{34}$$

and the quantities of the other components from the equation

$$\ell_{n,i} = L_n\, x_{n,i} \tag{35}$$

where $i \neq j$. The quantities of all components except absorber oil in the vapor to the top plate, V_{n-1}, were obtained by material balance,

$$v_{n-1,i} = v_{n,i} + \ell_{n,i} - \ell_{n+1,i} \tag{36}$$

and the total quantity of the stream as the summation of $v_{n-1,i}$. Since the temperatures and thus the molal enthalpies of streams L_{n+1}, L_n, and V_n were known, the molal enthalpy and then the temperature of V_{n-1} could be obtained by an energy balance:

$$\underline{H}_{V_{n-1}} = \frac{V_n \underline{H}_{V_n} + L_n \underline{H}_{L_n} - L_{n+1} \underline{H}_{L_{n+1}}}{V_{n-1}} \tag{37}$$

Thus, the complete set of properties of V_{n-1} was obtained. The above sequence of steps was repeated down the column, adding the heavier components at intervals, until a point was reached where the mole fraction of the key component in the vapor stream was about equal to that in the rich gas. This point was designated the bottom plate. The places where heavier components had been added to the vapor stream were changed, based on a comparison of the computed rich gas stream with the known rich gas, and the procedure was repeated until reasonable values for all components were obtained. Thus the procedure was not a complete method for the design of absorbers, but merely a way of checking material and energy relationships and determining the number of ideal stages furnished by a given absorber under certain conditions.

D. Machine Computation Methods

A rather large number of machine methods for continuous, multicomponent distillation and absorption calculations have appeared in recent years. A few will be discussed here, the purpose being either to illustrate machine adaptation of hand methods mentioned earlier or to show current trends in the art of plate-to-plate computation.

McIntire and Shelton(69) described two fractionator design programs for use with the Datatron. One, the "product mesh" method, used to determine the number of ideal stages necessary to make a given separation, was roughly the Lewis-Matheson procedure programmed for machine use. The other, the "feed mesh" method, used to calculate the separation achieved by a given column, corresponded to the Thiele-Geddes procedure. Both methods used Antoine-type equations for K values and third-order polynomial approximations for enthalpies.

The "feed mesh" method consisted of the following steps: Given the properties of the feed and the number of ideal stages in each section of the column, the enthalpy and separation of the feed were obtained by a flash calculation. A distribution of components in the product streams was assumed, and some of each component, even if an infinitesimal amount, was included in each product stream. A reflux ratio was assumed, and the heat flux in each section of the column was determined. Starting with the assumed overhead stream, a plate-to-plate calculation downward through the enriching section was made. Heat and material balances and equilibrium calculations were made on each step. The procedure was terminated when the liquid from the feed plate was reached. A bottom-up calculation through the stripping section was made, again terminating at the feed plate liquid. A feed plate mesh ratio was used to provide a revised estimate of the quantity of each component in the product streams.

$$R_i = \frac{x_{f,i} \text{ (down)}}{x_{f,i} \text{ (up)}} \qquad (38)$$

where

Ri was the feed plate mesh ratio of component i

$x_{f,i}$ was the mole fraction of component i in the liquid calculated for the feed plate.

R_i would be less than 1 if too little of component i had been assumed in the overhead, greater than 1 if too much had been assumed. The mass fluxes of each light component, δ, were then revised to give δ' according to the equations

$$\delta'_{s,i} = R_i \, \delta_{s,i} \qquad (39)$$

and

$$\delta'_{e,i} = \delta'_{s,i} - f_i \qquad (40)$$

and the mass fluxes of each heavy component according to the equations

$$\delta'_{e,i} = (1/R_i)(\delta_{e,i}) \qquad (41)$$

and

$$\delta'_{s,i} = \delta'_{e,i} + f_i \qquad (42)$$

where the mass flux was defined as the quantity of component i in any liquid stream minus the quantity in the adjacent or passing vapor, and

$\delta_{s,i}$ was the mass flux of component i in the stripping section

$\delta_{e,i}$ was the mass flux of component i in the enriching section

f_i was the quantity of component i in the feed.

Using the established heat flux and the revised product estimates, the plate-to-plate calculations were repeated. The procedure was continued until convergence was obtained, usually within one or two hours of machine computation.

Two interesting features of the feed plate mesh method are (1) the use of quantity ratios for correcting, in effect, the assumed quantities of components in the product streams and (2) the necessity of having at least a token quantity of each component in every stream. The avoidance of discontinuities such as the sudden introduction of a component, however small the quantity of it, in a stream partway through the column is typical of machine computation methods.

Bonner(16) presented an IBM 650 program similar to the feed plate mesh method described above. Relative volatilities, rather than K values, were used to describe the equilibrium relationships, and "activity coefficient corrections" were employed to account for the different volatility characteristics found with aromatic and paraffinic absorber oils.

Greenstadt, Bard, and Morse(42) wrote a distillation program for the IBM 704. Interesting facets of the procedure include (1) the use of the Benedict-Webb-Rubin equation of state(15) for computing K values, enthalpies, and their derivatives; (2) the formal consideration of the distillation problem as a series of simultaneous equations; and (3) the use of the Newton method for forcing convergence of an iterative procedure. Discussion of points (2) and (3) follows.

The equations describing a distillation or absorption column can be considered a set of n simultaneous equations in n unknowns:

$$f_i(x_1, x_2, \ldots, x_n) = 0. \qquad (i = 1, 2, \ldots, n) \tag{43}$$

We wish to solve them for the set of roots, the vector $\overline{x}_i$, satisfying all the equalities. (The vector x_i without the superscript bar denotes a set of values which occur during the iterative solution and still contain errors.) According to the Newton approximation,

$$f_i(\overline{x}) = f_i(x) + \Sigma_j \left(\frac{\partial f_i}{\partial x_j}\right) (\overline{x}_j - x_j) \tag{44}$$

Setting $f_i(\overline{x})$ equal to zero and denoting $(\overline{x}_j - x_j)$ by δx_j, we obtain

$$\Sigma_j \left(\frac{\partial f_i}{\partial x_j}\right)(\delta x_j) = -f_i(x) \tag{45}$$

Equation (45) is only an approximation, but it may be iterated in order to obtain as close an approximation as is desired.

We may consider certain of the variables as final variables (superscript F)

$$f_j^F \ (x_i^F) = 0 \tag{46}$$

Others may be considered initial variables, x_k^I. In a distillation column, initial variables might be the quantities of each component assumed in the product streams; the final variables, the quantities calculated for the feed plate by the enriching and stripping section calculations; and the final functions, the requirements that the two final quantities of each component be equal. Similar functions may be found in absorption columns.

Given a set of initial variables, x_k^I, we may, by solving a series of equations, arrive at values of the final variables, x_i^F, so that the final variables are functions (ultimately, but not explicitly) of the initial variables, denoted functionally

$$x_i^F = x_i^F \ (x_k^I) \tag{47}$$

and further

$$f_j^F\ [x_i^F\ (x_k^I)] = 0 \tag{48}$$

To employ the Newton approximation, we must solve

$$\Sigma_k\ \left(\frac{\partial f_j^F}{\partial x_k^I}\right)\ (\delta x_k^I) = -\ f_j^F\ (x_k^I) \tag{49}$$

The partial derivatives may be obtained by the so-called "chain rule" for partial derivatives,

$$\frac{\partial f_j^F}{\partial x_k^I} = \Sigma_i\ \left(\frac{\partial f_j^F}{\partial x_i^F}\right)\ \left(\frac{\partial x_i^F}{\partial x_k^I}\right) \tag{50}$$

and the problem reduces to that of finding the derivatives of the final variables with respect to the initial variables.

In a plate-to-plate calculation, we might assume the properties of the bottoms stream and, by the usual mass and energy balances and equilibrium relations, obtain the properties of the streams above the first or bottom plate of the column. We write the relationships

$$f_j^1\ (x_m^1,\ x_k^I) = 0 \tag{51}$$

and solve them iteratively by Newton's method,

$$\Sigma_m\ \left(\frac{\partial f_j^1}{\partial x_m^1}\right)\ (\delta x_m^1) = -\ f_j\ (x^1,\ x^I) \tag{52}$$

Equation (51) may be differentiated,

$$\Sigma_m\ \left(\frac{\partial f_j^1}{\partial x_m^1}\right)\ \left(\frac{\partial x_m^1}{\partial x_k^I}\right) + \frac{\partial f_j^1}{\partial x_k^I} = 0 \tag{53}$$

and having obtained the values of x_m^1, we may evaluate the partial derivatives of f_j^1 with respect to x_m^1 and x_k^I at the correct values of x_m^1

and then solve for the set $\frac{\partial x_m^1}{\partial x_k^I}$. Proceeding to plate 2, we write the equations

$$f_j^2 \, (x_r^2, x_m^1, x_k^I) = 0 \tag{54}$$

solve them iteratively as before for the values x_r^2, and then differentiate Equation (54) to obtain

$$\Sigma_r \, (\frac{\partial f_j^2}{\partial x_r^2}) \, (\frac{\partial x_r^2}{\partial x_k^I}) + \Sigma_m \, (\frac{\partial f_j^2}{\partial x_m^1}) \, (\frac{\partial x_m^1}{\partial x_k^I}) + \frac{\partial f_j^2}{\partial x_k^I} = 0 \tag{55}$$

and again we may solve for the set of partial derivatives $\frac{\partial x_r^2}{\partial x_k^I}$.

Proceeding tray-to-tray, we ultimately arrive at values of $\frac{\partial x_i^F}{\partial x_k^I}$ and $f_j(x_k^I)$ and are able to solve Equation (49) for the δx_k^I, obtain new approximations to the set of initial variables x_k^I, and finally obtain the values $\overline{x}_k^I$, $\overline{x}_m^1$, $\overline{x}_r^2$, etc., satisfying the complete set of equations.

Using the above method, Greenstadt and associates have obtained the solution of a four-component, twenty-plate column in about three minutes(41).

Amundson and Pontinen(7) recently described a distillation method developed on the Univac Scientific Computer Model 1103. If properties of the feed and the number of ideal stages in both sections of the column are known, the flow rates and compositions of bottoms and overhead may be estimated. Constant molal overflow may be assumed and later corrected by an energy balance. With plates in the stripping section numbered from the bottom up, a material balance around the reboiler (plate 0) and the bottom m plates gives

$$L_{m+1} = V_m + B \tag{56}$$

where B is the bottoms product flow rate. A component balance around plate m is

$$V_{m-1}\, y_{m-1,i} - L_m\, x_{m,i} - V_m\, y_{m,i} + L_{m+1}\, x_{m+1,i} = 0 \qquad (57)$$

Employing the equilibrium relation

$$y_{m,i} = K_{m,i}\, x_{m,i} \qquad (58)$$

and Equation (56), we obtain

$$(V_{m-1})(K_{m-1,i}\, x_{m-1,i}) - (V_{m-1} + B)(x_{m,i}) - (V_m)(K_{m,i}\, x_{m,i}) + (V_m + B)(x_{m+1,i}) = 0 \qquad (59)$$

or, collecting terms,

$$(V_{m-1}\, K_{m-1,i})(x_{m-1,i}) - (V_{m-1} + B - V_m\, K_{m,i})(x_{m,i}) + (V_m + B)(x_{m+1,i}) = 0 \qquad (60)$$

We now have a component material balance around plate m in terms of the liquid mole fractions on plates m-1, m, and m+1. If there are n plates plus reboiler and j components, a system of (n+1)(j) equations may be written, the equations for the top plate, general enriching section plate, feed plate, and bottom plate differing only slightly from the one given. If the total stream flow rates and temperatures are known ($K_{m,i}$ assumed to be a function only of temperature and the constant pressure), the system of equations may be solved for the mole fractions, $x_{m,i}$. By a somewhat similar procedure, a system of m heat balance equations in terms of the variables V_m may be derived.

The authors' method of determining the temperature profile and flow rate profiles necessary to produce the equality

$$f_m = \Sigma_i\ (x_{m,i}) \equiv \Sigma_i\ (K_{m,i}\, x_{m,i}) = 1 \qquad (61)$$

on each plate is of interest. They began by assuming a temperature on each plate m of t'_m. Computing the K values by power series approximations

$$K_{m,i} = \alpha_i + \beta_i\, t_m + \gamma_i\, t_m^2 + \delta_i\, t_m^3 \qquad (62)$$

and solving the set of simultaneous equations produced a set of values of $x_{m,i}$ and a value of the function f'_m on each plate. The values of $x_{m,i}$ in general did not sum to 1 on each plate. They were "normalized" by dividing each by the sum. Then the partial derivative of f_m with respect to t_m was computed

$$\left(\frac{\partial f_m}{\partial t_m}\right)_{t'_m} = \Sigma_i\, x_{m,i}[\beta_i + 2\gamma_i\, t'_m + 3\delta_i (t'_m)^2] \qquad (63)$$

and a new value of t_m was computed by the Newton approximation

$$t_m = t'_m + [1 - f_m(t'_m)]\, \left[\frac{\partial f_m}{\partial t_m}\right]^{-1}_{t'_m} \qquad (64)$$

In a typical 15-plate column, the authors alternated re-estimation of temperatures with recalculation of vapor rates and found 15 iterations to be sufficient for convergence.

Rose, Sweeny, and Schrodt(83) discussed a relaxation method for continuous distillation suitable for intermediate-size computers. Given feed conditions, flow rates of product streams, number of plates, and reflux ratio, the product compositions were calculated using certain simplifying assumptions and a material balance equation for the holdup of each component on each plate. The assumptions (which may be replaced by rigorous calculation) were (1) constant molal overflow, (2) ideal stages, (3) negligible vapor holdup, and (4) the composition of liquid holdup on plate m being identical to the composition of stream L_m. The holdup equation for any component on plate m was

$$(\Lambda)(x_m)_{k+1} = (\Lambda)(x_m)_k + (V_{m-1}\ y_{m-1})_k + (L_{m+1}\ x_{m+1})_k - (V_m\ y_m)_k - (L_m\ x_m)_k \tag{65}$$

where

Λ was the total holdup on plate m

k and k+1 were successive time intervals

V and L were in the units of moles/time interval.

Each equation was solved for $(x_m)_{k+1}$,

$$(x_m)_{k+1} = (x_m)_k + \frac{1}{\Lambda}[(V_{m-1}\ y_{m-1})_k + (L_{m+1}\ x_{m+1})_k - (V_m\ y_m)_k - (L_m\ x_m)_k] \tag{66}$$

and the process was repeated for successive time intervals. It was found necessary to make the time interval short enough that the quantity of flow during the interval was one-fifth to one-tenth of the total holdup.

Continuing now to the category of absorber calculation by digital computer, Mieth and Moore(70) reported using the Edmister effective absorption factor method(28) on a medium size computer. This program was part of a larger program, the object being the design of an entire absorption plant.

Norman(76) programmed a modification of the Harbert method(46) for the IBM 650. The program used second-order polynomial approximations for K values and enthalpies. Program specifications included the number of equilibrium stages, the complete properties of inlet streams, heat loss, and allowable errors in L/V ratios and enthalpy balances. The supplying of initial approximations of L/V ratios and the temperature profile was optional; the program generated its own initial values if none were furnished. Beginning with these approximations, the machine computed K values and absorption factors for each component on every plate. Using Equations (26) and (27), the quantity of each component in every liquid and vapor stream was computed, the quantities were summed to give the total liquid and vapor streams from each plate, and the L/V ratios were re-computed. These new L/V ratios were compared with the previous values, and if the maximum difference exceeded the allowable error, the procedure was repeated until all L/V ratios were within the bound. Having converged on a mass balance for a given temperature distribution, the machine then computed the enthalpy balance error on each plate, picked the largest one, and compared it to the maximum allowable error. If the error was too large, the temperature on that one plate was revised by the formula

$$(t_m)_{k+1} = (t_m)_k - E_m/F \qquad (67)$$

where

$(t_m)_{k+1}$	was the temperature on plate m for iteration k+1
$(t_m)_k$	was the temperature used in iteration k
E_m	was the enthalpy balance error on plate m
F	was an empirical correlation parameter.

The mass balance convergence and enthalpy balance were then repeated until final convergence was obtained. Machine computation time varied from 15 minutes to two hours depending upon the complexity of the problem.

An absorber program using a method similar to that of Holcomb(54) was discussed by Cobb and McIntire(22). The machine calculated the recovery obtained with specified input streams and number of plates.

III. ENGINEERING CONCEPTS

A. The Non-Ideal Stage

The character of the non-ideal or non-equilibrium vapor-liquid stage contact may be explained by comparison with the ideal or equilibrium stage. The term "equilibrium stage" implies that equilibrium is reached with respect to both mass and heat transfer. In the non-ideal stage, neither of these conditions need be the case.

In the ideal stage (1) V_m is a dew point vapor, (2) L_m is a bubble point liquid, (3) the composition of V_m is related to that of L_m by the expression

$$y_{m,i} = K_{m,i}\, x_{m,i} \tag{3}$$

(4) the temperatures of V_m and L_m are the same and equal to the temperature at which $K_{m,i}$ is evaluated, (5) the compositions of the liquid on plate m and the liquid leaving plate m are the same, and a similar statement holds for the vapor, and (6) time is not a factor in any of the mass or heat transfer relationships. In the non-ideal stage, (1) V_m is at its dew point temperature or higher, (2) L_m is at its bubble point temperature or lower, (3) V_m and L_m are not necessarily in equilibrium with respect to mass transfer, but their compositions may be related by expressions based on mass transfer rates, (4) the temperatures of V_m and L_m are not necessarily the same, but they may be related by expressions based on heat transfer rates, and (5) differences in both vapor and liquid compositions at various points in the zone of vapor-liquid contact may need to be considered.

It will be shown in the following sections that the non-ideal stage is more complicated than might be supposed, and that attempts to use existing efficiency concepts according to their original definitions have impeded, rather than aided, the present investigation.

B. Mass Transfer Relationships

The Problem

For purposes of discussion, let us consider the following problem: We are performing a plate-to-plate calculation upward through a multicomponent, non-ideal stage gas absorber. Pressure is constant and known. There is no heat gain or loss from the column. Having arrived at plate m, we have complete information on streams V_{m-1} and L_m; i.e., composition, temperature, and flow rate; and desire to calculate the properties of streams V_m and L_{m+1}. We wish to avoid simplifying assumptions as much as possible.

Material and energy balances around plate m may be made:

$$\ell_{m+1,i} + v_{m-1,i} = \ell_{m,i} + v_{m,i} \qquad (68)$$

$$H_{L_{m+1}} + H_{V_{m-1}} = H_{L_m} + H_{V_m} \qquad (69)$$

(H without underlining designates the total enthalpy of a stream) and by rearrangement,

$$\ell_{m+1,i} = v_{m,i} + (\ell_{m,i} - v_{m-1,i}) = v_{m,i} + \delta s_i \qquad (70)$$

$$H_{L_{m+1}} = H_{V_m} + (H_{L_m} - H_{V_{m-1}}) = H_{V_m} + \delta q \qquad (71)$$

Thus we may relate the adjacent or "passing" streams above plate m by the same "δ" quantities that apply to the streams below the plate. The problem of relating streams V_m and L_m remains.

The Murphree Plate Efficiency

The classic equation for specifying the degree to which conditions on an actual plate approach those of an equilibrium plate was proposed by Murphree(71) and is called, when based on the vapor phase, the Murphree vapor plate efficiency. For component i on plate m,

$$E_{MV,i} = \frac{y_{m,i} - y_{m-1,i}}{y^*_{m,i} - y_{m-1,i}} \qquad (72)$$

or in words, the change in mole fraction of component i which actually takes place in the vapor stream as it rises through the froth on plate m, divided by the change which would take place if plate m were an equilibrium contact. (The term "froth" is defined as the volume of continuous liquid phase containing entrained vapor as distinguished from the continuous vapor phase with entrained liquid which exists just above the froth.) Equation (72) is written for a complete plate and applies to concentrations in the average or completely mixed streams. If the expression is applied to a particular location on a plate, it is called the Murphree point efficiency, E_p. Various authors(34,67) have proposed methods of estimating the effect of liquid mixing on a plate and thus connecting E_{MV} and E_p.

Returning to our problem and recalling that we wish to compute the properties of stream V_m, knowing those of V_{m-1} and L_m, we may solve Equation (72) for $y_{m,i}$

$$y_{m,i} = y_{m-1,i} + E_{MV,i}\,(y^*_{m,i} - y_{m-1,i}) =$$

$$y_{m-1,i} + E_{MV,i}\,(K_{m,i}\,x_{m,i} - y_{m-1,i}) \qquad (73)$$

where $K_{m,i}$ is the equilibrium ratio $(y^*_{m,i}/x_{m,i})$. Assuming that the $E_{MV,i}$ are either constant and known or may be estimated for each plate, $y_{m,i}$ for each component may be calculated. Now only fortuitously will the $y_{m,i}$ sum to 1, and several methods of adjusting the $y_{m,i}$ to make them sum to 1 have been tried:

(1) An additional variable, t_m, the temperature at which K values were evaluated, was introduced. Changing t_m, and thus the $K_{m,i}$, caused the sum of the $y_{m,i}$ to equal 1, but the difference between t_m and either t_{L_m} or t_{V_m} was often many times the temperature variation which might be expected to occur on any plate. Furthermore, the use of this adjustment introduced computational instability, and so it was abandoned.

(2) The adjustment

$$y_{m,i} = \frac{y'_{m,i}}{\sum_i y'_{m,i}} \tag{74}$$

where the $y'_{m,i}$ were obtained from Equation (73) was employed. Again, computational instability prevented the obtaining of a solution.

(3) A method was tried which involved adjusting the $K_{m,i}$, in effect, in such a way that constant relative volatility among the components was preserved. Equation (73)may be written and then summed, term by term, for all components to give

$$\sum_i y_{m,i} = \sum_i y_{m-1,i} + \sum_i (E_{MV,i}\ K_{m,i}\ x_{m,i}) - \sum_i (E_{MV,i}\ y_{m-1,i}) \tag{75}$$

The consequence of both $\sum_i y_{m,i}$ and $\sum_i y_{m-1,i}$ being equal to 1 is that

$$\sum_i (E_{MV,i}\ K_{m,i}\ x_{m,i}) = \sum_i (E_{MV,i}\ y_{m-1,i}) \tag{76}$$

The products $(E_{MV,i}\ K_{m,i}\ x_{m,i})'$ (before adjustment) were then "normalized" to produce the equality (76) by the equation

$$E_{MV,i}\ K_{m,i}\ x_{m,i} = \frac{(E_{MV,i}\ K_{m,i}\ x_{m,i})'\ \sum_i (E_{MV,i}\ y_{m-1,i})}{\sum_i (E_{MV,i}\ K_{m,i}\ x_{m,i})} \qquad (77)$$

and then Equation (73) was used to calculate the $y_{m,i}$. Method (3), a direct calculation, was much faster than method (1), an iterative procedure. Furthermore, it produced a convergent sequence in many cases.

(4) The necessity of adjusting the $y_{m,i}$ produced by Equation (73) led to the conclusion that only i-1 of the set of $E_{MV,i}$ may be set independently. Consider the binary mixture of components a and b. Any mole fraction of component b will always be equal to 1 minus the mole fraction of component a in that mixture. Then

$$E_{MV,b} = \frac{(1 - y_{m,a}) - (1 - y_{m-1,a})}{(1 - y^*_{m,a}) - (1 - y_{m-1,a})} = \frac{y_{m,a} - y_{m-1,a}}{y^*_{m,a} - y_{m-1,a}} = E_{MV,a} \qquad (78)$$

The interdependence, but not necessarily equality, of the $E_{MV,i}$ for the various components of a multicomponent mixture may be similarly demonstrated. A fourth method of producing a set of $y_{m,i}$ summing to 1 involved computing $y_{m,i}$ of the major component, methane, by difference and in effect adjusting E_{MV} of methane to produce the desired result. This method also resulted in convergence in some cases.

Having computed the composition of stream V_m, we may estimate its temperature with an equation similar to the plate efficiency expressions. For the present, let us state it in general terms:

$$t_{V_m} = f(t_{V_{m-1}}, t_{L_m}, E_q) \qquad (79)$$

where E_q is some measure of the efficiency of heat transfer. The problem of determining the quantity of V_m then remains. Several methods have been tried, each of them involving the postulation of a step-wise series of conditions through which V_{m-1} and L_{m+1} might pass, ultimately emerging as V_m and L_m. In all cases where convergence has been obtained using the methods of determining compositions and quantities just discussed, the result has been the calculation of negative quantities of the lighter components in the liquid streams. It is for this reason that the use of the Murphree plate efficiency has proved unsatisfactory for absorbers. Examination of the efficiency expression and the conditions occurring in gas absorbers will furnish more conclusive evidence.

According to the definition of the Murphree vapor plate efficiency,

$$E_{MV,i} = \frac{y_{m,i} - y_{m-1,i}}{y^*_{m,i} - y_{m-1,i}} \tag{72}$$

if net absorption of component i is to take place on plate m, the denominator will be negative. If $E_{MV,i}$ is to be positive, the numerator must be negative and the mole fraction of component i must decrease as the vapor stream passes through the plate. Yet it has been found, both from machine computation and experimental results, (e.g., the Phillips absorber data - see Results) that the lightest components of a vapor stream may undergo absorption as the vapor passes through the upper stages of the column, yet increase in mole fraction because of the more rapid absorption of heavier components and consequent decrease of the quantity of the vapor stream. This would produce a negative plate efficiency, which is contrary to the general use of the word "efficiency", the existing methods of estimating plate efficiency, and the supposed intention of Murphree, who derived his efficiency expression for an "isothermal" column with negligible change in the quantity of the vapor stream.

The conclusion reached by the foregoing experience is that the Murphree plate efficiency (1) may be useful in the analysis of binary distillation or the case of a carrier gas and one absorbed component, and (2) may be a convenient index of the behavior of a key component in a multicomponent mixture, but it is an oversimplification for multicomponent systems generally.

An Expression Based on Mass Transfer Coefficients

Continuing with the problem of relating the properties of V_m, the vapor leaving plate m, with those of L_m, the liquid leaving the plate, we may write an expression for the rate of mass transfer of a component from the body of the vapor phase to a vapor-liquid interface in the froth layer and thence to the body of the liquid phase. Considering one component and dropping the subscript i,

$$dN = - d(Vy) = - dv = k_G a(f_G - f_I)A_{cs}dz = k_L a(f_I - f_L)A_{cs}dz \qquad (80)$$

where

N is the number of moles/sec of the component transferred

k_G is the vapor phase mass transfer coefficient in moles/sec ft^2 atm

k_L is the liquid phase mass transfer coefficient in the same units

f_G, f_I, and f_L are the fugacities of the transferred component in the body of the vapor, at the vapor-liquid interface, and in the body of the liquid. The unit is atm.

a is the surface area per unit volume of the froth, ft^2/ft^3

A_{cs} is the horizontal cross-sectional area of the froth, ft^2

z is vertical distance in the froth, ft.

Implicit in the above expression is the assumption that there is no resistance to mass transfer at the interface. If we make the usual assumptions that fugacities are proportional to concentrations and (to justify use of the overall coefficient, K_{OG}) that the operating lines (concentration gradients) are straight lines, we have

$$- dv = k_G a(y - y_I)pA_{cs}dz = k_L a(f_I - f_L)A_{cs}dz = K_{OG}a(y - y^*)pA_{cs}dz \qquad (81)$$

where

K_{OG} is the overall mass transfer coefficient based on the vapor phase

y^* is the mole fraction in the vapor which would be in equilibrium with the mole fraction in the liquid.

Assuming that the liquid phase is completely mixed, that the vapor phase is uniform in any horizontal section, and that $y^* = Kx$, we have

$$- \frac{dv}{y - Kx} = K_{OG}apA_{cs}dz \qquad (82)$$

Dividing both sides by V and integrating,

$$- \int \frac{dv}{V(y - Kx)} = \int \frac{K_{OG}apA_{cs}dz}{V} = K_{OG}apA_{cs} \int \frac{dz}{V} \qquad (83)$$

Since Equation (83) is really i such equations, one for each component, and V is the sum of the v of each component, Equation (83) must be integrated numerically, taking increments δz sufficiently small and re-computing V for each increment. Such a process would be quite tedious and would not be justified by the accuracy with which K_{OG} is estimated. Instead, let us use a constant vapor rate $\overline{V}$ defined as the value of V which, when considered constant, will result in the same value of the integral as would be obtained if the integration were done in small increments with V a variable. Note that this is not equivalent to considering the vapor rate to be a constant. With this approximation,

$$- \int \frac{dv}{(\bar{V}y - \bar{V}Kx)} = - \int \frac{dv}{(v - \bar{V}Kx)} = \frac{K_{OG}apA_{cs}z}{\bar{V}} = N_{OG} \qquad (84)$$

N_{OG} is the number of overall gas transfer units on the plate as proposed by Chilton and Colburn(20). One further approximation should be noted in passing, that of letting $\bar{V}y$ equal v, when actually Vy = v. Integrating the left side of Equation (84) through the froth layer,

$$- \int_{m-1}^{m} \frac{dv}{v - \bar{V}Kx_m} = -\ln \left[\frac{v_m - \bar{V}Kx_m}{v_{m-1} - \bar{V}Kx_m}\right] = N_{OG} \qquad (85)$$

and

$$\frac{v_m - \bar{V}Kx_m}{v_{m-1} - \bar{V}Kx_m} = e^{-N_{OG}} \qquad (86)$$

Solving for v_m,

$$\begin{aligned} v_m &= \bar{V}Kx_m + e^{-N_{OG}}(v_{m-1} - \bar{V}Kx_m) \\ &= v_{m-1} + \bar{V}Kx_m + e^{-N_{OG}}v_{m-1} - e^{-N_{OG}}\bar{V}Kx_m - v_{m-1} \\ &= v_{m-1} + (1 - e^{-N_{OG}})(\bar{V}Kx_m - v_{m-1}) \qquad (87) \end{aligned}$$

The expression $(1 - e^{-N_{OG}})$ will be recognized as the formula for E_p derived for the case of a carrier gas and one absorbed component, with suitable simplifying assumptions. Equation (87) should not be considered the result of multiplying the equation

$$y_m = y_{m-1} + E_p (Kx_m - y_{m-1}) \qquad (88)$$

by $\bar{V}$ since $\bar{V}$ occurs only in the term $\bar{V}Kx_m$ and is not a common factor of v_m and v_{m-1}.

In using Equation (87), one might first let $\overline{V}$ be equal to V_{m-1}, compute V_m as the sum of the v_m, replace $\overline{V}$ by some sort of average of V_{m-1} and the first approximation of V_m, recompute the values of the v_m and of V_m, etc. This procedure was found to be undesirable since (1) it resulted in a much longer calculation than the direct computation of v_m, and (2) the sequence of values of v_m sometimes became non-convergent. Instead, $\overline{V}$ was set equal to V_{m-1}, and it was found that the value of V_m produced by the direct calculation did not differ appreciably from that produced by the iterative procedure mentioned above. The reason for this small difference is that for light components, where the K values and therefore the terms $\overline{V}Kx_m$ are large, the factor $(1 - e^{-N_{OG}})$ is small; for the heavy components, where $(1 - e^{-N_{OG}})$ is appreciable, K and $\overline{V}Kx_m$ are small.

One final alteration may be made. The various methods of accounting for the effect of liquid phase concentration gradients and relating E_p and E_{MV} are compatible with the derivation above. We may, therefore, relax the restriction of constant liquid composition and include the slight increase of mass transfer this affords. The final equation is

$$\begin{aligned} v_m &= v_{m-1} + (E_{MV})(V_{m-1}Kx_m - v_{m-1}) \\ &= V_{m-1}\,[y_{m-1} + (E_{MV})(Kx_m - y_{m-1})] \qquad (89) \end{aligned}$$

and the mass transfer factor is given the name E_{MV} for convenience and in recognition of the way in which its values are predicted, but not because of being used as Murphree defined it.

C. The Mass Transfer-Heat Transfer Analogy

The subject of heat transfer in vapor-liquid stage contact has received very little attention by comparison with mass transfer. Nord(75) restricting his discussion to the case of equimolar counter-diffusion in a binary system with vapor phase resistance controlling, showed how the Colburn "j" factor analogy(19) led to a temperature efficiency expression. Kirschbaum(60) discussed temperature differences and heat transfer in a distillation column; his model, however, was restricted to a binary system, ideal stages, and constant liquid-to-vapor ratio. The fact remains, as stated by Curtiss and Hirschfelder(25), that the effect of mass transfer on heat transfer is not well-known. One may postulate the release of heat at a vapor-liquid interface caused by absorption of material and even estimate the quantity of heat involved. The disposition of this heat and its effect on the convective transfer of heat are not known.

A Consequence of the Colburn Analogy

Colburn(19) defined "j factors" for heat and mass transfer as follows:

$$j_H = \frac{f}{2} = \left(\frac{h}{c\rho u}\right)\left(\frac{c\mu}{k}\right)^{2/3} = \left(\frac{h}{c\rho u}\right)(Pr)^{2/3} \qquad (90)$$

$$j_D = \frac{f}{2} = \left(\frac{Kp}{\rho u}\right)\left(\frac{\mu}{\rho D}\right)^{2/3} = \left(\frac{Kp}{\rho u}\right)(Sc)^{2/3} \qquad (91)$$

where

j_H is the j factor for heat transfer

j_D is the j factor for mass transfer (diffusion)

f is the Fanning friction factor

h is the heat transfer coefficient

c is specific heat

ρ is density

u is linear velocity

μ is viscosity

k is thermal conductivity

K is the individual phase mass transfer coefficient

p is pressure

D is the diffusion coefficient or diffusivity

Pr is the dimensionless Prandtl number

Sc is the dimensionless Schmidt number

The equality of j_H and j_D has been found to hold even when they are not mutually equal to f/2. Equating j_H and j_D on the basis of the vapor phase and making the very important assumption that the Colburn analogy may be applied to overall coefficients in a two-phase system,

$$\frac{h}{c_p\ \rho_V\ u} = \left(\frac{K_{OG}}{\rho_V\ u}\right)\left(\frac{Sc}{Pr}\right)^{2/3} = \left(\frac{K_{OG}}{\rho_V\ u}\right)(Le)^{2/3} \tag{92}$$

where h and K_{OG} are now the overall heat and mass transfer coefficients based upon the vapor phase. The ratio of the Schmidt to the Prandtl numbers is sometimes called the Lewis number. Since

$$\rho_V\ u = \frac{V}{A_{cs}} \tag{93}$$

then

$$\frac{h\ A_{cs}}{c_p\ V} = \frac{K_{OG}\ p\ A_{cs}}{V}\ (Le)^{2/3} \tag{94}$$

and multiplying both sides by az,

$$\frac{h\ A_{cs}\ a\ z}{c_p\ V} = \frac{K_{OG}\ a\ p\ A_{cs}\ z}{V}\ (Le)^{2/3} = (N_{OG})(Le)^{2/3} \qquad (95)$$

Equation (95) suggests that the quantity $(\frac{h\ A_{cs}\ a\ z}{c_p\ V})$ might be given the symbol N_{GH}, the number of heat transfer units based on the vapor phase, and that it might be related to N_{OG} by the Lewis number to the arbitrary 2/3 power. We shall now see that the symbol N_{GH} is appropriate.

The Heat Transfer Efficiency

If the vapor passes through a liquid phase of constant temperature and if we consider heat transfer without reference to mass transfer taking place, then in a form similar to the differential equation for mass transfer,

$$\begin{aligned} dQ &= h\ a\ A_{cs}\ (t_L - t_V)\ dz \\ &= c_p\ V\ dt_V \end{aligned} \qquad (96)$$

where Q is the heat flow rate. Rearranging,

$$\frac{dt_V}{t_V - t_L} = -\frac{h\ a\ A_{cs}\ dz}{c_p\ V} \qquad (97)$$

Integrating,

$$\ell n[\frac{t_{V_m} - t_{L_m}}{t_{V_{m-1}} - t_{L_m}}] = -\frac{h\ a\ A_{cs}\ z}{c_p\ V} = -N_{GH} \qquad (98)$$

and

$$\begin{aligned} t_{V_m} &= t_{L_m} + (e^{-N_{GH}})(t_{V_{m-1}} - t_{L_m}) \\ &= t_{V_{m-1}} + (1 - e^{-N_{GH}})(t_{L_m} - t_{V_{m-1}}) \end{aligned} \qquad (99)$$

and the factor $(1 - e^{-N_{GH}})$ might be called the heat transfer efficiency, E_q.

In view of Equation (95), a reasonable way of evaluating E_q for a multicomponent system might be by way of N_{OG}:

$$N_{GH} = \Sigma_i (y_i \ N_{OG,i})(Le)_i^{2/3} \tag{100}$$

However, since (1) E_{MV} is readily available, (2) the process of computing logarithms and exponentials is relatively slow, and (3) E_{MV} of the lighter components (which form the bulk of the vapor phase) does not differ greatly from N_{OG} because both are in the range 0.001 to 0.100, nor are the Lewis numbers in the vapor phase much different from 1, the following formula has been selected:

$$E_q = C_q \ \Sigma_i (y_i \ E_{MV,i})(Le)_i^{2/3} \tag{101}$$

where C_q is an empirical factor necessitated by the fact that this particular use of the Colburn analogy is not exact.

D. Prediction of the Murphree Plate Efficiency

It should be emphasized that there is presently no proven method of predicting Murphree plate efficiencies for hydrocarbon mixtures. Methods have been proposed by Bakowski(9), Chu(21), Geddes(35), and Walter and Sherwood(90), but none has found general acceptance.

In the present investigation, the Murphree vapor plate efficiency, defined

$$E_{MV} = \frac{y_m - y_{m-1}}{y_m^* - y_{m-1}} \tag{72}$$

was computed as a function of the point efficiency, E_p, itself a function of N_{OG}, the number of transfer units based on the vapor phase. N_{OG} was in turn computed from the separate resistances of the vapor and liquid phases, and these were estimated from data obtained with other systems in laboratory-size apparatus. The charge may be made that data extrapolated this far are of little value, and no defense can be made except to point out the following facts: (1) the correlation to be discussed was based on physical properties believed to be the basic ones in mass transfer operations, and (2) the basic purpose of the investigation was, after all, to make the fullest possible use of present data and to show where the need for further knowledge exists.

E_{MV} Based on Separate Phase Transfer Units

The Murphree efficiency, as originally intended, applied only to a "point", that is, to a particular location on a plate where a vapor stream, whose composition does not vary in any horizontal direction, flows up through a liquid of unvarying composition. The plate efficiency, E_{MV}, which is applied to the completely mixed vapor and liquid streams before and after their contact on the plate, is thus seen to refer to an "integration" of changes which occur in the various parts of the vapor stream as they contact liquid whose composition varies both horizontally and vertically on the plate. The integration may be expressed by computing a "point efficiency", E_p, based on the average conditions existing on the plate and correlating the plate efficiency with the point efficiency and other pertinent variables.

Gautreaux and O'Connell have proposed such a correlation(34):

$$E_{MV} = \frac{L}{mV} \left[\left(1 + \frac{E_p\, m\, V}{n\, L} \right)^n - 1 \right] \qquad (102)$$

where m is the slope of the equilibrium curve, $m = dy_i^*/dx_i$, and n is the number of stages in series.

In this case, the stages are imaginary "mixing pools" across the width of the plate. A graphical correlation of n versus x, the length of the liquid path in feet, has been fitted by the equation

$$n = 1 + 0.7\,x \tag{103}$$

Further, in multicomponent systems the slope of the equilibrium curve becomes a rather nebulous concept and, for small mole fractions, the slope of a chord from the origin to a point on the equilibrium curve, which is of course the K value, y^*/x, may be used as an approximation to the slope of a tangent to the curve, dy^*/dx.

Gerster, Colburn, et al(38) have related E_p to N_{OG}, the number of overall mass transfer units based upon the vapor phase, by the equation

$$E_p = 1 - e^{-N_{OG}} \tag{104}$$

and N_{OG} is in turn related to N_G and N_L, the number of mass transfer units in the vapor and liquid phases, respectively.

$$\frac{1}{N_{OG}} = \frac{1}{N_G} + \left(\frac{mV}{L}\right)\left(\frac{1}{N_L}\right) = \frac{1}{N_G} + \left(\frac{KV}{L}\right)\left(\frac{1}{N_L}\right) \tag{105}$$

The substitution of K for m is used as in Equation (102).

The Effect of System Properties

The A.I.Ch.E. Committee on Tray Efficiencies in Distillation Columns(1) indicates that N, the number of transfer units in the liquid or vapor phase of system 2 may be related to N in the corresponding phase of system 1 by the equation

$$N_2 = N_1 \left[\frac{(Sc)_1}{(Sc)_2}\right]^{1/2} \tag{106}$$

under similar conditions of vapor and liquid rates and in columns of similar construction. Sc, equal to $(\mu/\rho D)$, is the dimensionless Schmidt number, and μ, ρ, and D are the absolute viscosity, density, and diffusion coefficient, respectively, all in consistent units. The Committee also states, however, that the effect of density might be represented better by an exponent of 0.13 rather than 0.5 and that the effect of viscosity is supposed to be small, though appreciable(5). Equation (106) may also be used to correlate values of k_G and k_L, the mass transfer coefficients, and Gerster(37) has suggested that for mass transfer coefficients, the following equation serves equally well.

$$(k_G)_2 = (k_G)_1 \left[\frac{(D_G)_2}{(D_G)_1}\right]^{1/2} \qquad (107)$$

The following relationships were finally chosen for the present correlation:

$$(N_L)_2 = (N_L)_1 \left[\frac{(Sc)_1}{(Sc)_2}\right]^{1/2} \qquad (108)$$

where system 1 was the air-water-carbon dioxide system with $(Sc)_1$ of 550 under the conditions at which the correlation of $(N_G)_1$ was made, and

$$(N_G)_2 = (N_G)_1 \left[\frac{(D_G)_2}{(D_G)_1}\right]^{1/2} \qquad (109)$$

where subscript 1 referred to the air-water-ammonia system with $(D_G)_1$ of 0.96 ft^2/hr or 0.000267 ft^2/sec.

<u>The Effect of Operating Variables</u>

In the air-water-ammonia system, N_G has been correlated graphically against θ_G, the vapor residence time in seconds, with u, the linear vapor velocity in ft/sec, as a parameter(2). The graphs are straight lines through the origin and the slope of each line is a simple function of u. The same applies to N_L as a function of θ_L, the liquid residence time in seconds, and u in the air-water-carbon dioxide system. Algebraic correlations were developed:

$$(N_G)_1 = \left(\frac{25\ u}{u + 0.8}\right)\theta_G \tag{110}$$

and

$$(N_L)_1 = \left(\frac{0.8\ u}{u + 3.0}\right)\theta_L \tag{111}$$

The vapor residence time is the quotient of the quantity of vapor in the froth layer and the vapor rate. The liquid residence time involves the quantity of liquid in the froth layer and the liquid rate.

$$\theta_L = \frac{z\ A_{cs}\ \varphi\ \rho_L}{L} \tag{112}$$

$$\theta_G = \frac{z\ A_{cs}\ (1 - \varphi)\ \rho_V}{V} \tag{113}$$

where

φ is the "froth density", actually the volume fraction of liquid in the froth

θ_L and θ_G are the liquid and vapor phase residence times.

Correlations of froth height and froth density in the actual columns operating with hydrocarbon streams were required. They were not available, and so data from other systems were used. In the air-water-ammonia system, a curve fit of graphical data(6) gave

$$z = w + 0.14 + 0.0071\ F \tag{114}$$

where

w is the weir height in ft

F is the quantity $(u)(\rho_V)^{1/2}$ and has the dimensions $(\mathrm{ft/sec})(\mathrm{lb/ft^3})^{1/2}$.

In the air-water system(4),

$$\varphi = \frac{0.20\ F + 0.20}{F + 0.20} \tag{115}$$

Correlations of the form of Equations (110), (111), and (115) were chosen in preference to functions involving exponentials or fractional powers for two reasons: (1) their values are bounded for large and small values of the independent variable and are thus not able to give grossly unreasonable values, and (2) the expressions may be evaluated on a digital computer much more quickly than those containing logarithms or exponentials.

The Plate Efficiency Correlation

The equations given in the previous paragraphs made possible a correlation of E_{MV} based upon characteristics of the column and properties of the vapor and liquid streams being contacted on a particular plate. The correlation was developed in the following way:

From Equations (110), (113), (114), and (115),

$$\theta_G = \frac{(w + 0.14 + 0.0071\ F)(A_{cs})(0.80\ F)(\rho_V)}{(V)(F + 0.20)} \tag{116}$$

$$(N_G)_1 = \frac{(20\ u)(w + 0.14 + 0.0071\ F)(A_{cs})(F)(\rho_V)}{(u + 0.8)(V)(F + 0.20)} \tag{117}$$

From Equations (111), (112), (114), and (115),

$$\theta_L = \frac{(w + 0.14 + 0.0071\ F)(A_{cs})(0.20)(F + 1)(\rho_L)}{(L)(F + 0.20)} \tag{118}$$

$$(N_L)_1 = \frac{(0.16\ u)(w + 0.14 + 0.0071\ F)(A_{cs})(F + 1)(\rho_L)}{(u + 3)(L)(F + 0.20)} \tag{119}$$

From Equations (105), (108), (109), (117), and (119),

$$\frac{1}{N_{OG}} = \frac{1}{(N_G)_2} + [\frac{KV}{L}][\frac{1}{(N_L)_2}] = [\frac{1}{(N_G)_1}][\frac{(D_G)_1}{(D_G)_2}]^{1/2} + [\frac{KV}{L}][\frac{1}{(N_L)_1}][\frac{(Sc)_2}{(Sc)_1}]^{1/2}$$

$$= \frac{(u + 0.8)(V)(F + 0.20)(0.01635)}{(20\ u)(w + 0.14 + 0.0071\ F)(A_{cs})(F)(\rho_V)(D_G)_2^{1/2}} +$$

$$\frac{(K)(V)(u + 3)(L)(F + 0.20)(Sc)_2^{1/2}}{(L)(0.16\ u)(w + 0.14 + 0.0071\ F)(A_{cs})(F + 1)(\rho_L)(23.5)}$$

$$= \frac{(u + 0.80)(V)(F + 0.20)}{(1223\ u)(w + 0.14 + 0.0071\ F)(A_{cs})(F)(\rho_V)(D_G)_2^{1/2}} +$$

$$\frac{(K)(V)(u + 3)(F + 0.20)(Sc)_2^{1/2}}{(3.76\ u)(w + 0.14 + 0.0071\ F)(A_{cs})(F + 1)(\rho_L)}$$

$$= F_{NV}/(D_G)_2^{1/2} + (F_{NL})(K)(Sc)_2^{1/2} \qquad (120)$$

E_p and E_{MV} were then calculated from Equations (104) and (102).

The factors F_{NV} and F_{NL} were common to all components on a particular plate. The quantities $(D_G)_2$ and $(Sc)_2$ varied for each component. The quantities $F_{NV}/(D_G)_2^{1/2}$ and $(F_{NL})(K)(Sc)_2^{1/2}$ are sometimes called the vapor and liquid phase resistances.

Comparison of Predicted Values with Test Data

The sample calculation found in Table 1 occurred in a computation based on a set of test data designated as column B. Data with which to compare the estimated efficiencies are quite scarce. Walter and Sherwood(90) submit the following data for hydrocarbons in bubble cap absorbers:

TABLE 1

SAMPLE CALCULATION OF MURPHREE PLATE EFFICIENCY

Component	x_m	y_{m-1}	K	D_G	Vapor Resistance	D_L
Nitrogen	0.0010	0.0410	18.95	3.502×10^{-6}	1.754	4.797×10^{-8}
Methane	0.1164	0.8026	4.900	2.922	1.920	4.272
Ethane	0.0531	0.0723	1.167	2.914	1.922	3.413
Propane	0.0800	0.0597	0.4489	2.466	2.090	2.813
Isobutane	0.0158	0.0059	0.2345	2.092	2.269	2.418
n-Butane	0.0440	0.0135	0.1804	2.115	2.257	2.435
Isopentane	0.0095	0.0016	0.09266	1.889	2.388	2.164
n-Pentane	0.0112	0.0014	0.07408	1.886	2.390	2.155
Hexane	0.0074	0.0004	0.03203	1.726	2.498	1.942
Heptane	0.0007	0.0016	0.01292	1.606	2.590	1.775
Octane	0.0011	--	0.00511	1.500	2.679	1.640
Nonane	0.0118	--	0.00215	1.414	2.760	1.524
Decane	0.0200	--	0.00096	1.339	2.836	1.425
Abs.Oil 1	0.1084	--	0.00038	1.251	2.934	1.312
Abs.Oil 2	0.5196	--	0.00006	1.108	3.117	1.131

$t = 114\,°F$

$p = 740$ psia

$L = 0.3790$ lb moles/sec

$V = 0.9324$ lb moles/sec

$A_{cs} = 15.708\ ft^2$

$\rho_V = 2.705\ lb/ft^3$

$u = 0.4470$ ft/sec

$F = 0.7352$

$\rho_L = 45.66\ lb/ft^3$

$w = 0.25$ ft

$z = 0.395$ ft

$\varphi = 0.3711$

TABLE 1

SAMPLE CALCULATION OF MURPHREE PLATE EFFICIENCY (CONT'D)

Component	$(Sc)_L$	Liquid Resistance	N_{OG}	E_p	E_{MV}
Nitrogen	247.0	156.20	0.00633	0.0063	0.0070
Methane	277.4	42.79	0.02237	0.0221	0.0244
Ethane	347.2	11.40	0.07505	0.0723	0.0780
Propane	421.2	4.831	0.1445	0.1345	0.1421
Isobutane	490.1	2.722	0.2004	0.1816	0.1887
n-Butane	486.7	2.087	0.2302	0.2056	0.2127
Isopentane	547.7	1.137	0.2837	0.2470	0.2522
n-Pentane	549.9	0.911	0.3030	0.2614	0.2660
Hexane	610.3	0.415	0.3433	0.2906	0.2930
Heptane	667.6	0.175	0.3617	0.3035	0.3046
Octane	722.7	0.072	0.3634	0.3047	0.3052
Nonane	777.4	0.031	0.3583	0.3011	0.3013
Decane	831.3	0.014	0.3508	0.2959	0.2960
Abs.Oil 1	902.9	0.006	0.3402	0.2884	0.2884
Abs.Oil 2	1047.3	0.001	0.3207	0.2743	0.2742

θ_G = 0.557 sec

θ_L = 1.926 sec

F_{NV} = 0.003282

F_{NL} = 0.5243

μ_L = 0.8051 cp

x = 4.00 ft (liquid path)

n = 3.8 mixing stages

E_{MV} of isobutane in heavy naphtha	36 %
E_{MV} of isobutane in gas oil	17
E_{MV} of isobutane in gas oil and lube oil	9 - 10
E_{MV} of propane in heavy naphtha	22 - 24
E_{MV} of propane in gas oil	11 - 13
E_{MV} of propane in gas oil and lube oil	5 - 11

E. Enthalpy Procedures

Estimation of the enthalpy of vapor and liquid hydrocarbon mixtures has been the subject of many publications in recent years(10,31,77,82). Each method involves certain assumptions and approximations, and no one method can be considered best for all purposes. In the present investigation, methods were evolved which would optimize a function of rigor, accuracy, machine computation time, and machine storage.

The datum point for the enthalpy procedures was the ideal gas state at 0°R. Enthalpy was evaluated by (1) postulating a series of "steps" or changes of the variables temperature and pressure, each of which could be characterized thermodynamically, and (2) computing the enthalpy change associated with each step. Reference to Figures 2 and 3 will clarify description of the various steps, and the detailed evaluation of the enthalpy changes is covered in the section on physical properties. Sample calculations are given in Table 2.

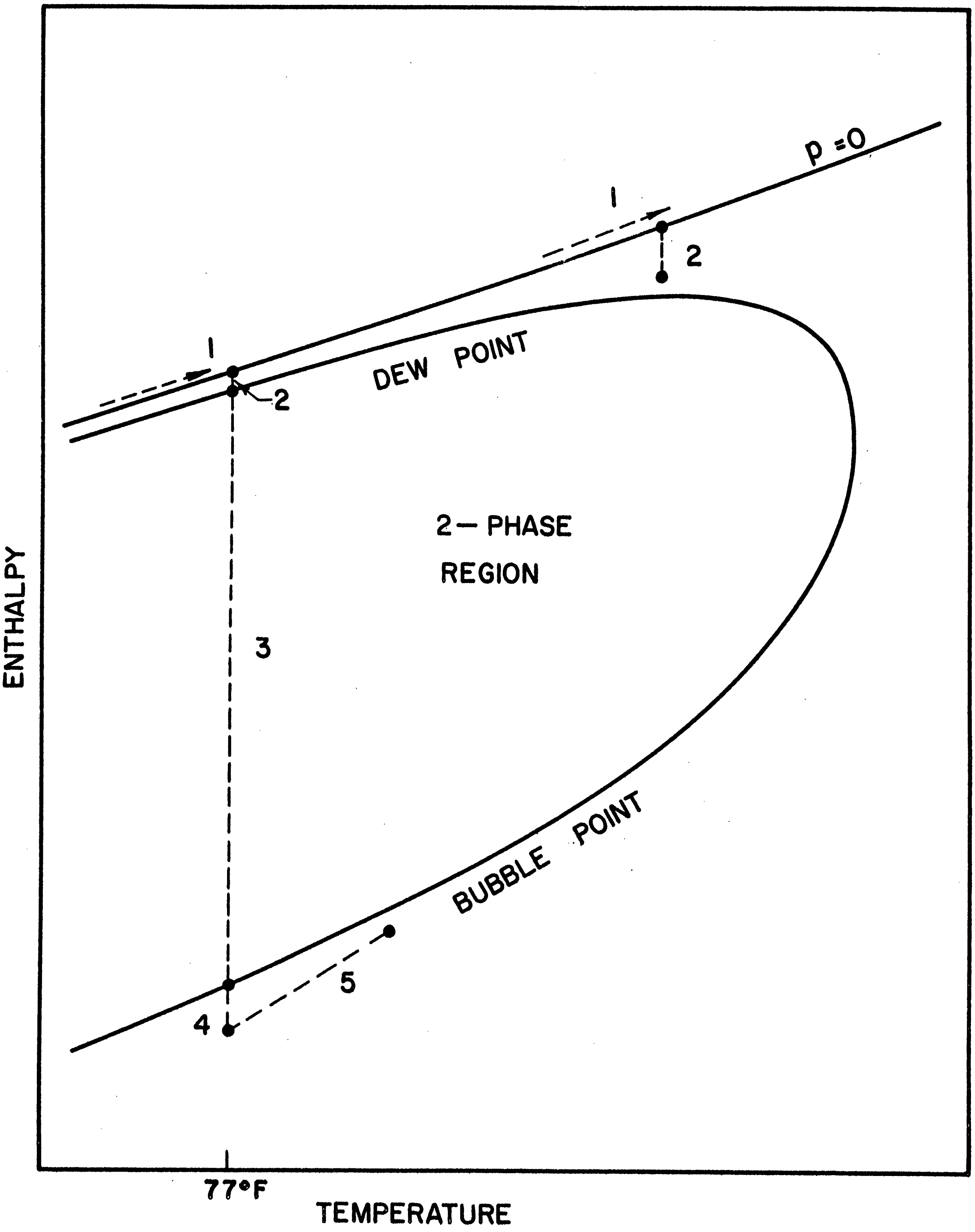


Figure 2. Enthalpy Evaluation Steps

Vapor Enthalpy

The enthalpy of a vapor mixture at temperature t_V and pressure p was computed as the sum of the enthalpy changes involved in (1) heating the ideal gas mixture to the temperature t_V and then (2) raising the pressure isothermally to p.

$$\underline{H}_V = \underline{H}^\circ + \Delta\underline{H}_t^{pc} \tag{121}$$

where

$\underline{H}_V$ is the molal enthalpy of the vapor

$\underline{H}^\circ$ is the ideal gas enthalpy at temperature t_V

$\Delta\underline{H}_t^{pc}$ is the pressure correction to the ideal gas enthalpy at constant temperature t_V.

Liquid Enthalpy, Method I

The liquid enthalpy procedure which was found to be successful consisted of the following steps: (1) heating of the ideal gas at zero pressure to the arbitrary standard temperature 77 °F (25 °C), followed by isothermal compression of the gas mixture (2) to the dew point pressure, then (3) to the bubble point pressure, and finally (4) to the condition of subcooled liquid at the existing pressure of the column, and (5) isobaric heating or cooling of the liquid phase to the temperature t_L. Enthalpy changes were computed only for steps (1), (3), and (5), the other two changes being neglected.

$$\underline{H}_L = \underline{H}^\circ - \Delta\underline{H}_t^{V} + \Delta\underline{H}^{sc} \tag{122}$$

where

$\underline{H}_L$ is the molal enthalpy of the liquid

TABLE 2

SAMPLE ENTHALPY CALCULATIONS

<u>Vapor Enthalpy</u>		
A typical rich gas at 88 °F, 740 psia:		
Ideal gas enthalpy at 88 °F	4680	Btu/lb mole
Pressure correction*	- 519	
	4161	Btu/lb mole
A typical lean gas at 112 °F, 740 psia:		
Ideal gas enthalpy at 112 °F	4643	Btu/lb mole
Pressure correction	- 339	
	4304	Btu/lb mole
<u>Liquid Enthalpy</u>		
A typical lean oil at 103 °F, 740 psia:		
Ideal gas enthalpy at 77 °F	25,069	Btu/lb mole
Heat of vaporization	- 26,265	
Subcooled liquid enthalpy change	2,378	
	1,182	Btu/lb mole
A typical rich oil at 114 °F, 740 psia		
Ideal gas enthalpy at 77 °F	19,078	Btu/lb mole
Heat of vaporization	- 19,656	
Subcooled liquid enthalpy change	2,603	
	2,025	Btu/lb mole

---

* For detail, see Table 7.

$\Delta\underline{H}_t^V$ is the heat of vaporization at constant temperature

$\Delta\underline{H}^{sc}$ is the enthalpy change accompanying heating or cooling of the subcooled liquid.

Since the liquid phase usually contained large quantities of heavy components, the dew point pressure at 77°F was a rather high vacuum, and the enthalpy change over this very small pressure change was considered negligible. The enthalpy change caused by compression of the liquid phase, although not negligible, was ignored because (1) it was small by comparison with the probable errors in the other enthalpy changes, (2) the temperature was considerably below the critical point of the mixture, (3) the enthalpy change would not change much for the various streams found in a given column and its effects would thus be minimized, and (4) no convenient methods were available for evaluating the enthalpy change.

A variation of the above method was found to be unsuccessful. It consisted of using the molal average boiling point as the reference temperature (instead of 77°F) and evaluating the heat of vaporization with an equation proposed by Kistyakowsky$^{(61)}$ for non-polar liquids:

$$\Delta\underline{H}^V = (T_b)(7.58 + 1.985 \ln T_b) \qquad (123)$$

where

$\Delta\underline{H}^V$ is in Btu/lb mole

T_b is the normal boiling temperature in °R.

Enthalpies for wide-boiling-range liquids, e.g., rich oils, were inaccurate and incompatible with enthalpies of narrow-boiling-range liquids. The conclusion was that for purposes of using the Kistyakowsky equation, the molal average boiling point was not a sufficiently sensitive indicator of the composition of wide-boiling-range liquids.

Liquid Enthalpy, Method II

An alternate method of computing liquid enthalpy was investigated and found to have some merit, but was finally abandoned. It consisted of calculating the dew point and bubble point temperatures of the liquid at the column pressure and then evaluating the changes of enthalpy corresponding to (1) heating the ideal gas to the dew point temperature, (2) increasing the pressure isothermally to the dew point, (3) lowering the temperature to the bubble point and thus condensing the vapor at constant pressure, and (4) subcooling the liquid to the temperature t_L.

$$\underline{H}_L = \underline{H}^\circ + \Delta\underline{H}_t^{pc} - \Delta\underline{H}_p^V + \Delta\underline{H}^{sc} \qquad (124)$$

where $\Delta\underline{H}_p^V$ is the isobaric heat of vaporization.

Enthalpies computed for lean, well-stripped oils were found to be inconsistent with those for rich oils, and reference to Figure 3 will help to explain the difficulty. In a typical case, both streams might have dew points in the vicinity of 900°F. The bubble point of the lean oil might be 850°F; that of the rich oil, 100°F. Thus, the rich oil enthalpy includes a large heat of vaporization, the lean oil enthalpy includes a large enthalpy of subcooling, and both include a large ideal gas enthalpy change and are computed as the difference of large numbers. Accuracy of the individual step enthalpy correlations is not sufficient to cover these wide temperature ranges. Furthermore, the pressure correction to the ideal gas enthalpy must span the range of zero pressure to the column pressure, and the upper limit of the reduced pressure in the correlation is 2.0, or about 400 psia for the heaviest components, which are the major constituents of the liquid streams. Finally, the

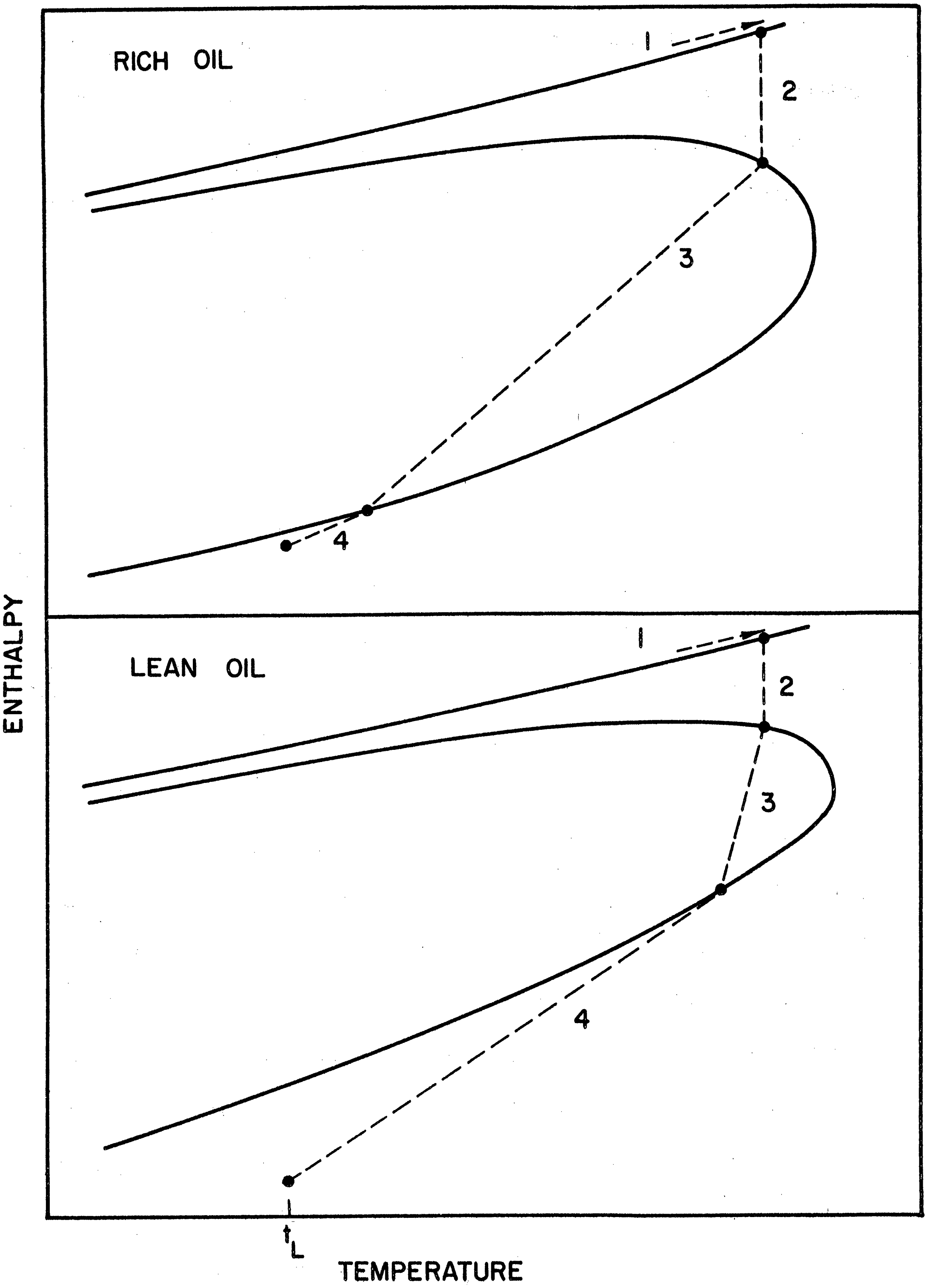


Figure 3. Liquid Enthalpy - Method II

bubble point is quite sensitive to the presence of light components, and the use of Method II was found to be unstable computationally.

Method II is unsuitable for gas absorbers, particularly those operating at high pressures, but it is thermodynamically sound and may find application in distillation columns at low or moderate pressure.

F. K Values and Convergence Pressure

The K value or equilibrium vaporization ratio, defined

$$K = \frac{y^*}{x^*} \tag{125}$$

is a most useful property, having been used in the present investigation for determining vapor compositions, calculating bubble points and dew points, computing the isobaric and partial molal heats of vaporization, and estimating individual component plate efficiencies.

Functional Dependence

K values, strictly speaking, are functions of temperature, pressure, and the compositions of both the vapor and liquid in equilibrium. Methods for predicting K values subject to the above conditions are available(26,32,58). For most applications, dependence of K on both phases produces lengthy trial-and-error calculations, and usually little error will be introduced by neglecting the effect of the vapor composition. Most well-known K value correlations(43,72,95) involve only the liquid phase composition through the artifice of the "convergence pressure". (This is one point in favor of plate-to-plate calculations from the bottom of the column upward -- liquid phase compositions are used to calculate vapor compositions.) For rough work, particularly at low pressures, the liquid composition need not be considered either, provided that the set of K values used be determined using liquid phase compositions of approximately the same composition as those in the problem at hand. Most intermediate size computer programs use K values or relative volatilities on this basis.

Convergence Pressure

For binary systems, the locus of critical points of mixtures is a continuous line between the critical points of the two pure compounds. With three or more components, a multiplicity of binary loci is produced, and any prediction of the critical point of a mixture becomes unreliable.

The convergence pressure of a binary has been described as the pressure coordinate of the intersection of a constant (system) temperature line with the locus of critical points. See Figure 4. For multicomponent mixtures, convergence pressure becomes just a simple correlation parameter defined as the pressure at which K values of all components in the system appear to converge to unity.

Hadden(45) proposed a method for estimating convergence pressure, which consists of treating a multicomponent mixture as a binary mixture composed of the lightest component of the mixture and a heavy "pseudo-component" which is a function of all other components of the mixture. Lenoir and White(65) devised a method utilizing two pseudo-components in a manner easily adaptable to machine computation, and this latter method was used in the present investigation.

K as a Function of Convergence Pressure

Winn(95) has presented K values as a function of convergence pressure through the use of a parameter "grid pressure". The functional

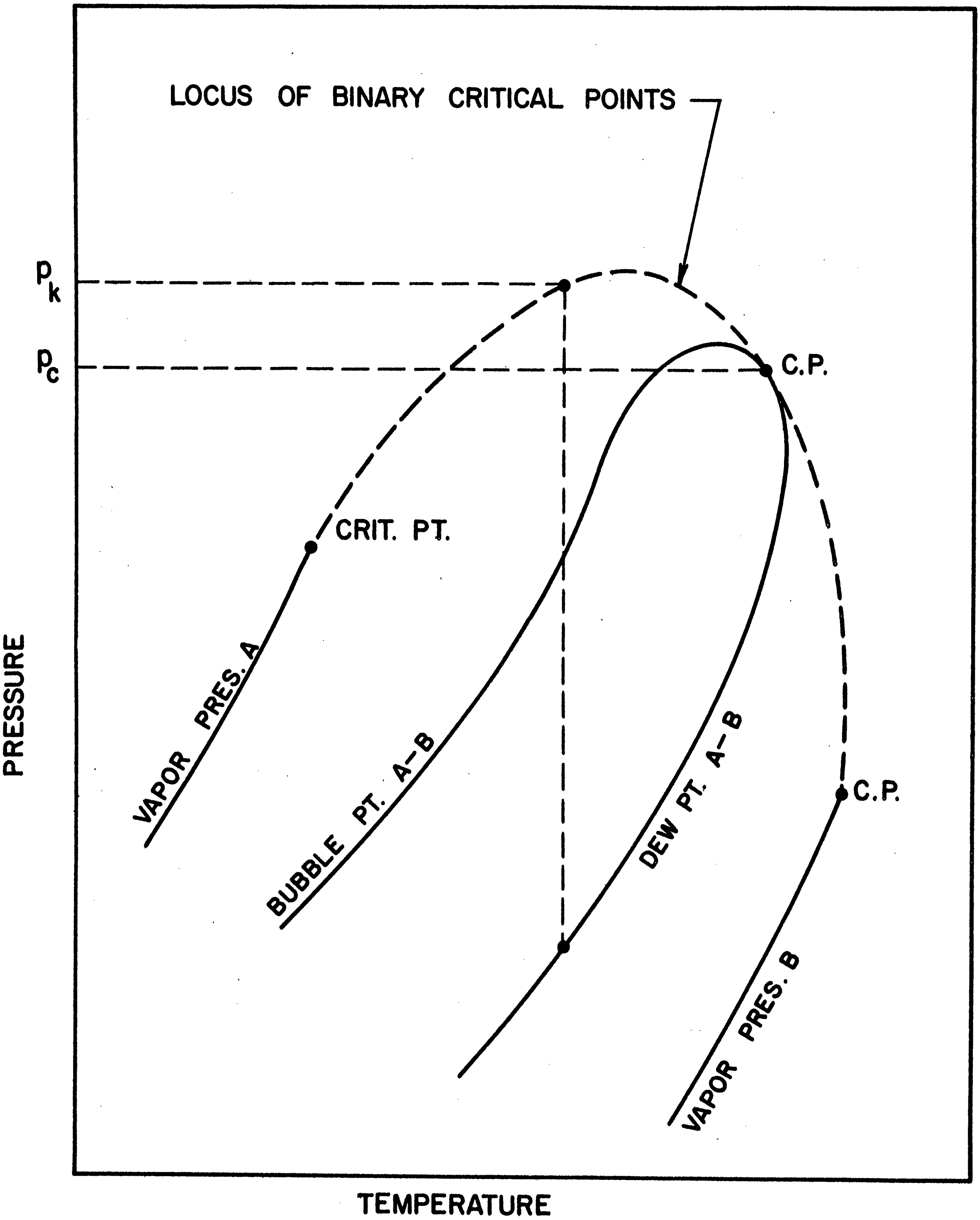


Figure 4. Critical Region of a Binary Mixture

relationship is given by nomograph, and Winn has stated$^{(96)}$ that it is probably too complex for algebraic representation. Hadden$^{(44)}$ has discussed the dependence of K on convergence pressure in the vicinity of the critical pressure for binary systems. The N.G.A.A. Equilibrium Ratio Committee$^{(73)}$, having furnished K values at a set of nine different convergence pressures, merely implies that one should use the set at convergence pressure closest to that of the system being investigated. Hinshaw$^{(52)}$, using a "correlating pressure" equivalent for most purposes to convergence pressure, suggests plotting three values of $\ell n(K)$ versus the corresponding values of $\ell n(p_k)$ and interpolating graphically.

The K value subroutine correlated the natural logarithm of K as a function of temperature for a fixed value of a system pressure at two convergence pressures, the expected extremes of those found in the gas absorber. When K was required at an intermediate convergence pressure, interpolation was performed according to the formula

$$\ell n(K)_{p_k} = \ell n(K)_{p_{k1}} + \left[\frac{\ell n(p_k) - \ell n(p_{k1})}{\ell n(p_{k2}) - \ell n(p_{k1})}\right]\left[\ell n(K)_{p_{k2}} - \ell n(K)_{p_{k1}}\right] \quad (126)$$

IV. PHYSICAL PROPERTIES

A. Vapor Density

The volume-explicit form$^{(11)}$ of the Beattie-Bridgeman equation of state$^{(12)}$ was used for calculating vapor density.

$$\underline{V} = [\frac{RT}{p} + B_o(1 - \frac{bp}{RT})][1 - \frac{cp}{RT^4}] - [\frac{A_o}{RT}][1 - \frac{ap}{RT}] \tag{127}$$

The constants for a mixture were computed from those for pure components with the following formulas proposed by Beattie, Stockmayer, and Ingersoll$^{(14)}$:

$$A_o = (\Sigma_i\ y_i \sqrt{A_{o,i}})^2 \tag{128}$$

$$B_o = (1/4)(\Sigma_i\ y_i\ B_{o,i}) + (3/4)(\Sigma_i\ y_i\ B_{o,i}{}^{1/3})(\Sigma_i\ y_i\ B_{o,i}{}^{2/3}) \tag{129}$$

$$a = \Sigma_i\ y_i\ a_i \tag{130}$$

$$b = \Sigma_i\ y_i\ b_i \tag{131}$$

$$c = (\Sigma_i\ y_i \sqrt{c_i})^2 \tag{132}$$

where

$\underline{V}$ is molal volume in liters/g mole

R is the universal gas constant in liter atm/g mole °K

T is temperature in °K

p is pressure in atm

A_o, B_o, a, b, and c are parameters in units consistent with the above.

Values of $A_o{}^{1/2}$, $B_o{}^{1/3}$, a, b, and $c^{1/2}$ as tabulated by Beattie and Stockmayer$^{(13)}$ from the work of many investigators, were available for hydrogen, nitrogen, methane, ethylene, ethane, propane, isobutane, normal butane, normal pentane, heptane, oxygen, and carbon dioxide. Values for propylene, isopentane, hexane, and octane were estimated by plotting values of neighboring compounds versus number of carbon atoms in the molecule and interpolating on a smooth curve. The implication here is not that quantities so obtained are of any value in predicting the behavior of the pure components; merely that a smaller error is introduced by using these values in calculating constants for a mixture than by leaving them out entirely and in effect assuming that the unknown values are equal to those of the mixture.

Table 3 contains Beattie-Bridgeman constants used in computing vapor density.

B. Liquid Density

Liquid density was assumed additive volume-wise and the following expression was derived:

$$\rho_L^{60} = \frac{\sum_i x_i M_i}{\sum_i (x_i M_i / \rho_{L,i}^{60})} \tag{133}$$

where

ρ_L^{60} was the density of the liquid at 60°F

M was molecular weight.

The mean coefficient of expansion was assumed equal to 0.0005 as suggested by Nelson$^{(74)}$ for 50.9 to 35.0 °API materials, and the liquid density at temperature t was then given by the expression

$$\rho_L^t = \frac{\rho_L^{60}}{1 + (0.0005)(t - 60)} \tag{134}$$

TABLE 3

BEATTIE-BRIDGEMAN CONSTANTS

Component	$(A_o)^{1/2}$	$(B_o)^{1/3}$	a	b	c
Hydrogen	0.44441	0.275717	-0.00506	-0.04359	22.45
Nitrogen	1.15953	0.369529	0.02617	-0.00691	204.94
Methane	1.50894	0.382290	0.01855	-0.01587	358.19
Ethylene	2.48032	0.495371	0.04964	0.03597	476.24
Ethane	2.42487	0.454684	0.05861	0.01915	948.68
Propylene	3.5	0.58	0.07	0.06	1000.
Propane	3.45254	0.565665	0.07321	0.04293	1095.45
Isobutane	4.07476	0.617451	0.11171	0.07697	1732.05
n-Butane	4.21829	0.626752	0.12161	0.09423	1870.83
Isopentane	5.2	0.72	0.142	0.131	1950.
n-Pentane	5.31601	0.733104	0.15099	0.13960	2000.
Hexane	6.35	0.81	0.178	0.168	2000.
Heptane	7.38377	0.891341	0.20066	0.19179	2000.
Octane	8.5	0.98	0.22	0.213	2000.
Oxygen	1.22111	0.358927	0.02562	0.004208	219.09
Carbon Dioxide	2.23752	0.471410	0.07132	0.07235	812.40

The effect of pressure was neglected since temperatures were considerably below the pseudocritical.

The average apparent densities suggested by Brown, et al(17) were used for methane and ethane. The value suggested for ethane was used for ethylene also. Specific gravities for the other hydrocarbons were obtained from Rossini(84). Table 9 contains the values used.

C. Vapor Diffusivity

Gilliland(39) has proposed the following equation for the gas diffusion constant of component a in a mixture of a and b:

$$D_{ab} = 0.0043 \frac{T^{3/2} \ (M_a + M_b/M_a \ M_b)^{1/2}}{p \ (v_a^{1/3} + v_b^{1/3})^2} \qquad (135)$$

where

D_{ab} is the diffusion coefficient in cm^2/sec

T is the temperature in °K

M_a and M_b are the molecular weights of a and b

p is the pressure in atm

v_a and v_b are molecular volumes at the normal boiling point in cm^3/g mole.

If the units of D_{ab} are changed to ft^2/sec, those of T to °R, of p to psia, and those of v left unchanged, the constant becomes 2.79×10^{-5}. The exponent of T is not constant, and the equation is recommended only for the range 0 - 100°C.

Wilke(93) has given an expression for the coefficient of diffusion of component i through a stagnant multicomponent layer in terms of the various possible binaries.

$$D_{G,i} = \frac{1 - y_i}{\sum_{i \neq j} (y_j / D_{i,j})} \qquad (136)$$

and when Equation (135) is substituted,

$$D_{G,i} = \frac{(2.79 \times 10^{-5})(T^{3/2})(1/p)(1 - y_i)}{\sum_{j \neq i} y_j \dfrac{(v_i^{1/3} + v_j^{1/3})^2}{\left(\dfrac{M_i + M_j}{M_i\ M_j}\right)^{1/2}}} \tag{137}$$

Eighteen components were included in the computation: hydrogen, nitrogen, and the hydrocarbons methane through decane plus two absorber oil components. Other non-hydrocarbon components were neglected on the grounds that they occurred in small concentrations and that Equation (136) was intended for components of similar molecular configuration. If values for these components were needed, values of others were substituted in the following manner: the diffusion constant of nitrogen for that of carbon monoxide, oxygen, and water vapor; ethylene for hydrogen sulfide; and propylene for carbon dioxide. The criteria for selection of components whose coefficients were to be substituted were these: (1) Use a compound of molecular weight close to the one for which the coefficient is substituted. (2) Use a component likely to occur in low concentration and thus not be affected much by the factor $(1 - y_i)$.

The values of the expression $(v_i^{1/3}+v_j^{1/3}) \left(\frac{M_i\ M_j}{M_i + M_j}\right)^{1/2}$ were constant, and it was expedient to use them in tabular form. The two absorber oil components were not included since their values changed with whatever absorber oil properties were used. They were recomputed and inserted for each absorber oil. The values are given in matrix form as Table 4. The matrix is, of course, symmetric and has a zero main diagonal. The molecular weights and molecular volumes, given by Rossini(86), are shown in the consolidated table of physical properties, Table 9.

TABLE 4

VAPOR DIFFUSIVITY CONSTANTS

Component	Hydrogen	Nitrogen	Methane	Ethylene	Ethane	Propylene
Hydrogen	--	42.61	44.75	50.91	53.35	59.14
Nitrogen	42.61	--	135.15	173.89	184.06	215.69
Methane	44.75	135.15	--	157.61	165.86	189.71
Ethylene	50.91	173.89	157.61	--	195.90	247.74
Ethane	53.35	184.06	165.86	195.90	--	261.88
Propylene	59.14	215.69	189.71	247.74	261.88	--
Propane	61.61	225.62	197.69	258.56	273.25	322.67
Isobutane	69.03	261.43	224.83	297.70	314.84	374.80
n-Butane	68.67	260.22	223.82	296.41	313.49	373.25
Isopentane	75.24	291.26	247.29	330.16	349.29	418.31
n-Pentane	75.36	291.70	247.59	330.62	349.81	418.87
Hexane	81.71	320.76	269.54	362.02	383.10	460.67
Heptane	87.62	347.46	289.67	390.74	413.54	498.86
Octane	93.33	372.78	308.80	417.89	442.26	534.85
Nonane	98.88	397.10	327.22	443.90	469.74	569.21
Decane	104.37	420.81	345.21	469.16	496.43	602.46
Abs. Oil 1*	118.26	480.76	390.50	532.90	563.69	686.41
Abs. Oil 2*	142.86	584.42	469.10	642.42	679.04	829.50

* Absorber Oil 1 is a typical light absorber oil with molecular weight of 184 and molecular volume of 304 cm^3/g mole.

* Absorber Oil 2 is a typical heavy absorber oil with molecular weight of 269 and molecular volume of 444 cm^3/g mole.

TABLE 4

VAPOR DIFFUSIVITY CONSTANTS (CONT'D)

Component	Propane	Isobutane	n-Butane	Isopentane	n-Pentane	Hexane
Hydrogen	61.61	69.03	68.67	75.24	75.36	81.71
Nitrogen	225.62	261.43	260.22	291.26	291.70	320.76
Methane	197.69	224.83	223.82	247.29	247.59	269.54
Ethylene	258.56	297.70	296.41	330.16	330.62	362.02
Ethane	273.25	314.84	313.49	349.29	349.81	383.10
Propylene	322.67	374.80	373.25	418.31	418.87	460.67
Propane	--	391.38	389.79	436.93	437.51	481.19
Isobutane	391.38	--	455.68	513.14	513.79	566.98
n-Butane	389.79	455.68	--	511.20	511.84	564.91
Isopentane	436.93	513.14	511.20	--	578.48	640.27
n-Pentane	437.51	513.79	511.84	578.48	--	641.03
Hexane	481.19	566.98	564.91	640.27	641.03	--
Heptane	521.08	615.63	613.43	696.87	697.67	775.36
Octane	558.62	661.38	659.08	750.12	750.97	835.88
Nonane	594.44	704.95	702.56	800.81	801.69	893.51
Decane	629.11	747.03	744.54	849.73	850.65	949.07
Abs. Oil 1*	716.58	853.52	850.81	973.85	974.85	1090.51
Abs. Oil 2*	865.41	1033.77	1030.73	1183.45	1184.58	1328.98

* Absorber Oil 1 is a typical light absorber oil with molecular weight of 184 and molecular volume of 304 cm^3/g mole.

* Absorber Oil 2 is a typical heavy absorber oil with molecular weight of 269 and molecular volume of 444 cm^3/g mole.

TABLE 4

VAPOR DIFFUSIVITY CONSTANTS (CONT'D)

Component	Heptane	Octane	Nonane	Decane	Abs.Oil 1*	Abs.Oil 2*
Hydrogen	87.62	93.33	98.88	104.37	118.26	142.86
Nitrogen	347.46	372.78	397.10	420.81	480.76	584.42
Methane	289.67	308.80	327.22	345.21	390.50	469.10
Ethylene	390.74	417.89	443.90	469.16	532.90	642.42
Ethane	413.54	442.26	469.74	496.43	563.69	679.04
Propylene	498.86	534.85	569.21	602.46	686.41	829.50
Propane	521.08	558.62	594.44	629.11	716.58	865.41
Isobutane	615.63	661.38	704.95	747.03	853.52	1033.77
n-Butane	613.43	659.08	702.56	744.54	850.81	1030.73
Isopentane	696.87	750.12	800.81	849.73	973.85	1183.45
n-Pentane	697.67	750.97	801.69	850.65	974.85	1184.58
Hexane	775.36	835.88	893.51	949.07	1090.51	1328.98
Heptane	--	914.18	978.29	1040.10	1198.08	1464.23
Octane	914.18	--	1058.40	1126.20	1300.07	1593.10
Nonane	978.29	1058.40	--	1208.40	1397.68	1716.92
Decane	1040.10	1126.20	1208.40	--	1491.98	1836.91
Abs. Oil 1*	1198.08	1300.07	1397.68	1491.98	--	2152.49
Abs. Oil 2*	1464.23	1593.10	1716.92	1836.91	2152.49	--

* Absorber Oil 1 is a typical light absorber oil with molecular weight of 184 and molecular volume of 304 cm^3/g mole.

* Absorber Oil 2 is a typical heavy absorber oil with molecular weight of 269 and molecular volume of 444 cm^3/g mole.

D. Liquid Diffusivity

The liquid diffusivity was estimated by a formula of Wilke and Chang(94).

$$D_{L,i} = 7.4 \times 10^{-8} \frac{(xM)^{1/2}\, T}{\mu v_i^{0.6}} \tag{138}$$

where

$D_{L,i}$ is the liquid diffusivity of component i in the mixture

x is an "association factor"

M is the molecular weight of the solvent

T is the temperature in °K

μ is the viscosity of the solvent in centipoises

v_i is the molal volume of the solute in cm^3/g mole.

When the dimensions of $D_{L,i}$, T, and μ are changed to those involving pounds, feet, seconds, and degrees Rankine, the constant becomes 2.97×10^{-14}. The factor x may be taken as 1 in dilute solutions of unassociated liquids. Furthermore, little error is introduced by computing M as the molecular weight of the entire liquid phase.

E. Liquid Viscosity

According to Partington(79), one of the more satisfactory of the convenient additive formulas for viscosity was proposed by Kendall(59).

$$\eta^{1/3} = \Sigma_i\, x_i\, \eta_i^{1/3} \tag{139}$$

where η is the kinematic viscosity in centistokes. By definition,

$$\eta = \mu/\rho \tag{140}$$

where μ is the absolute viscosity in centipoises and ρ is in g/cm^3. A relation for the temperature dependence of the kinematic viscosity was proposed by Cornelissen and Waterman(24).

$$\ell n(\eta) = \frac{A}{T^x} + B \tag{141}$$

where A and B are empirical constants. The exponent x, for moderate changes of temperature, is approximately equal to 2.

Values of the kinematic viscosity were obtained from Rossini(85) at 60 and 200°F. The kinematic viscosities of a mixture at each of these temperatures were then computed by Equation (139), the constants A and B were evaluated from the equations

$$A = \frac{\ell n(\eta_1/\eta_2)\ T_1^2\ T_2^2}{T_2^2 - T_1^2} = 7.11847 \times 10^{-5}\ (\ell n\ \eta_{60} - \ell n\ \eta_{200}) \tag{142}$$

and

$$B = \ell n\ \eta_1 - \frac{A}{T_1^2} = \ell n\ \eta_{60} - (3.7026 \times 10^{-6})(A) \tag{143}$$

and the kinematic viscosity at temperature t was computed from Equation (141). Multiplying η in cs by the density in lb/ft^3 and dividing by the constant 92,900 produced the absolute viscosity in lb/ft sec.

One further correction for the effect of pressure was then made.

$$\mu_p = \mu_o \exp(0.00014\ p) \tag{144}$$

where μ_o is the viscosity "at zero pressure" and does not differ appreciably from that at 1 atm, and p is the pressure in psia. The form of Equation (144) is given in Perry's Handbook(80) and the value of the constant was based on the statement, "At 1000 atm the viscosities of many common organic liquids are approximately doubled in the temperature range 30° to 75°C..."

F. Vapor Thermal Conductivity

The temperature dependence of the thermal conductivity of gases was computed by the equation of Sutherland(88).

$$k_T = (k_{32\,°F})\left(\frac{491.7 + C_s}{T + C_s}\right)\left(\frac{T}{491.7}\right)^{3/2} \qquad (145)$$

where C_s is the Sutherland constant for a particular compound. Values of the thermal conductivities of the various compounds were taken from the collection in Perry's Handbook(81), and Sutherland constants for the compounds hydrogen, nitrogen, methane, ethylene, propane, n-butane, carbon monoxide, oxygen, carbon dioxide, and water vapor were given by Partington(78). The others were calculated from the approximate formula of Arnold(8).

$$C_s = 1.47\ T_b \qquad (146)$$

G. Ideal Gas Enthalpy

In the ideal gas state, the pure component enthalpy is equal to the partial molal enthalpy, the molal enthalpy of a mixture then being equal to the summation, by mole fraction, of the individual component enthalpies.

$$\underline{H}^o = \Sigma_i\ y_i\ \overline{H}_i^o = \Sigma_i\ y_i\ \underline{H}_i^o \qquad (147)$$

where

$\overline{H}_i^o$ is the partial molal enthalpy of component i in the ideal gas state

$\underline{H}_i^o$ is the molal enthalpy of pure component i in the ideal gas state.

The ideal gas enthalpy of a component may be correlated with temperature by a fifth-order power-series approximation

$$\underline{H}_i^o = \Sigma_{j=0}^{5} A_{j,i} \ (t/100)^j \tag{148}$$

the expression (t/100), where t is in °F, being used for convenience. The ideal gas enthalpy of a mixture then becomes

$$\underline{H}^o = \Sigma_i \ y_i \ \Sigma_{j=0}^{5} A_{j,i} \ (t/100)^j \tag{149}$$

Values of $A_{j,i}$ for hydrogen and methane through n-octane, based on the data of A.P.I. Project 44(87), were furnished by Edmister(30). Values for the non-hydrocarbon gases were derived from heat capacity equations by Kobe and Long(62), and the constants for nonane, decane, and the absorber oil components were obtained by using an equation for hydrocarbon specific heats given by Fallon and Watson(33)

$$c_p = (0.0450 \ K' - 0.233) + (0.440 + 0.0177 \ K')(10^{-3} \ t) - (0.1530 \times 10^{-6})(t^2) \tag{150}$$

where K' is the characterization factor. In cases where heat capacity equations were used, integration produced constants $A_{1,i}$ through $A_{3,i}$ for nonane, decane, and the absorber oils, $A_{4,i}$ and $A_{5,i}$ being zero; and $A_{1,i}$ through $A_{4,i}$ for the other components, $A_{5,i}$ being zero. For components other than absorber oil, $A_{0,i}$, the constant of integration (equal to the molal enthalpy at 0 °F) was obtained from the literature(62,87). $A_{0,i}$ for the absorber oils was arbitrarily set at $(103)(M_i)$, where M_i was the molecular weight, any error thus introduced being cancelled by the fact that enthalpies were used for energy balances, where enthalpy changes, rather than absolute values, are important. The value of 103 is quite close to the enthalpies, in Btu/lb, of the heavier paraffin hydrocarbons. Values of $A_{j,i}$ are given as Table 5.

H. Pressure Correction to Ideal Gas Enthalpy

The pressure correction to the ideal gas enthalpy is given thermodynamically as

$$\Delta \underline{H}_t^{pc} = \int_0^p \left(\frac{\partial H}{\partial p}\right)_t dp = \int_0^p \left[\underline{V} - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp \qquad (151)$$

The integration may be carried out using a suitable equation of state, but this method is cumbersome and not recommended for machine use.

Edmister and Canjar$^{(31)}$ have published a graphical correlation of the partial molal enthalpy correction for pressure (in the form $\overline{\Delta H}/T_c$) as a function of the reduced temperature, pressure, and normal boiling point.

$$(T_r)_i = \frac{T}{(T_c)_i} \qquad (152)$$

$$(p_r)_i = \frac{p}{(p_c)_i} \qquad (153)$$

$$(B_r)_i = \frac{\sum_j x_j (T_b)_j}{(T_b)_i} = \frac{\text{molal average normal boiling point}}{(T_b)_i} \qquad (154)$$

where

T_r is the reduced temperature

T_c is the critical temperature in °R

p_r is reduced pressure

p_c is critical pressure in psia

B_r is reduced boiling point

T_b is normal boiling point in °R

TABLE 5

IDEAL GAS ENTHALPY CONSTANTS

Component	A_0	A_1	A_2	A_3	A_4	A_5
Hydrogen	3,109.	675.02	14.127	-4.955	0.879	-0.057
Nitrogen	3,192.	692.2	1.323	0.1445	-0.0029	--
Methane	3,667.	825.5	9.33	8.375	-1.333	0.092
Ethylene	3,781.	920.8	93.08	-15.417	3.917	-0.350
Ethane	4,214.	1146.3	65.62	7.125	-1.125	0.058
Propylene	4,708.	1372.7	89.75	7.750	-1.250	0.083
Propane	5,043	1568.2	114.17	9.250	-1.667	0.083
Isobutane	6,014.	2044.0	164.83	8.875	-1.833	0.092
n-Butane	6,639.	2125.8	120.92	19.500	-3.417	0.200
Isopentane	7,476.	2479.1	231.33	0.375	-0.833	0.058
n-Pentane	7,951.	2743.6	50.12	62.750	-11.125	0.700
Hexane	9,439.	3012.8	267.29	-1.792	-0.292	0.008
Heptane	10,823.	3508.6	300.25	-0.583	-0.250	-0.017
Octane	12,270.	3889.6	372.83	3.208	-2.833	0.225
Nonane	13,671.	4326.3	426.00	-6.541		
Decane	15,066	4805.3	472.72	-7.256		
Abs. Oil 1	18,988	6334.7	614.63	-9.402		
Abs. Oil 2	27,656	9726.6	905.05	-13.694		

TABLE 5

IDEAL GAS ENTHALPY CONSTANTS (CONT'D)

Component	A_0	A_1	A_2	A_3	A_4	A_5
Carbon Monoxide	3,194	690.3	2.644	0.0902	-0.0023	
Oxygen	3,188	690.6	7.83	-0.1511	0.0013	
Carbon Dioxide	3,358.	844.8	28.78	-0.720	0.0076	
Hydrogen Sulfide	3,449.	794.6	10.20	0.0783	-0.0034	
Water	3,642.	796.8	1.588	0.1917	-0.0037	

Twenty charts, one for each value of B_r from 0.3 to 2.2 at increments of 0.1, contain graphs of the function $(\overline{\Delta H}/T_c)$ versus T_r with p_r as a parameter. Values of p_r ranged from 0.1 to 1.1 (in some cases 0.8) at increments of 0.1; values of T_r, from 0.3 to 2.4, although no one graph covered the whole range. The charts of B_r of 1.3 and greater were actually the writer's cross-plots of data given as $(\overline{\Delta H}/T_c)$ versus T_r with B_r as the parameter.

The curves, 178 in all, were fit with equations of the form

$$(\overline{\Delta H}/T_c) = c_1 T_r^{-2} + c_2 T_r^{-1} + c_3 + c_4 T_r \qquad (155)$$

using the method of least squares with from six to fifteen points per curve spaced at approximately equal distances along the curve, slightly closer in regions of maximum curvature. Each of the constants was then further correlated against p_r with the equation

$$c_j = k_{1,j} p_r^2 + k_{2,j} p_r + k_{3,j} \qquad (156)$$

giving, for each value of B_r, a set of twelve constants required to reproduce the set of eight or eleven curves. Table 6 contains values of k; Table 7, a sample calculation; Table 9, the critical data used in the calculation.

The pressure correction is given by the expression

$$\underline{\Delta H}^{pc} = \Sigma_i (y_i)(T_c)_i (\overline{\Delta H}/T_c)_i \qquad (157)$$

TABLE 6

CROSS-CORRELATION CONSTANTS FOR PRESSURE CORRECTION CURVES

B_r	$k_{1,1}$	$k_{2,1}$	$k_{3,1}$	$k_{1,2}$
0.3	0.76515201	-1.0896985	0.048774930	-2.5260888
0.4	0.65641733	-1.8188528	0.0076648226	-0.79829508
0.5	0.053625970	-2.0889816	0.10234174	0.012211400
0.6	-2.7204796	-1.2274600	-0.029616518	6.0421819
0.7	6.8463816	-10.905157	1.4236963	-16.755093
0.8	-7.2901857	-1.0717085	-0.56703191	10.957736
0.9	-21.957863	5.2381433	-1.3307538	37.844393
1.0	-4.9646741	-14.042670	0.19602834	5.3078301
1.1	-13.001823	4.0844344	-1.1619453	24.366139
1.2	-24.619161	16.703230	-2.6743881	43.492558
1.3	-15.707064	10.345823	-1.1954760	28.052020
1.4	-9.1706785	2.3486746	-0.15448517	19.607486
1.5	-5.0820381	-3.2345288	0.0025136118	9.6589914
1.6	-26.281748	8.7038198	-2.6813022	48.158575
1.7	-12.221984	-40.224737	4.5784289	14.952675
1.8	-47.376168	-81.148598	13.192791	55.946835
1.9	707.86697	-558.01626	71.988096	-1035.1484
2.0	1017.0506	-750.86950	96.835324	-1354.2093
2.1	136.63509	-91.321110	18.977083	-128.21982
2.2	-104.80550	96.437031	14.509830	170.78796

TABLE 6

CROSS-CORRELATION CONSTANTS FOR PRESSURE CORRECTION CURVES (CONT'D)

B_r	$k_{2,2}$	$k_{3,2}$	$k_{1,3}$	$k_{2,3}$
0.3	1.6424300	-0.36092828	2.7965679	-1.7766868
0.4	1.6141758	-0.052154370	-0.78930334	0.16169519
0.5	1.8278866	-0.43011532	-0.38639856	-0.87145890
0.6	-1.0986707	-0.081923870	-4.3500451	0.68778619
0.7	20.553221	-3.5128029	11.801998	-14.253674
0.8	-0.85629380	0.95173645	-5.5902836	0.25957340
0.9	-12.116760	2.0630605	-21.535105	6.6800258
1.0	24.352870	-0.55029913	-1.8256805	-15.202776
1.1	-12.710789	2.1576869	-14.819421	8.3165842
1.2	-32.864472	4.6783490	-24.953644	18.711362
1.3	-18.654170	1.8166865	-14.345968	8.4351253
1.4	-3.9948665	0.42651519	-11.718348	1.6332848
1.5	8.9914864	0.25360696	-4.9646483	-5.8217500
1.6	-10.848954	5.6598528	-30.341967	8.4778520
1.7	83.637982	-6.7041671	-8.0142457	-47.282593
1.8	164.54885	-19.217993	-23.512913	-94.294868
1.9	852.77109	-101.73664	498.65291	-420.67737
2.0	1056.0718	-127.91437	592.46645	-481.80108
2.1	132.71598	-19.060167	30.318558	-53.165091
2.2	-94.395823	-17.957405	-92.486516	40.103620

TABLE 6

CROSS-CORRELATION CONSTANTS FOR PRESSURE CORRECTION CURVES (CONT'D)

B_r	$k_{3,3}$	$k_{1,4}$	$k_{2,4}$	$k_{3,4}$
0.3	0.64216386	-1.0992639	0.48136410	-0.31815297
0.4	-0.0035042948	0.76794306	-0.84538628	0.050396749
0.5	0.42106418	0.10041700	-0.00055905000	-0.10956390
0.6	0.18301313	0.88428910	-0.073278290	-0.050436775
0.7	2.5661826	-2.6288551	3.1468000	-0.56924327
0.8	-0.53552344	0.91443227	-0.025887490	0.10964841
0.9	-0.98585531	4.0084568	-1.2217063	0.14369424
1.0	0.39329410	0.24077358	2.9094673	-0.070760689
1.1	-1.2553654	2.9583135	-1.7954403	0.24046920
1.2	-2.5634896	4.7181227	-3.5407984	0.45245450
1.3	-0.71359150	2.2243009	-1.1973324	0.064486269
1.4	-0.31806367	2.2550089	-0.45210724	0.082852748
1.5	-0.31050288	0.68967455	0.93653583	0.090312239
1.6	-3.8718402	6.2494725	-2.5319863	0.84497597
1.7	3.2100072	1.6771271	7.9035915	-0.49863798
1.8	9.2360967	3.4846976	16.501281	-1.4641740
1.9	47.507386	-79.379934	67.576609	-7.3347124
2.0	55.755917	-85.244240	71.647827	-8.0187174
2.1	5.5848900	-0.32240363	5.7549133	-0.38698325
2.2	7.2650072	16.415901	-7.2277083	-0.95281385

TABLE 7

SAMPLE CALCULATION OF PRESSURE CORRECTION TO IDEAL GAS ENTHALPY

Component	y	T_r	p_r	B_r	$-\overline{\Delta H}/T_c$	$-y\overline{\Delta H}$
Nitrogen	0.0410	2.4118	1.5031	1.6374	0.4486	4.177
Methane	0.8026	1.5954	1.0994	1.1343	0.8766	241.539
Ethane	0.0723	0.9962	1.0448	0.6864	2.3711	94.249
Propane	0.0597	0.8224	1.1986	0.5481	2.9205	116.111
Isobutane	0.0059	0.7455	1.3986	0.4845	3.3258	14.416
n-Butane	0.0135	0.7156	1.3437	0.4646	3.2259	33.329
Isopentane	0.0016	0.6600	1.5321	0.4208	3.6019	4.782
n-Pentane	0.0014	0.6477	1.5117	0.4096	3.4785	4.118
Hexane*	0.0004	--	--	--	--	--
Heptane	0.0016	0.5633	1.8644	0.3409	4.0546	6.308
						519.029

$$* \quad \frac{519.029}{0.9996} = 519.237$$

$$t_V = 88°F$$

$$p = 740 \text{ psia}$$

$$\Sigma_i \, (y_i)(T_{b,i}) = 228.006$$

* The machine program, to save time, neglects mole fractions less than 0.001 and "normalizes" the result.

I. Isobaric Heat of Vaporization

The isobaric heat of vaporization was computed with an equation proposed by Edmister$^{(29)}$:

$$\underline{\Delta H}_p^V = \Sigma_i \left[\frac{R\ T_1\ T_2}{T_2 - T_1}\ \ln \frac{K_{2,i}}{K_{1,i}}\right] + \Sigma_i\ z_i\ \underline{\Delta H}_i^o \tag{158}$$

where

$\underline{\Delta H}_p^V$ is the isobaric heat of vaporization in Btu/lb mole

R is the universal gas constant in Btu/lb mole °R

T_1 is the bubble point temperature in °R

T_2 is the dew point temperature in °R

$K_{2,i}$ is the K value of component i at the dew point

$K_{1,i}$ is the K value of component i at the bubble point

z_i is the mole fraction of component i

$\underline{\Delta H}_i^o$ is the ideal gas enthalpy change of component i over the range T_1 to T_2.

J. Isothermal Heat of Vaporization

According to the definition of the partial molal heat of vaporization,

$$\underline{\Delta H}_t^V = \Sigma_i\ z_i\ \overline{\Delta H}_{t,i}^V \tag{159}$$

where $\overline{\Delta H}_{t,i}^V$ is the partial molal isothermal heat of vaporization of component i. These partial quantities may be calculated from the van't Hoff equation

$$\overline{\Delta H}^V = RT^2 \left(\frac{\partial \ln K}{\partial T}\right) \tag{160}$$

and the values for nitrogen and the various hydrocarbons at 77°F (25°C) are shown in Table 9. These values were calculated by (1) reading K values at 10 psia from the N.G.A.A. K value charts, (2) plotting their natural logarithms versus temperature, (3) drawing smooth curves, (4) computing the slopes of the tangent lines at 77°F, and (5) applying Equation (159).

K values for absorber oils were not sufficiently accurate for the calculation of the partial molal heat of vaporization, so an approximation of the pure component heat of vaporization was used. Kistyakowsky's equation was employed to estimate the heat of vaporization at the normal boiling point,

$$\Delta \underline{H}^V = (T_b)(7.58 + 1.985 \ln T_b) \qquad (123)$$

and an equation suggested by Watson(91) was used to compute the heat of vaporization at 77°F as a function of the normal boiling point, the critical temperature, and the heat of vaporization at the normal boiling point.

$$\Delta \underline{H}^V_T = \Delta \underline{H}^V_{T_b} \left(\frac{T_c - T}{T_c - T_b}\right)^{0.38} \qquad (161)$$

A typical absorber oil with molecular weight of 223, boiling point of 535°F, and critical temperature of 845°F had a heat of vaporization of 21,200 Btu/lb mole at 535°F and 29,900 Btu/lb mole at 77°F.

K. Enthalpy Change of Subcooled Liquid

The change of enthalpy accompanying the temperature change of a liquid hydrocarbon mixture may be calculated by Fallon and Watson's specific heat equation(33).

$$c_p = [(0.355 + 0.128 \times 10^{-2}\ °\text{API}) + (0.503 + 0.117 \times 10^{-2}\ °\text{API}) \cdot (10^{-3}\ t)][0.05\ K' + 0.41] \qquad (162)$$

where

c_p is the specific heat in Btu/lb °F

°API is the API gravity

K' is the characterization factor.

Like many other equations for hydrocarbon fluids, Equation (162) is probably more accurate for narrow-boiling fractions than for wide-boiling ones. Since the equation is seldom applied over more than a 40-degree temperature change, the inaccuracy is probably no greater than that associated with many other correlations.

When the specific heat is evaluated at the arithmetic average of temperatures t_1 and t_2 to give $\overline{c_p}$, the formula for the enthalpy change becomes

$$\Delta\underline{H}^{sc} = (\overline{c_p})(M_L)(t_2 - t_1) \tag{163}$$

It can easily be demonstrated that this is equivalent to an integration over the temperature range $(t_2 - t_1)$. Generally,

$$\frac{\underline{\underline{H}}}{M_L} = (\overline{c_p})(t_2 - t_1) = [a + b(\frac{t_2 + t_1}{2})][t_2 - t_1] =$$

$$(a)(t_2 - t_1) + (b/2)(t_2^2 - t_1^2)$$

Integrating, we have

$$\frac{\underline{\underline{H}}}{M_L} = \int_{t_1}^{t_2} c_p \, dt = \int_{t_1}^{t_2} (a + bt)(dt) = [(a)(t) + \frac{(b)(t)^2}{2}]_{t_1}^{t_2} =$$

$$(a)(t_2 - t_1) + (b/2)(t_2^2 - t_1^2)$$

L. K Value

The Gram orthogonal polynomial approximation as discussed by Hildebrand(48) was used to correlate the natural logarithm of K as a function of temperature. K values at nine equally-spaced values of temperature were used, and for each component a set of five correlation coefficients was produced, corresponding to a fourth order polynomial approximation. For component i (subscripts on the K values indicate the nine temperature points and the subscript i has been dropped),

$$a_0 = \frac{1}{9}[\ln K_1 + \ln K_2 + \ln K_3 + \ln K_4 + \ln K_5 + \ln K_6 + \ln K_7 + \ln K_8 + \ln K_9] \tag{164}$$

$$a_1 = \frac{1}{15}[- 4 \ln K_1 - 3 \ln K_2 - 2 \ln K_3 - \ln K_4 + 0 + \ln K_6 + 2 \ln K_7 + 3 \ln K_8 + 4 \ln K_9] \tag{165}$$

$$a_2 = \frac{1}{99}[28 \ln K_1 + 7 \ln K_2 - 8 \ln K_3 - 17 \ln K_4 - 20 \ln K_5 - 17 \ln K_6 - 8 \ln K_7 + 7 \ln K_8 + 28 \ln K_9] \tag{166}$$

$$a_3 = \frac{7}{495}[- 14 \ln K_1 + 7 \ln K_2 + 13 \ln K_3 + 9 \ln K_4 + 0 - 9 \ln K_6 - 13 \ln K_7 - 7 \ln K_8 + 14 \ln K_9] \tag{167}$$

$$a_4 = \frac{7}{965}[14 \ln K_1 - 21 \ln K_2 - 11 \ln K_3 + 9 \ln K_4 + 18 \ln K_5 + 9 \ln K_6 - 11 \ln K_7 - 21 \ln K_8 + 14 \ln K_9] \tag{168}$$

Then at any temperature t the function ψ was evaluated,

$$\psi = \frac{t - t_5}{\Delta t} \tag{169}$$

where

t_5 was the fifth or center temperature point

Δt was the temperature interval between points, and five functions of the parameter ψ,

$$p_0 = 1 \tag{170}$$

$$p_1 = \frac{1}{4}\psi \tag{171}$$

$$p_2 = \frac{3\psi^2 - 20}{28} \tag{172}$$

$$p_3 = \frac{5\psi^3 - 59\psi}{84} \tag{173}$$

$$p_4 = \frac{35\psi^4 - 575\psi^2 - 1080}{840} \tag{174}$$

Then for any component i

$$K_i = \exp\,[\Sigma_{j=0}^{4} a_{j,i}\, p_j] \tag{175}$$

The K value data of Hinshaw(53) were used for absorber oils, Winn's nomograph(95) for water vapor, and the N.G.A.A. data(72) for all other components.

M. Convergence Pressure

An article by Lenoir and White(65) is the basis of the convergence pressure correlation. The authors define an effective light component, which is a function of all components in the mixture except the heaviest, and an effective heavy component, which is a function of all except the lightest.

Letting $t_{\ell e}$ and t_{he} be the light component and heavy component effective boiling points in °F, and $T_{b\ell}$ and T_{bh} be the absolute (°R) boiling points of the lightest and heaviest components of the mixture, then

$$t_{\ell e} = \frac{\Sigma_i\, x_i\, T_{b,i}\, (T_{b\ell}/T_{b,i})^{5.57}}{\Sigma_i\, x_i\, (T_{b\ell}/T_{b,i})^{5.57}} - 459.69 \tag{176}$$

where i does not include the heaviest component, and

$$t_{he} = \frac{\sum_i x_i \, T_{b,i}(T_{b,i}/T_{bh})^{2.10}}{\sum_i x_i (T_{b,i}/T_{bh})^{2.10}} - 459.69 \tag{177}$$

where i does not include the lightest component. In evaluating $t_{\ell e}$ and t_{he} on the machine, the exponent of the ratio $(T_{b\ell}/T_{b,i})$ in Equation (176) was changed to 6 and that of the ratio $(T_{b,i}/T_{bh})$ in Equation (177) was changed to 2. These changes resulted in a considerable saving of machine time, and an examination of the authors' figures indicated that the accuracy was not seriously affected.

Lenoir and White gave two graphical correlations of $\ell n(p_k)$ versus the temperature of the system, t, with t_{he} as a parameter, one of the charts with $t_{\ell e}$ corresponding to methane, -259°F, the other with $t_{\ell e}$ corresponding to ethane, -128°F. On each chart, $\ell n(p_k)$ was correlated with t by an equation of the type

$$\ell n(p_k) = (a)(t/100)^3 + (b)(t/100)^2 + (c)(t/100) + d \tag{178}$$

using the method of least squares. Each of the four constants was then cross-correlated with t_{he} by an equation of the type

$$a = (a_1)(t_{he}/100)^2 + (a_2)(t_{he}/100) + a_3 \tag{179}$$

and thus twelve constants served to reproduce each of the charts. Values of the constants are given in Table 8.

To find $\ell n(p_k)$ with a value of $t_{\ell e}$ other than -259°F or -128°F, $\ell n(p_k)$ was evaluated with $t_{\ell e}$ equal to each of these values, and then linear interpolation was performed. The authors have recently published a more complete article(66) furnishing graphs for twelve values of the effective light component, and it seems reasonable to expect that $\ell n(p_k)$ may be made a smooth function of $t_{\ell e}$ also.

TABLE 8

CONVERGENCE PRESSURE CORRELATION CONSTANTS

$t_{\ell e}$	$t_{he}/100$	a	b	c	d
-259	0	0.0224	-0.1971	0.1651	7.4077
	1.0	-0.0126	-0.0666	0.1597	7.7413
	2.0	-0.0088	-0.0457	0.1533	8.0347
	3.0	-0.0041	-0.0536	0.1821	8.3041
	4.0	-0.0039	-0.0402	0.1620	8.5793
	5.0	-0.0037	-0.0271	0.1316	8.8070
	6.0	-0.0029	-0.0301	0.1670	8.9733
	7.0	-0.0193	-0.2798	1.5663	12.2065
	8.0	-0.0210	-0.3873	2.6868	15.7365
-128	0	-0.0215	-0.0177	0.2279	6.4141
	1.0	-0.0076	-0.1045	0.5497	6.2478
	2.0	-0.0038	-0.1488	0.8883	5.9164
	3.0	-0.0132	-0.0378	0.6730	6.0768
	4.0	0.0028	-0.1567	1.0186	5.8432
	5.0	0.0009	-0.1272	0.9838	5.9152
	6.0	0.0036	-0.1568	1.1600	5.7595
	7.0	-0.0012	-0.0744	0.8209	6.2386
	8.0	0.0015	-0.0968	0.8791	6.3042

TABLE 8

CONVERGENCE PRESSURE CORRELATION CONSTANTS (CONT'D)

$t_{\ell e}$	j	j_1	j_2	j_3
-259	a	-0.00056	0.00587	-0.018
	b	0	0.00718	-0.0696
	c	0.000611	-0.0035	0.162
	d	-0.015	0.348	7.41
-128	a	-0.00090	0.00887	-0.0193
	b	0.0070	-0.0593	-0.023
	c	-0.0262	0.289	0.250
	d	0.0205	-0.205	6.37

TABLE 9

CONSOLIDATED PHYSICAL PROPERTIES

Component	Molecular Weight	Normal Boiling Point	Critical Temperature	Critical Pressure	Kinematic Viscosity at 60°F	Kinematic Viscosity at 200°F
		°R	°R	psia	cs	cs
Hydrogen	2.016	36.828	59.87	188.11	--	--
Nitrogen	28.020	139.25	227.09	492.32	--	--
Methane	16.042	201.01	343.30	673.1	--	--
Ethylene	28.052	305.01	509.51	742.1	--	--
Ethane	30.068	332.16	549.77	708.3	--	--
Propylene	42.078	405.83	657.20	667.0	--	--
Propane	44.094	415.96	665.95	617.4	0.230	0.145
Isobutane	58.120	470.58	734.65	529.1	--	--
n-Butane	58.120	490.79	765.31	550.7	0.314	0.185
Isopentane	72.146	541.82	829.80	483.0	--	--
n-Pentane	72.146	556.62	845.60	489.5	0.387	0.220
Hexane	86.172	615.42	914.10	439.7	0.4913	0.270
Heptane	100.20	668.86	972.31	396.9	0.6379	0.3551
Octane	114.22	717.89	1024.9	362.1	0.8177	0.4201
Nonane	128.25	763.13	1071.0	331.0	1.057	0.4975
Decane	142.28	805.11	1114.0	306.0	1.358	0.5857
Carbon Monoxide	28.010	146.09	239.69	507.01	--	--
Oxygen	32.000	162.29	278.57	736.27	--	--
Carbon Dioxide	44.010	350.39	547.49	1071.3	--	--
Hydrogen Sulfide	34.080	384.41	672.41	1306.5	--	--
Water	18.016	491.69	1165.2	3208.1	1.172	0.318

TABLE 9

CONSOLIDATED PHYSICAL PROPERTIES (CONT'D)

Component	Density at 60°F	Heat of Vaporization at 77°F	Molecular Volume	Thermal Conductivity at 32°F	Sutherland Constant
	g/cm^3	Btu/lb mole	cm^3/g mole	Btu/sec ft °F	°R
Hydrogen	--	--	14.3	2.78×10^{-4}	139
Nitrogen	--	1,339	31.2	3.89×10^{-5}	212
Methane	0.25	1,477	37.85	4.86	322
Ethylene	0.40	4,453	49.32	2.81	457
Ethane	0.40	5,478	55.03	2.94	473
Propylene	0.5215	7,292	69.13	2.30	603
Propane	0.5068	6,308	75.94	2.41	599
Isobutane	0.5626	8,786	97.75	2.22	660
n-Butane	0.5840	9,576	96.60	2.17	670
Isopentane	0.6241	10,490	117.94	2.00	733
n-Pentane	0.6303	11,210	118.40	2.05	774
Hexane	0.6633	12,020	140.90	2.00	876
Heptane	0.6875	12,930	163.58	1.94	980
Octane	0.7061	13,720	186.87	--	--
Nonane	0.7210	16,080	210.87	--	--
Decane	0.7335	19,270	235.79	--	--
Carbon Monoxide	--	--	30.7	3.75	212
Oxygen	--	--	25.6	3.95	248
Carbon Dioxide	--	2,220	34.0	2.36	493
Hydrogen Sulfide	--	5,080	32.9	2.11	596
Water	0.9991	18,920	18.90	3.67	995

V. PROBLEM-SOLVING PROCEDURE

A. The Overall Procedure

The procedure followed in solving a problem, as distinguished from the machine run procedure discussed in the Appendix, is shown in flow sheet form as Figure 5. Recalling the statement of the problem, given the complete properties of the rich gas and lean oil streams, the column pressure, the number and dimensions of the bubble plates, and data on heat losses from the column, we wish to calculate the properties of the output streams and the internal streams of the column. We do this by (1) making a first approximation to the properties of the rich oil stream, (2) computing the properties of the lean gas stream by material and energy balance, (3) computing these same properties by a plate-to-plate calculation upward through the column, (4) comparing the values obtained in steps (2) and (3) and, on the basis of this comparison, adjusting the properties of the rich oil, and (5) repeating steps (2) through (4) until convergence is obtained.

The complete sequence may be broken down into four phases: (1) data conversion, (2) initial approximation, (3) plate-to-plate calculation, and (4) output. Each of these phases corresponds to a subprogram and is covered by a detailed flow sheet. The two complex subroutines are also discussed.

B. Data Conversion

The data conversion phase (contained in Subprogram A) begins with the reading of a set of K values and absorber oil data. If the machine detects an error in reading the set, a remark is written to that

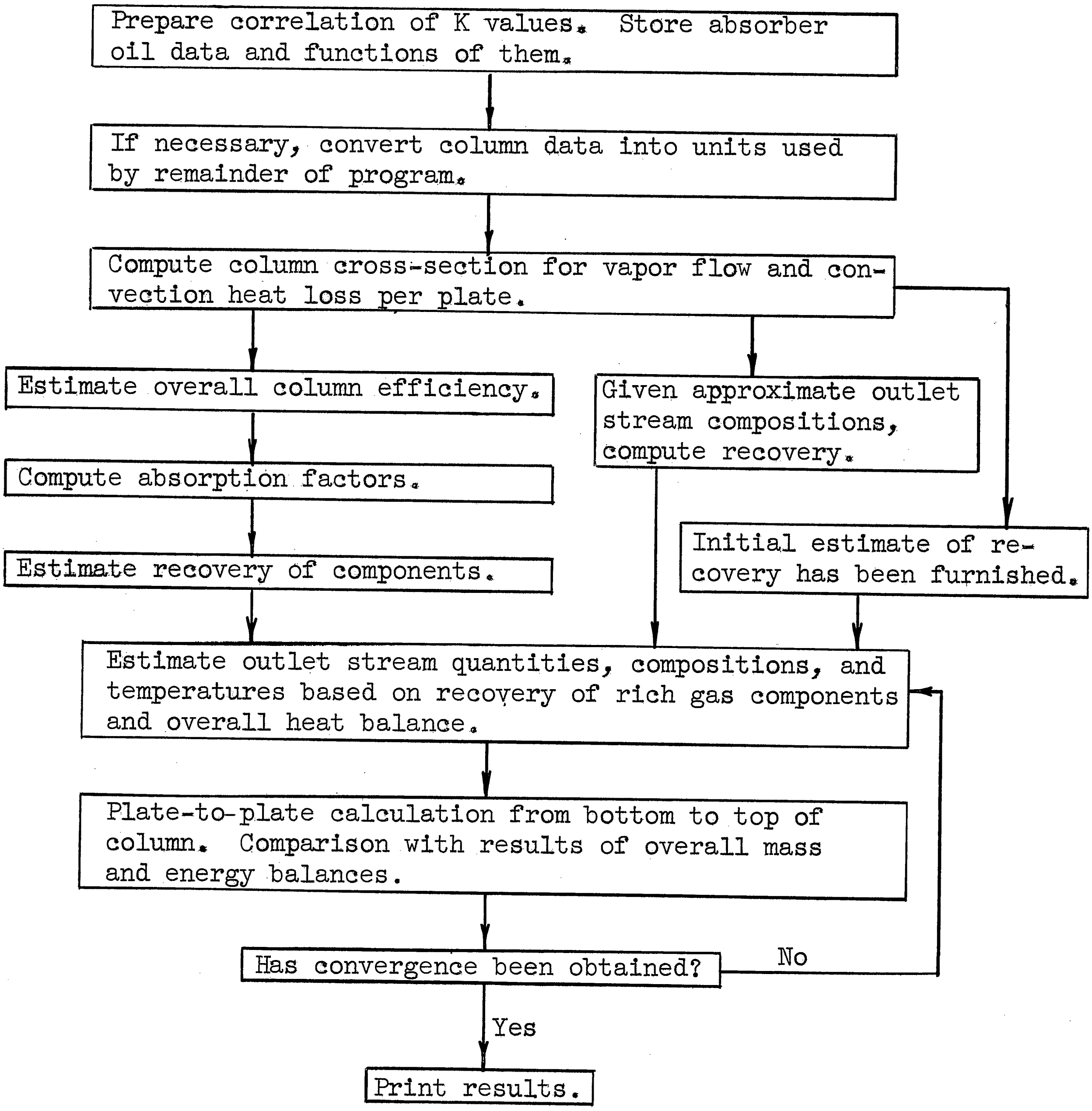
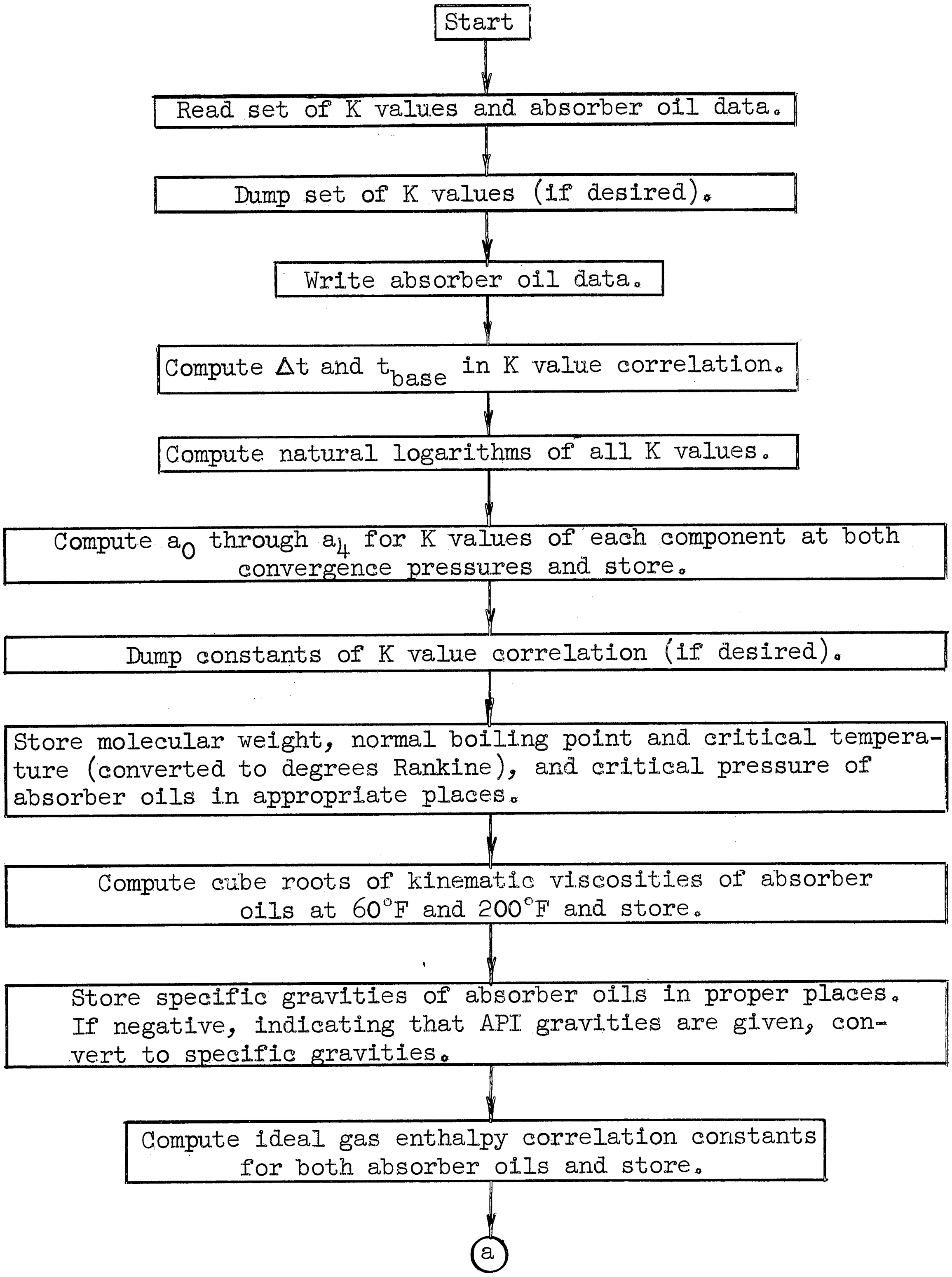


Figure 5. Problem-Solving Procedure.



(Continued)

Figure 6. Flow Diagram-Subprogram A.

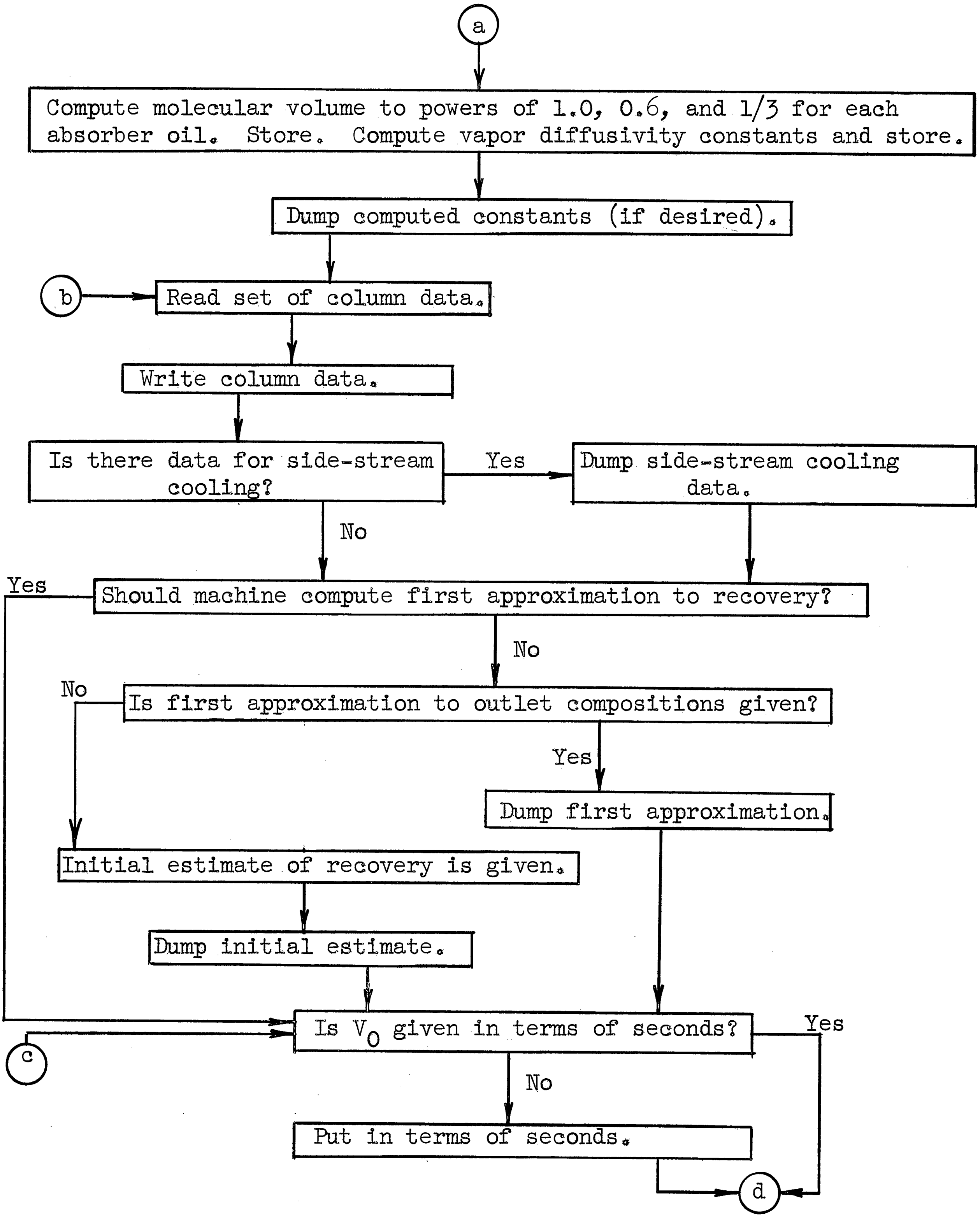


Figure 6. (Continued)

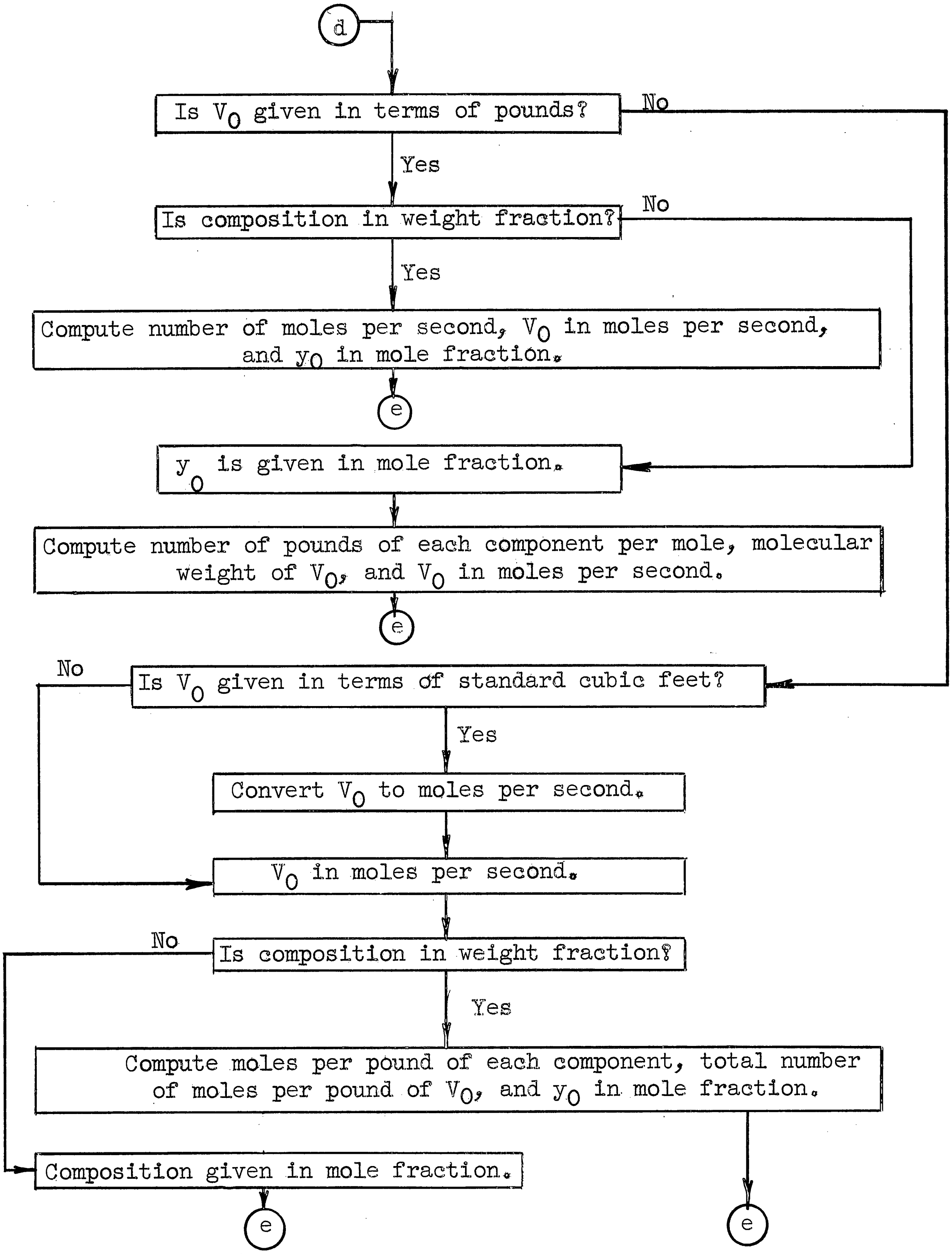


Figure 6. (Continued)

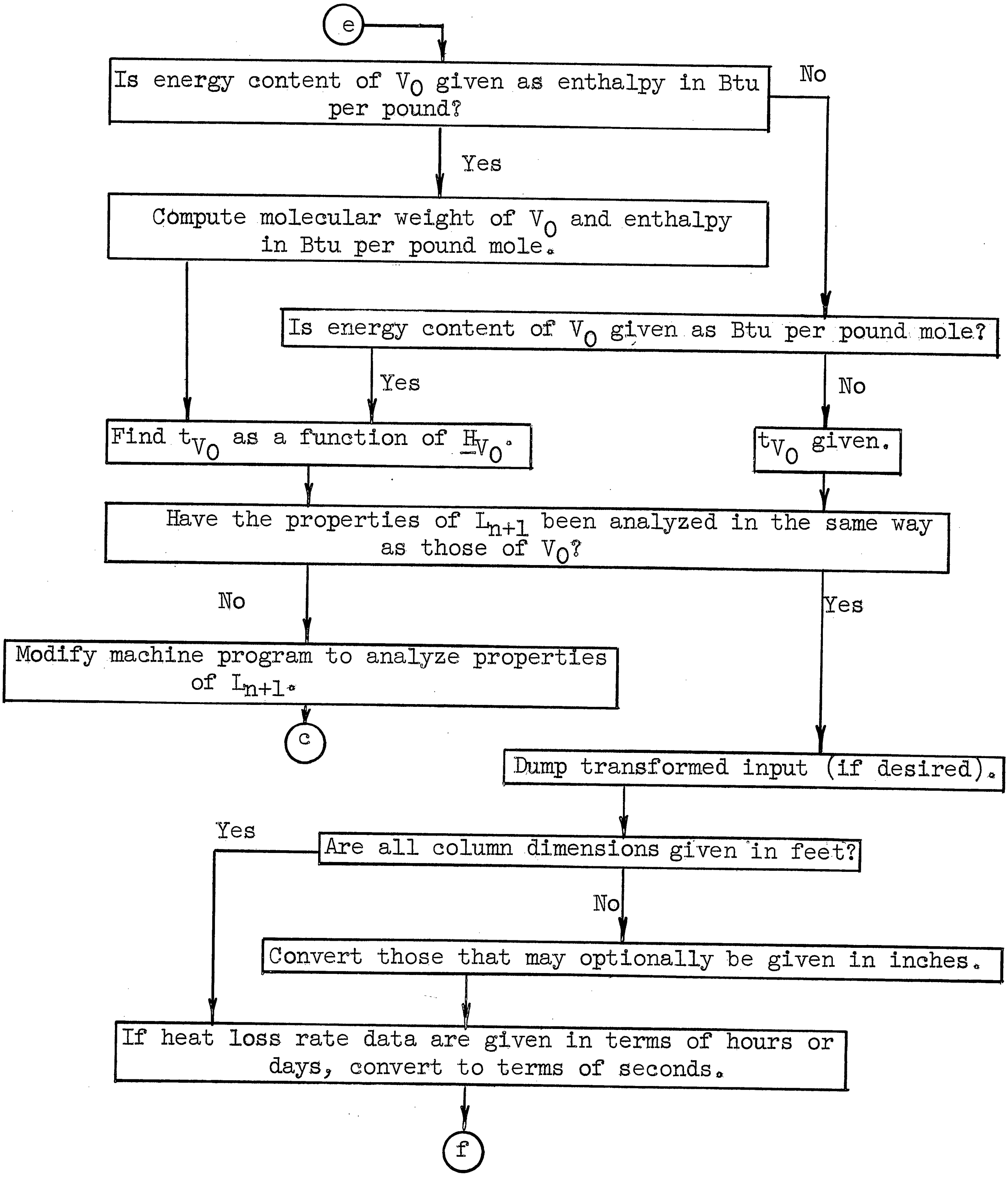


Figure 6. (Continued)

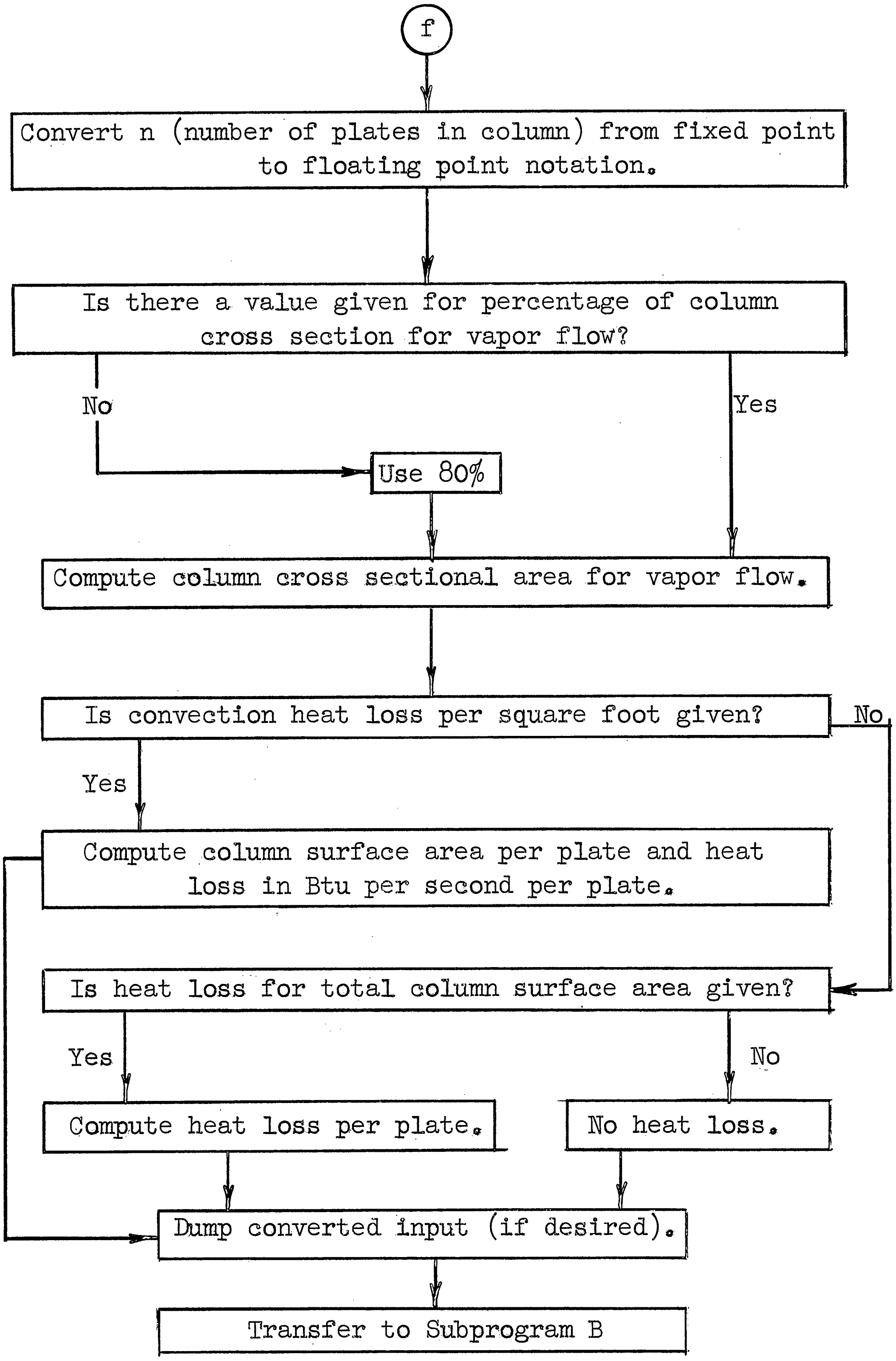


Figure 6. Flow Diagram-Subprogram A.

effect, all sets of column data following the set are ignored, and the machine attempts to read another set of K value and absorber oil data. If none is available, the entire program is transferred off the machine. The set of data, if correctly read, may be dumped (printed in a very simple and compact form) if desired for record purposes. The machine then proceeds to the correlation of the K values.

The fifth or middle one of the nine temperature values is designated t_{base}, the basic or datum temperature, and the difference between adjacent values is called Δt. The K values are correlated as the natural logarithm, so the machine then employs the GMLOG1 subroutine to obtain the natural logarithms. GMLOG1 gives an immediate error return if the argument is zero, and this feature is used to store zeros in all locations which originally contained zeros, i.e., for components not present in the column. All non-zero numbers are replaced by their natural logarithms. Note that K of 1.0 is also replaced by a zero. The machine then computes the orthogonal polynomial coefficients for each set of nine values of $\ell n(K_i)$. If $\ell n(K_{1,i})$ is zero, $\ell n(K_{2,i})$ is examined. If both are zero, the machine concludes that the component is missing, stores zeros for coefficients, and procedes to the next component. The machine may dump the coefficients if desired.

The molecular weight and critical pressure of each of the absorber oils are stored in the table of physical properties. Critical temperature and normal boiling point are converted to °R and stored. The cube roots of the kinematic viscosities at 60° and 200°F are computed and stored. If the API gravity of the absorber oils is given (designated by a negative sign), it is changed to specific gravity. Specific gravities are stored.

The machine then computes the characterization factor of each of the absorber oils and the constants for the ideal gas enthalpy correlation. The fifth and sixth constants are zero. The molecular volume is estimated as equal to 1.65 times the molecular weight (an average value for the heavy paraffin hydrocarbons), and the one-third and six-tenth powers are stored. The vapor diffusivity constants are computed and stored in the 18 x 18 matrix. The computed functions may be dumped if desired. This completes processing of the K values and absorber oil data.

The first set of column data is read. If an error is detected, a remark is printed and the machine reads the next set. If no set of column data is available, the machine returns to the reading of another set of K value and absorber oil data. The column data are printed for reference. If side stream cooling (intercooling) data is included, it is dumped. A first approximation of either outlet stream compositions or fractional recovery of components is dumped if supplied; otherwise the machine writes a remark saying that it will compute the first approximation.

The machine proceeds to an examination of the dimension and the column code flags and converts the input data to the standard units used by the program. These are seconds, feet, mole fractions, moles per second, and degrees Fahrenheit. The flow sheet (Figure 6) adequately explains this procedure.

The number of plates in the column, originally in fixed point form, is converted to floating point also. The mean column cross-sectional area and the area for vapor flow are computed. If no value for the fraction of the column area for vapor flow has been given, 0.8 is used. If data for convection and radiation heat loss have been given, they are converted to the units Btu/sec per plate, H_c/n.

This completes the data conversion phase, and control is transferred to Subprogram B.

C. Initial Approximation

The computing of a first approximation to the recovery of the various components or the use of such information if provided, together with preparation for the iterative, plate-to-plate procedure, constitutes the work of Subprogram B.

The machine begins by filling out the complete list of properties of the rich gas and lean oil streams. This consists of computing the flow rate of each component (the product of the mole fraction and the total stream flow rate), the molal enthalpy, and the total enthalpy. The properties of stream V_0 (the rich gas) are transferred to the corresponding locations for stream V_{m-1} in preparation for the plate-to-plate calculation.

The average temperature in the column, $\bar{t}$, is computed as the arithmetic average of t_{V_0} and $t_{L_{n+1}}$ plus 15°F. This has been found to be a fair approximation for most columns.

The computation code flag is examined. If the machine is to compute the first approximation, the overall column efficiency is required, and the Drickamer and Bradford formula(27) is used to approximate it.

$$E_{oc} = -1.78 - 0.268\ \ell n(\mu_f) \qquad (180)$$

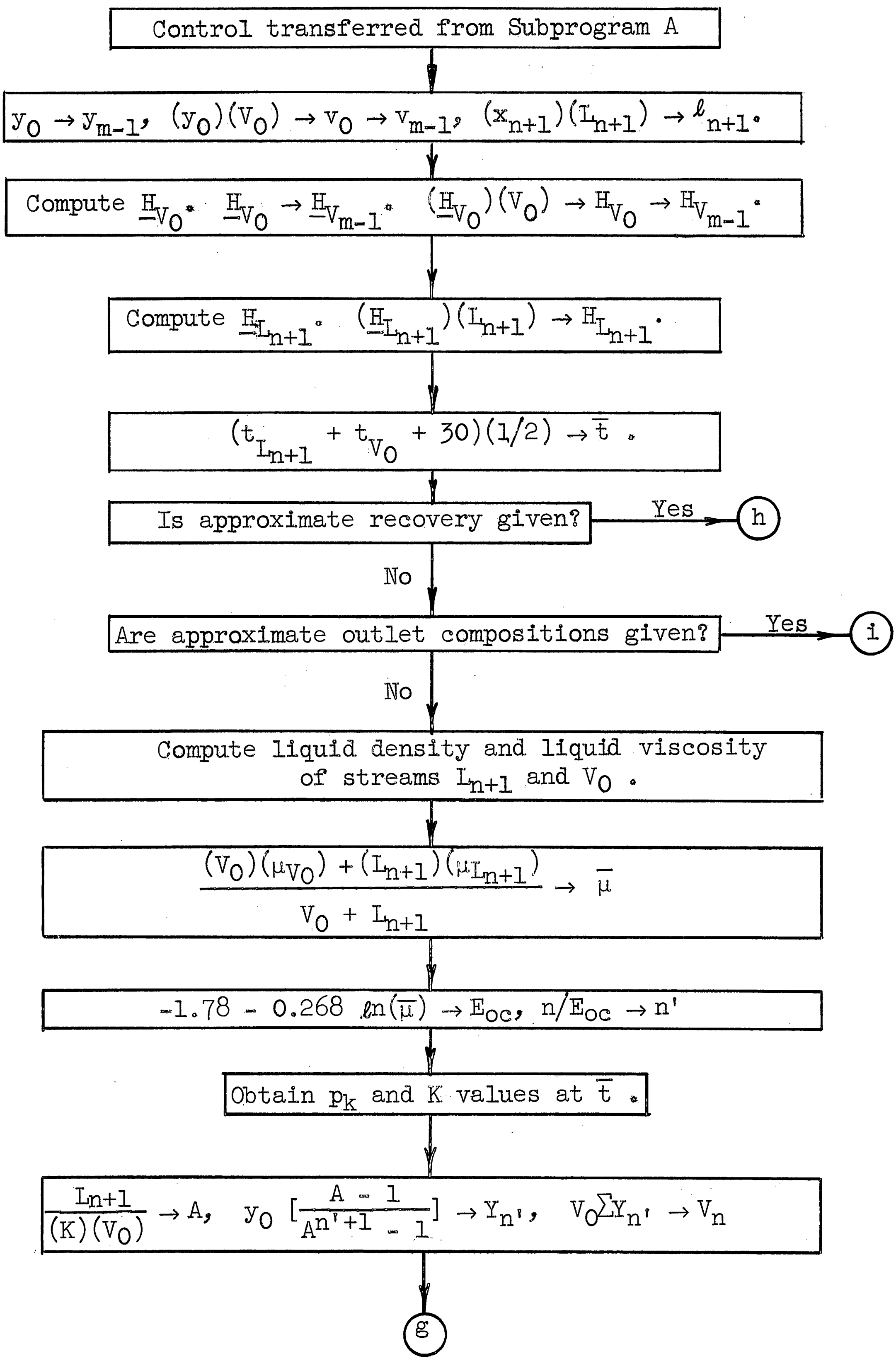


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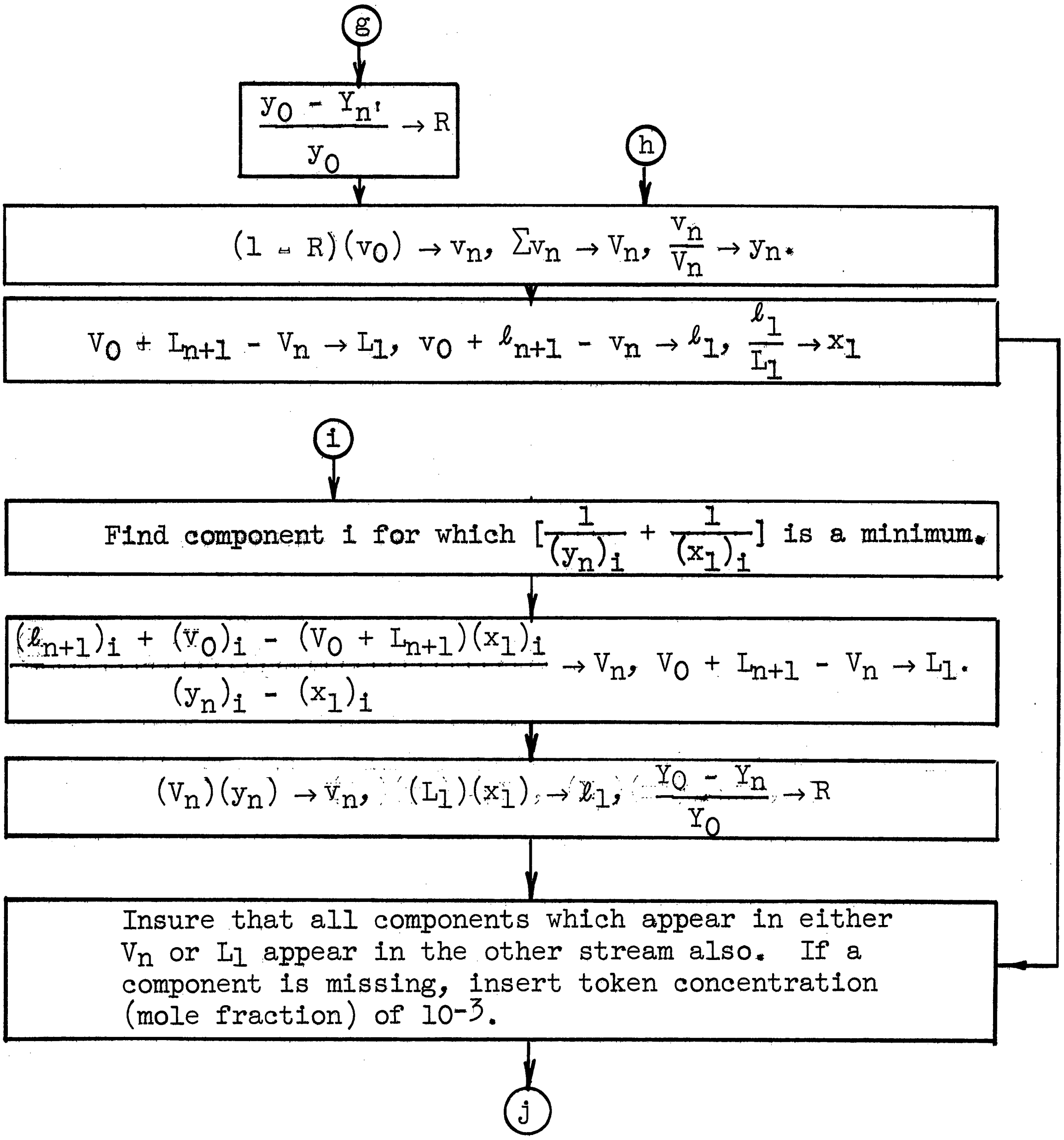
Figure 7. Flow Diagram-Subprogram B.



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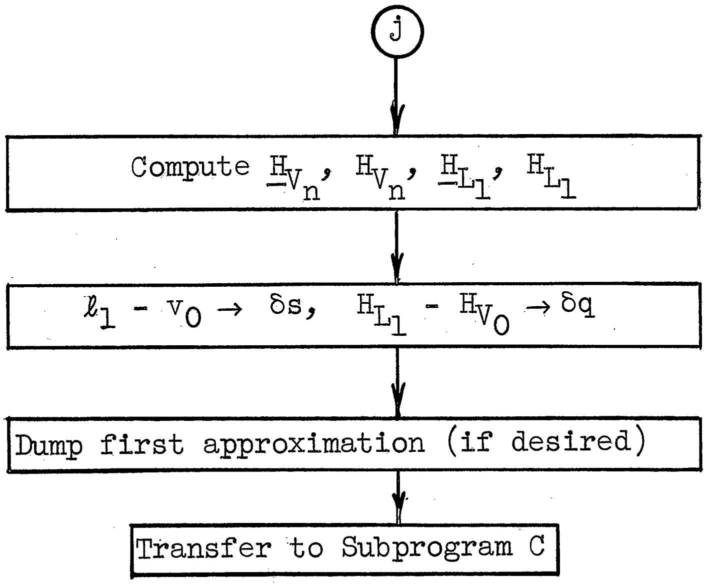

Figure 7. Flow Diagram-Subprogram B.

where μ_f is the viscosity of the feed in lb/ft sec. The viscosity of the "feed" is taken as the average of the liquid viscosities of the rich gas and lean oil, weighted by the flow rate of each stream. The number of theoretical plates, n', is obtained as the quotient of n divided by E_{oc}, and a set of K values is computed at $\bar{t}$.

The machine then makes use of an absorption factor technique quite similar to the Kremser-Brown method(18,63) to calculate $Y_{n'}$ of each component, the quantity of each component leaving the column in stream V_n <u>per mole of rich gas entering</u>. The absorption factor is computed as

$$A = \frac{L_{n+1}}{(K)(V_0)} \tag{181}$$

and

$$Y_{n'} = y_0\left[\frac{A - 1}{A^{n'+1} - 1}\right] \tag{182}$$

The sum of the $Y_{n'}$, multiplied by V_0, is equal to V_n. The recovery of any component is defined

$$R = \frac{y_0 - Y_{n'}}{y_0} \tag{183}$$

The remaining quantities and compositions of streams V_n and L_1 are obtained by an overall column material balance. All material entering in the lean oil is assumed to be completely recovered. The average temperature, $\bar{t}$, is used as the first approximation of t_{V_n} and t_{L1}.

If the approximate recovery of each component has been given with the column data, the machine proceeds with the overall column material balance as in the paragraph above and again uses $\bar{t}$ for approximating t_{V_n} and t_{L1}.

If a first approximation of the compositions of the outlet streams has been furnished, the machine picks out the component most likely to afford an accurate material balance. This component is taken as the one for which the sum $[(1/y_n) + (1/x_1)]$ is a minimum, the criterion being that it occur in appreciable concentration in both streams. An overall column material balance yields the quantities of the streams V_n and L_1. Temperatures of V_n and L_1 are furnished with the column data under the option of providing outlet compositions.

At this point, the three routes to making the first approximation of the product streams all join again. The machine insures that all components entering the column occur in both outlet streams and inserts a token mole fraction of 10^{-3} for any that are missing. The molal and total enthalpies of streams V_n and L_1 are computed, the delta quantities for heat and for each component are computed, and the machine then proceeds to the plate-to-plate calculation, Subprogram C.

D. Plate-to-Plate Calculation

Subprogram C begins with the transfer of the properties of stream L_1 to those of the liquid from the general plate, L_m. At this point, the machine enters the column calculation loop and the calculation loop for plate 1.

Using the temperature t_{L1} (now t_{Lm}), and the properties of streams L_1 and V_0 (now L_m and V_{m-1}), the machine computes values of convergence pressure, K values, and plate efficiencies. The quantity of each component in the stream V_1 (V_m) is computed from the formula

$$v_{m,i} = V_{m-1}[y_{m-1} + (E_{MV,i})(K_{m,i}\ x_{m,i} - y_{m-1,i})] \qquad (184)$$

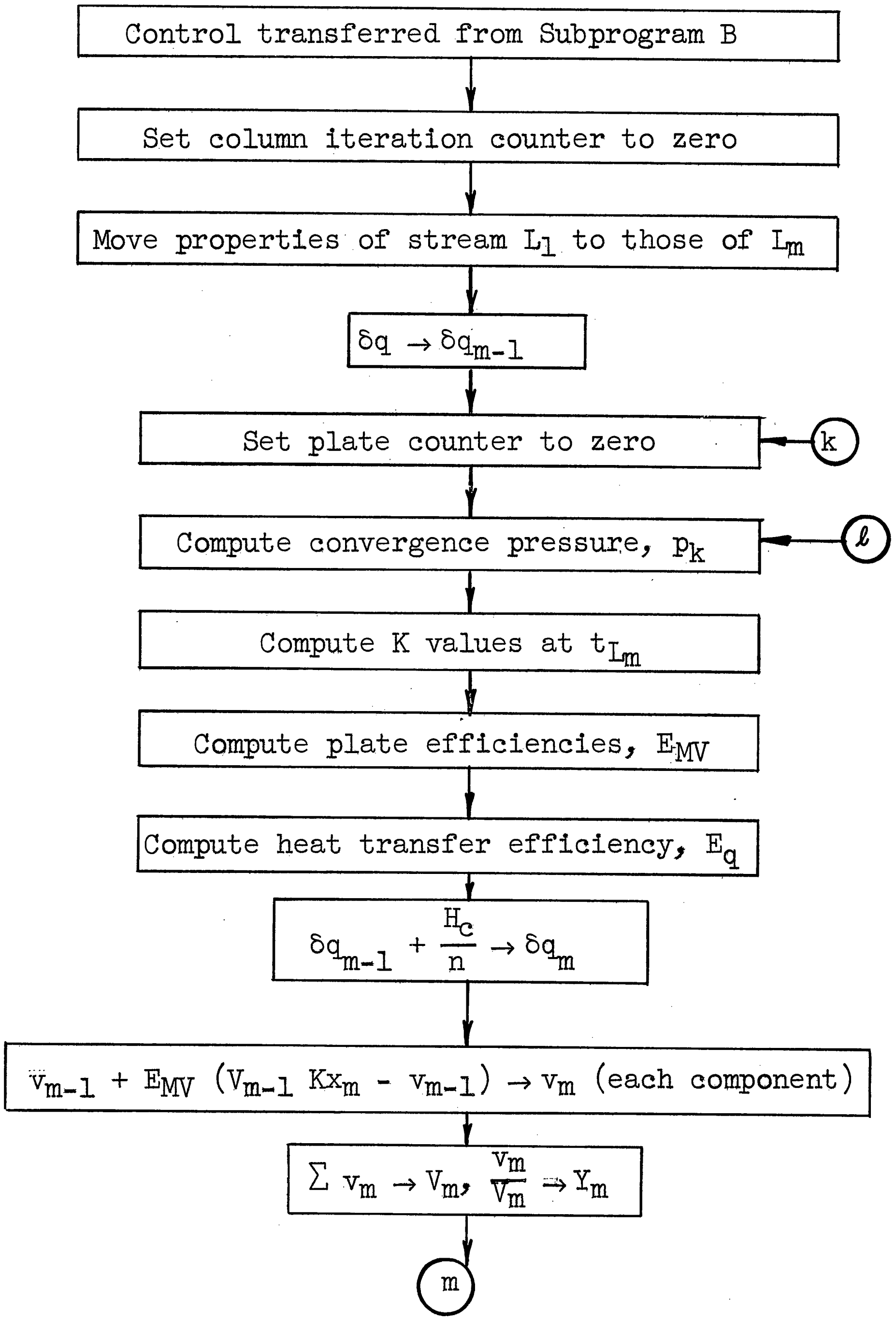

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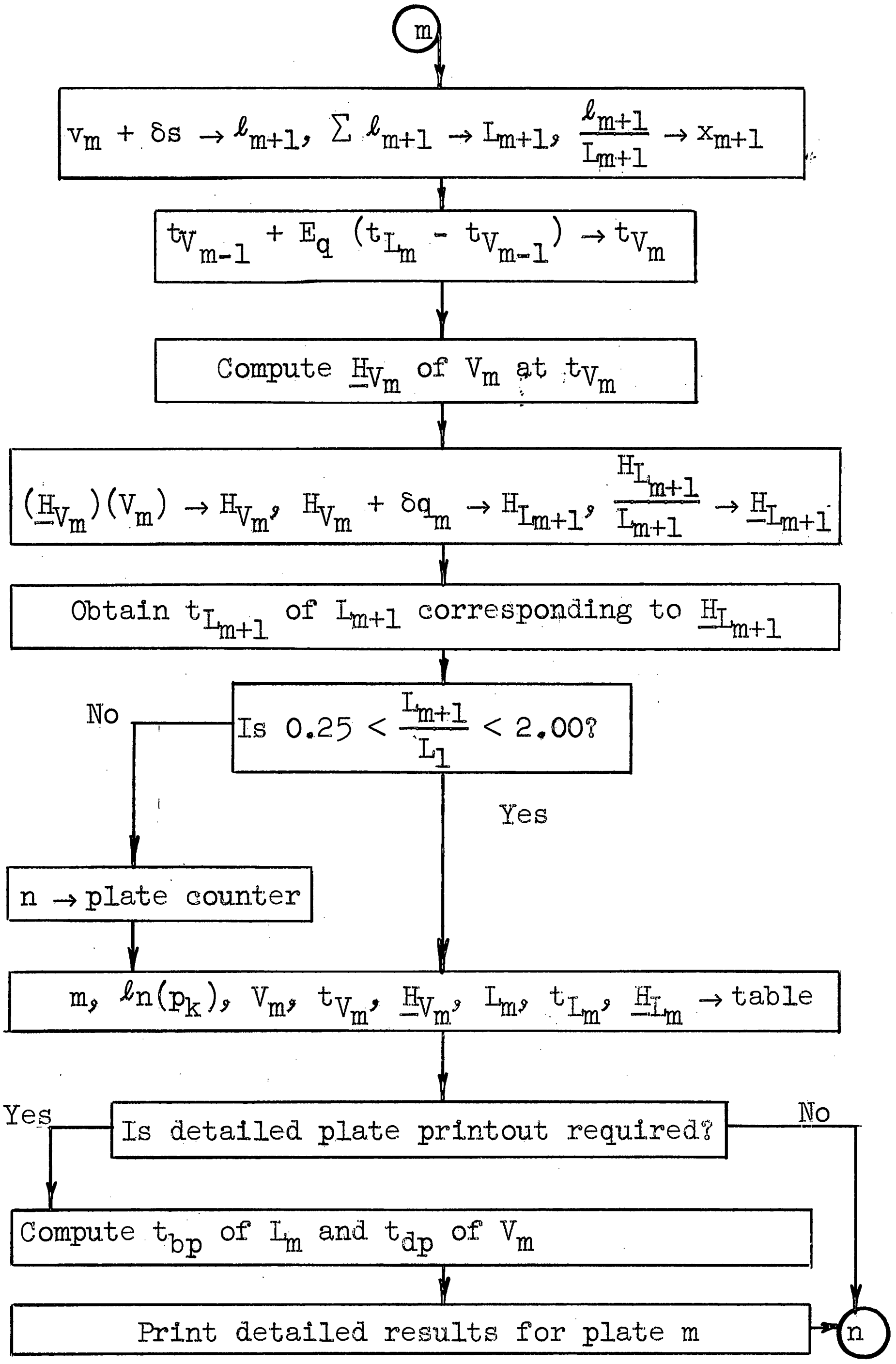
Figure 8. Flow Diagram-Subprogram C.



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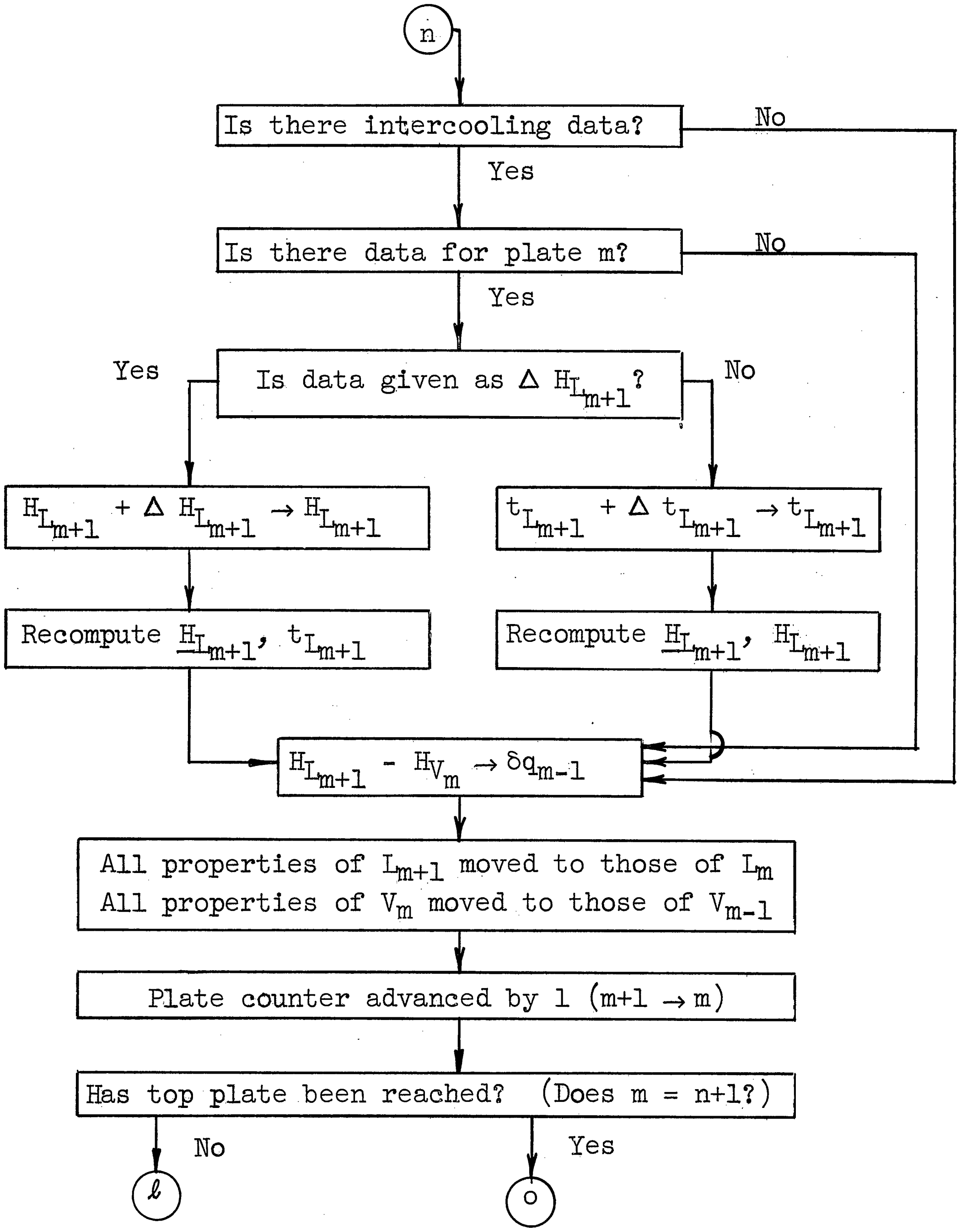

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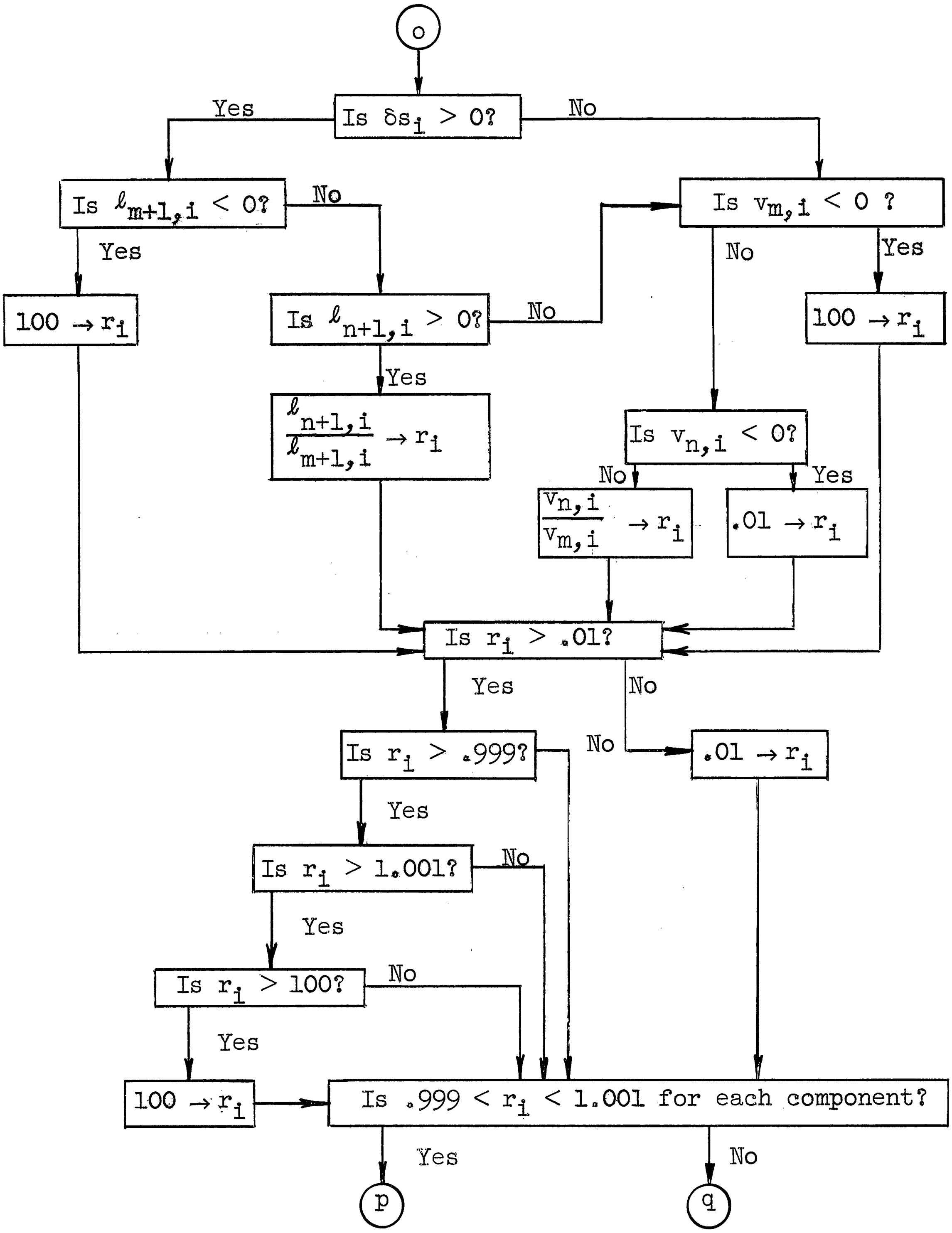

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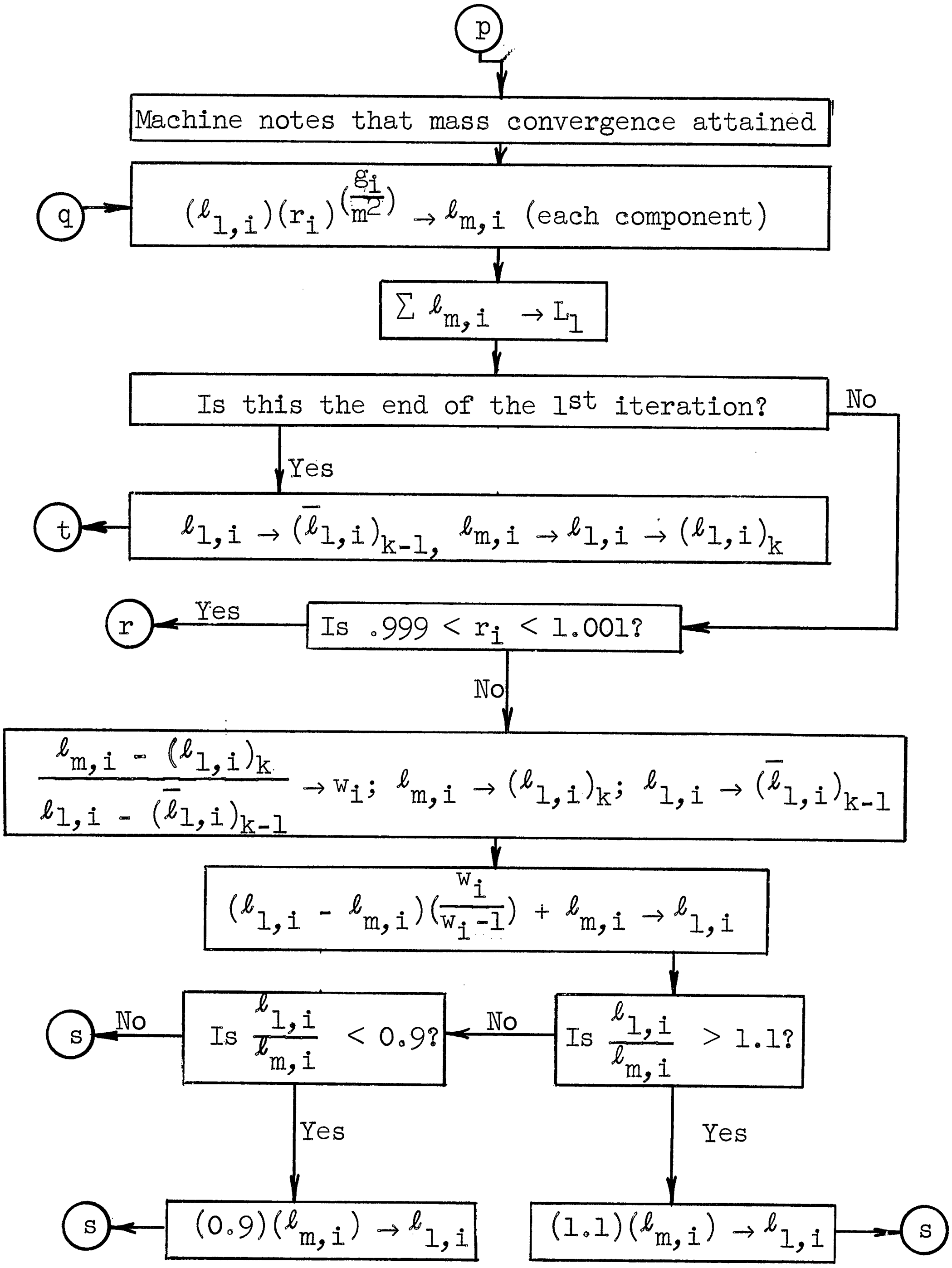

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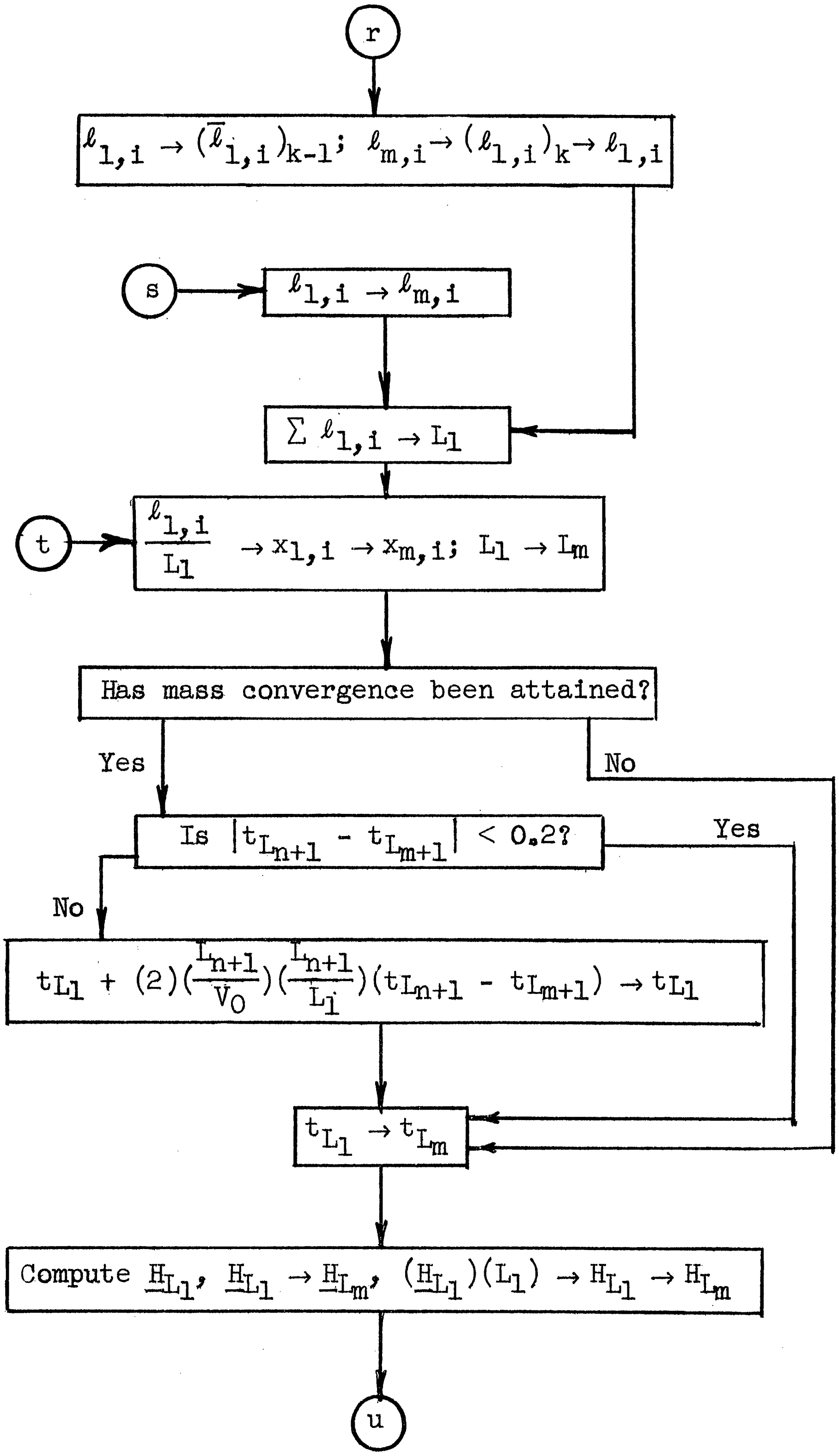

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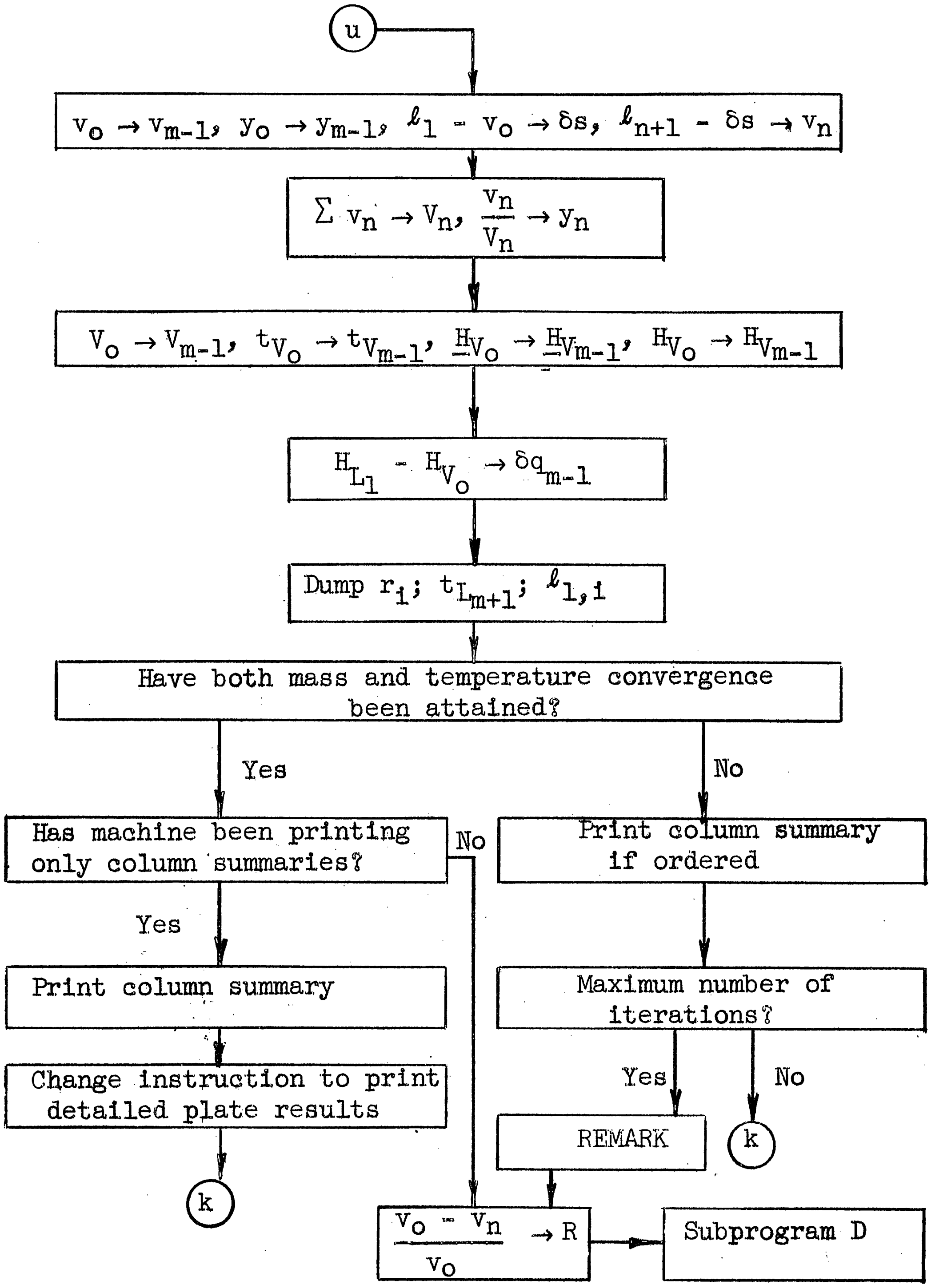


Figure 8. Flow Diagram-Subprogram C.

and the sum of them is V_m. Mole fractions, $y_{m,i}$, are computed, and then the quantity of each component in stream L_{m+1} is computed from the stream δs_i quantities.

$$\ell_{m+1,i} = v_{m,i} + \delta s_i \tag{185}$$

The sum of the $\ell_{m+1,i}$ is equal to L_{m+1} and the mole fractions, $x_{m+1,i}$, follow.

Using the properties of stream V_m, the machine obtains the heat transfer efficiency and computes the temperature of the vapor, t_{V_m}.

$$t_{V_m} = t_{V_{m-1}} + (E_q)(t_{L_m} - t_{V_{m-1}}) \tag{99}$$

The molal and total enthalpy of V_m are obtained, and the corresponding properties of L_{m+1} by energy balance.

$$H_{L_{m+1}} = H_{V_m} + \delta q_m \tag{186}$$

where

$$\delta q_m = \delta q_{m-1} + H_c/n \tag{187}$$

The temperature of the liquid stream, $t_{L_{m+1}}$, is obtained as a function of $\underline{H}_{L_{m+1}}$ and $x_{m+1,i}$.

Having completed a plate calculation, the machine checks the size of L_{m+1}. If the condition

$$0.25 < \frac{L_{m+1}}{L_1} < 2.00 \tag{188}$$

is not met, the machine advances the plate counter to n. The next time the plate counter is checked, plate m will be treated as the top plate, the rich oil properties will be revised, and the plate-to-plate calculation will be started again. Eight key properties of plate m are moved to the column summary table, and the tag of the computation code flag is examined. If it calls for a detailed plate printout, the bubble point of L_m and the dew point of V_m are computed and placed in the proper locations, and the plate printout is made. The machine examines the column code flag. If it indicates that there is any intercooling, the table of data is checked to see if there is any cooling just above or on plate m. If data have been given as a change in temperature of stream L_{m+1}, $t_{L_{m+1}}$ is increased by $\Delta t_{L_{m+1}}$ and $\underline{H}_{L_{m+1}}$ and $H_{L_{m+1}}$ are recomputed at the higher temperature. If the cooling has been expressed as a change of enthalpy, $H_{L_{m+1}}$ is increased and $\underline{H}_{L_{m+1}}$ and $t_{L_{m+1}}$ are revised. The heat flux, δq_m, is recalculated.

The plate calculation is now complete, and the machine prepares to continue with the next plate. The heat flux, δq_m, is moved to δq_{m-1}, the complete properties of stream L_{m+1} are moved to those of L_m, the properties of V_m are moved to those of V_{m-1}, and the plate counter is advanced by 1.

The plate counter is examined to see if the top plate has been reached. If not, the plate calculation is repeated; if so, the machine inquires about convergence of the mass balance, taking each component in order. The quantity δs_i is examined. If it is identically zero, the component is not present in the column. If it is positive, indicating a heavy component whose net flow is downward, the ratio $(\ell_{n+1,i}/\ell_{m+1,i})$ will be examined; if it is negative, indicating a light component with net flow upward, the ratio $(v_{n,i}/v_{m,i})$ will be used. For illustration, we assume the latter case. The quantity $v_{m,i}$ is first examined. If it is negative, the machine concludes that too little of component i has been assumed in the rich oil and sets the correction ratio r_i equal to the upper limit of all correction ratios, 10^2. Otherwise, the ratio

$$r_i = \frac{v_{n,i}}{v_{m,i}} \tag{189}$$

is computed. If it is less than the lower limit (including being negative), the lower limit, 10^{-2}, is used instead. A ratio for each component is obtained, and if one or more do not meet the condition

$$0.999 < r_i < 1.001 \tag{190}$$

the mass balance has not converged.

The assumed quantity of each component in the rich oil is revised by the following procedure: The convergence ratios are used in the equation

$$(\ell_{1,i})_{k+1} = (\overline{\ell}_{1,i})_k \, (r_i)_k^{\left(\frac{g_i}{m^2}\right)} \tag{191}$$

where

$(\ell_{1,i})_{k+1}$ is the quantity of component i proposed to be used in the rich oil for the next iteration (k+1)

$(\overline{\ell}_{1,i})_k$ is the quantity of component i in the rich oil used in the iteration just concluded (k)

$(r_i)_k$ is the convergence ratio obtained in the iteration just concluded

g_i, the numerator in the exponent on $(r_i)_k$, is an empirical parameter for each component

m is the highest plate reached during iteration k.

The significance of the bar over $(\ell_{1,i})_k$ is that it denotes a quantity actually used as the input of a plate-to-plate column calculation. Now if k equals 1, the quantity $(\ell_{1,i})_{k+1}$ is used for the next iteration.

$$(\overline{\ell}_{1,i})_2 = (\ell_{1,i})_2 \tag{192}$$

On all succeeding iterations, the Wegstein extrapolation procedure is employed (see Mathematical Analysis),

$$w_i = \frac{(\ell_{1,i})_{k+1} - (\ell_{1,i})_k}{(\bar{\ell}_{1,i})_k - (\bar{\ell}_{1,i})_{k-1}} \tag{193}$$

$$(\bar{\ell}_{1,i})_{k+1} = (\ell_{1,i})_{k+1} + [\frac{w_i}{w_i - 1}][(\bar{\ell}_{1,i})_k - (\ell_{1,i})_{k+1}] \tag{194}$$

and, lest any vagary in the extrapolation produce an unreasonable value, a further condition is imposed:

$$0.9 < \frac{(\bar{\ell}_{1,i})_{k+1}}{(\ell_{1,i})_{k+1}} < 1.1 \tag{195}$$

Revision of the quantities in the rich oil stream occurs whether mass convergence has been reached or not, but the extrapolation is not used on those components for which convergence has been obtained.

If mass convergence has been reached, the criterion of temperature convergence is applied.

$$|t_{L_{n+1}} - (t_{L_{m+1}})_k| < 0.2\,°\text{F} \tag{196}$$

If this requirement is not met, t_{L_1} is adjusted according to the equation

$$(t_{L_1})_{k+1} = (t_{L_1})_k + (2)[\frac{L_{n+1}}{V_0}][\frac{L_{n+1}}{(L_1)_{k+1}}][t_{L_{n+1}} - (t_{L_{m+1}})_k] \tag{197}$$

If mass convergence has not been reached, the assumed temperature t_{L_1} is not changed.

The machine now computes the total quantity of stream L_1, the mole fractions of the various components, enthalpies, the mass flux or δs_i quantities, and the properties of V_n obtainable by overall column material balance. The properties of L_1 are transferred to those of L_m and the properties of the rich gas to those of V_{m-1} in preparation for another column iteration. If the machine has been printing only column summaries on each previous iteration and mass and temperature convergence have been obtained, one more column iteration will *definitely* be made, printing detailed plate results. If one of the other two printout options has been employed and convergence has been obtained, the plate-to-plate phase of the computation is finished. If convergence of both mass and temperature has not been realized, another iteration will be made *conditionally*. The machine dumps the current set of values of r_i, $t_{L_{m+1}}$, and $(\bar{\ell}_{1,i})_{k+1}$ and then gives a column summary unless the option of printing only final results is in effect. If another conditional iteration is to be made, it is made unless the maximum specified number of column iterations has already been made, in which case the machine prints a remark to this effect and proceeds to terminate the plate-to-plate phase. The machine computes the fractional recovery of each component present and then transfers control to Subprogram D.

E. Output

Writing of the output in a convenient, tabular form is the function of Subprogram D. The machine transfers properties of the exit streams to their proper locations, transfers the compositions and temperatures to the locations used for the initial estimate of outlet compositions and temperatures, and changes the computation code flag to indicate that these data are furnished. This transferring of data is done to facilitate the running of a group of similar columns.

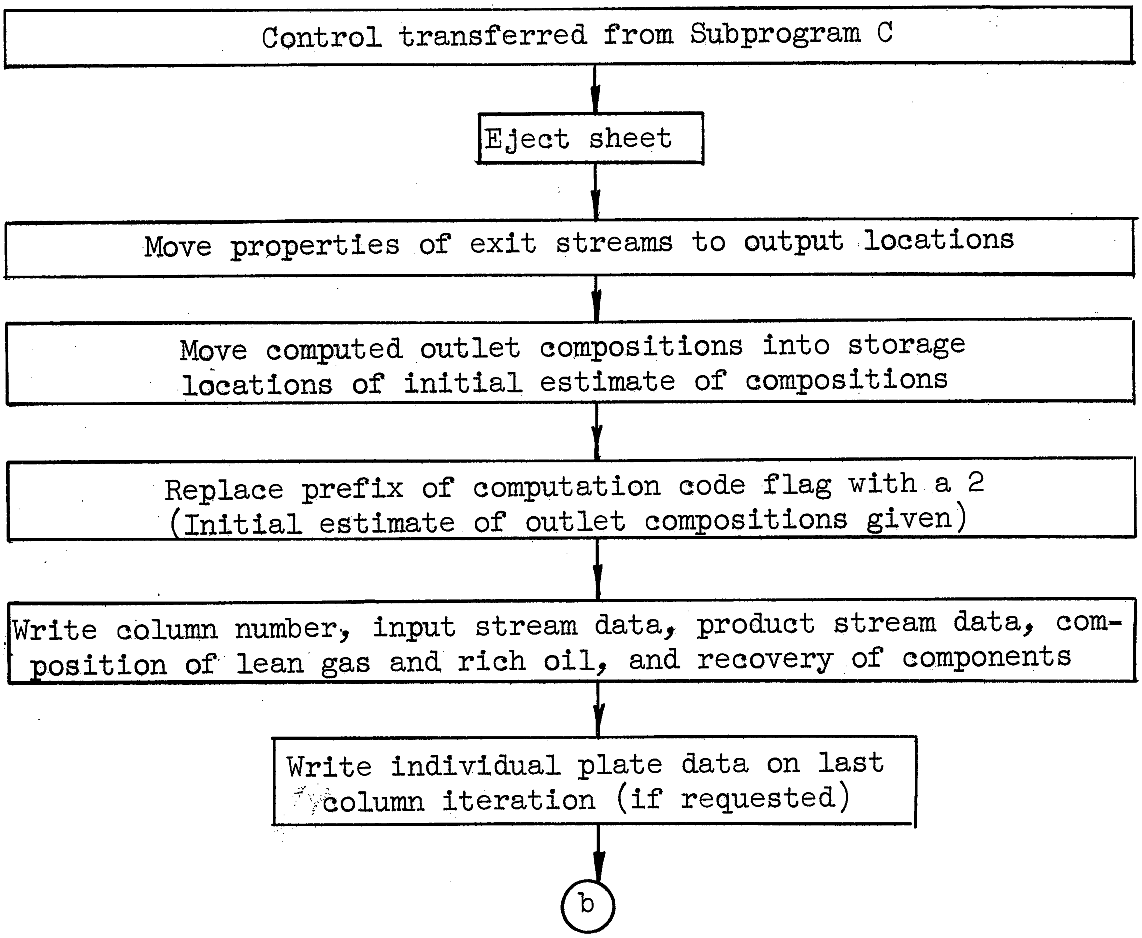


Figure 9. Flow Diagram-Subprogram D.

The machine then writes the results of the column calculation and returns control to Subprogram A for the reading of the next set of column data or K value and absorber oil data.

F. The Liquid Temperature Subroutine

The graph of $\underline{H}_L$ versus t_L is a smooth curve without inflection points. If we imagine that t_L is now a function of $\underline{H}_L$, we can write an extrapolation formula based upon the Newton method. Given a starting value t_k and desiring to find t corresponding to $\underline{H}$, we can write

$$t \approx t_k + \frac{dt}{d\underline{H}} (\underline{H} - \underline{H}_k) \tag{198}$$

Approximating the derivative by the slope of a chord cutting the curve at $t_k - \Delta t$ and $t_k + \Delta t$, the points k-1 and k+1, instead of the tangent at t_k,

$$t \approx t_k + \frac{(2)(\Delta t)(\underline{H} - \underline{H}_k)}{\underline{H}_{k+1} - \underline{H}_{k-1}} \tag{199}$$

We may substitute the point $(\underline{H}_{k-1}, t_k - \Delta t)$ for the point $(\underline{H}_k, t_k)$ and obtain

$$t \approx (t_k - \Delta t) + \frac{(2)(\Delta t)(\underline{H} - \underline{H}_{k-1})}{\underline{H}_{k+1} - \underline{H}_{k-1}} \tag{200}$$

or, in the notation used in the rest of the program,

$$t' = t + (2)(\Delta t)\left[\frac{\underline{H} - \underline{H}_{t-\Delta t}}{\underline{H}_{t+\Delta t} - \underline{H}_{t-\Delta t}} - \frac{1}{2}\right] \tag{201}$$

The liquid temperature subroutine operates in the following way: Given $\underline{H}_L$ and a first approximation to the corresponding temperature, t_L, and required to find the exact temperature t_L, the machine sets Δt

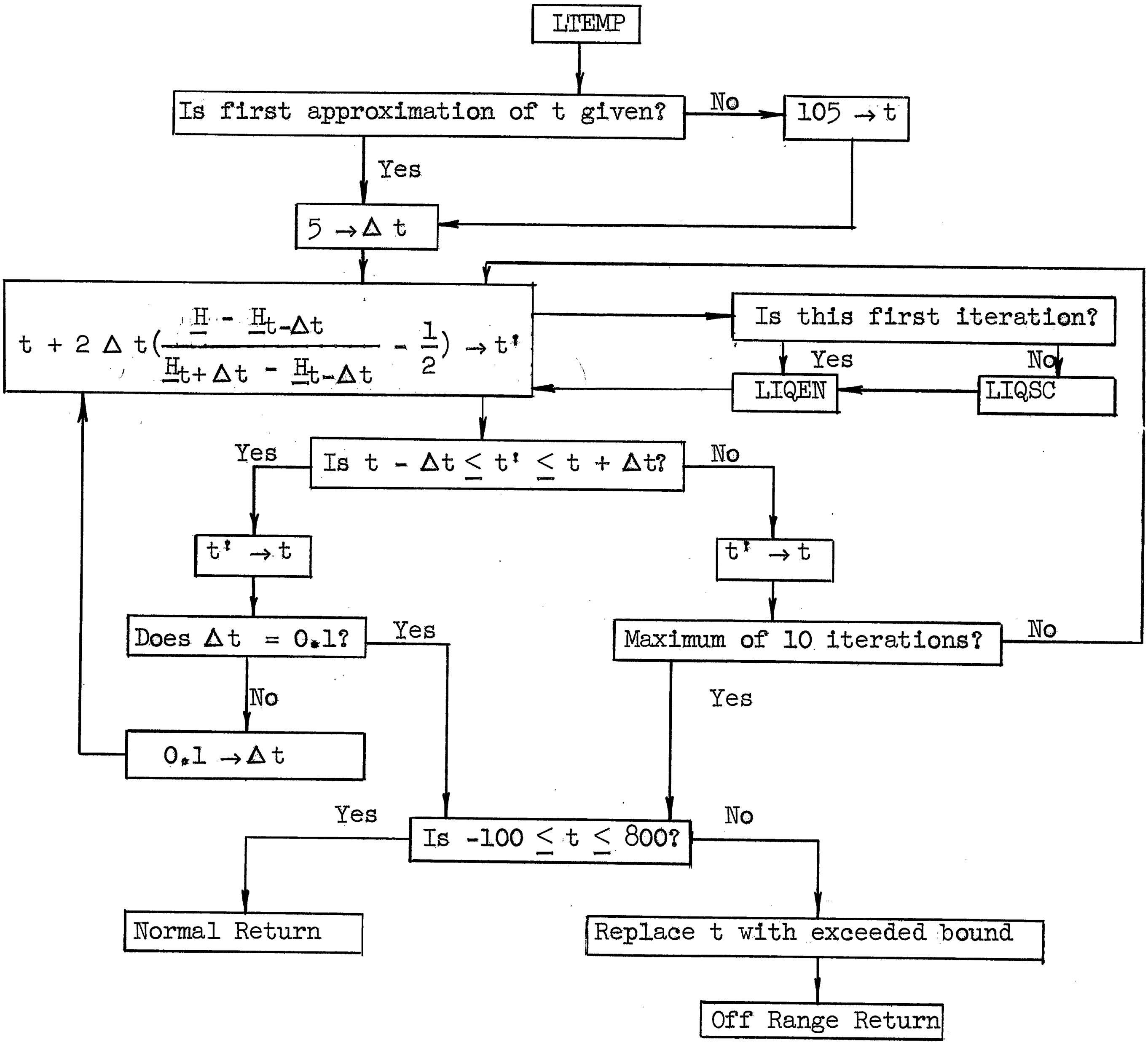


Figure 10. Flow Diagram-Liquid Temperature Subroutine.

equal to 5°F, uses formula (201) to compute a closer approximation, t', and then checks to see if t' lies between $t - \Delta t$ and $t + \Delta t$. If t' does not, t' replaces t and the process is repeated. As soon as a t' does lie within $t \pm \Delta t$, t' replaces t, t is set equal to 0.1°F and the above sequence is repeated until t' is again obtained as an interpolation or until a maximum of ten iteration of the process have been made. This t' is returned as the stream temperature, t_L. If t_L lies outside the range -100°F to 800°F, the off-range return is made.

G. The Dew Point Subroutine

The dew point temperature of a multicomponent mixture is that temperature at which

$$\Sigma_i \frac{y_i}{K_i} = 1 \tag{202}$$

We may therefore define the function

$$f(y_i, t) = \Sigma_i \frac{y_i}{K_i} - 1 = 0 \tag{203}$$

(since K is a function of temperature and composition) and find the value of t which satisfies the equality. (The subroutine actually uses $\Sigma_i y_i$ instead of 1 and ignores negative mole fractions.)

The logic of the dew point subroutine is given in Figure 11. Briefly, the machine uses the method of false position to find the root, t_{dp}. This consists of computing values of the function $f(y_i, t)$ for a series of temperatures (differing by Σt) until two values on either side of zero are found. Linear interpolation is performed to approximate t_{dp}, the interval Δt is shortened from 50°F to 2°F, and the procedure is repeated once more. The result of the second interpolation is taken as the dew point temperature.

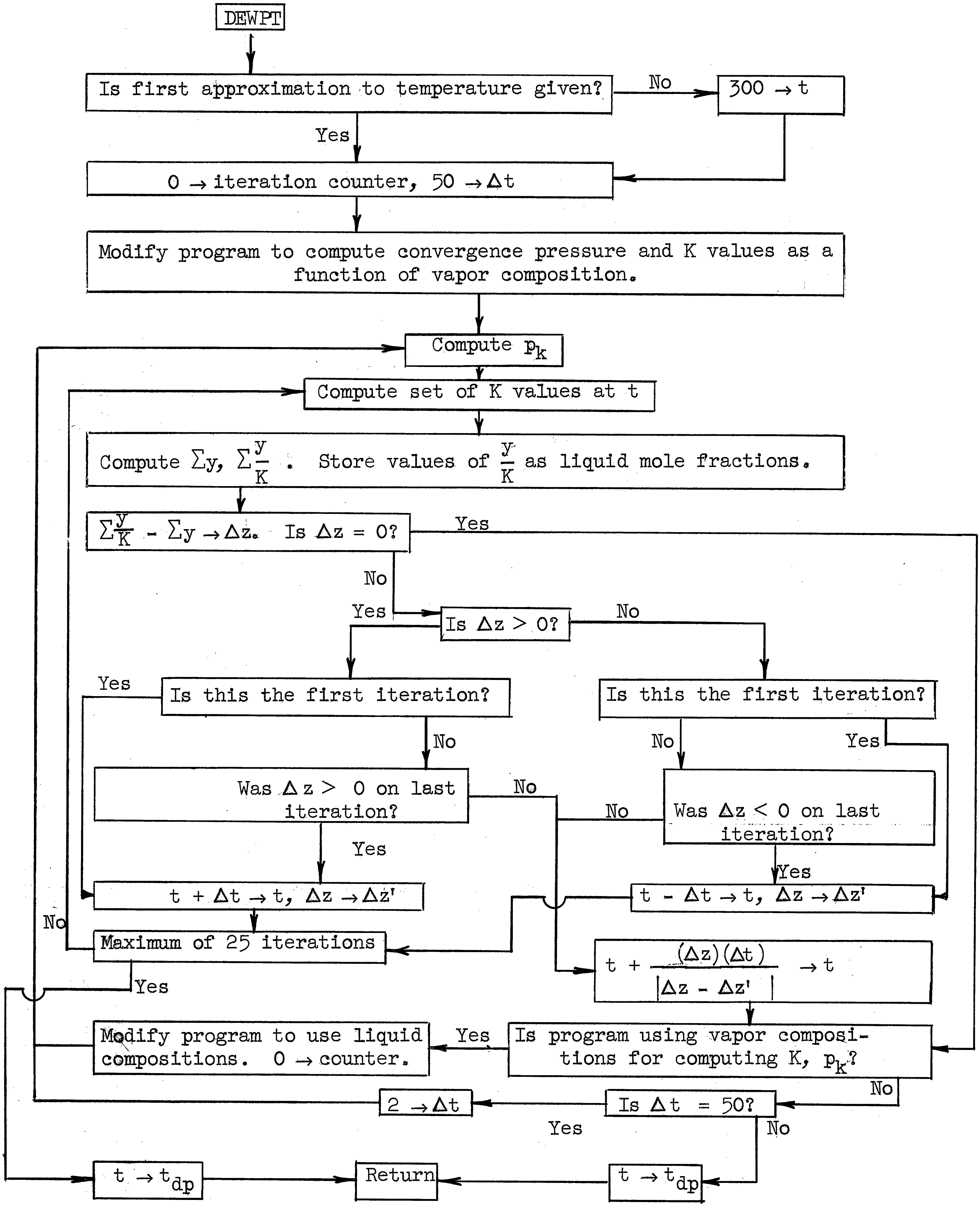


Figure 11. Flow Diagram-Dew Point Subroutine.

VI. MATHEMATICAL ANALYSIS

A. The System of Simultaneous Equations

In company with a great many other chemical engineering calculations, the solution of a multicomponent absorption or distillation problem may be considered as the solution of a set of simultaneous equations. The requirement for the existence of a unique solution is that the number of equations or relationships be equal to the number of variables, and that the equations be linearly independent; in other words, that no one of the equations be a linear combination of any others. The plate-to-plate procedure described here is an example of an iterative solution, exemplified (for a system of linear equations) by the Gauss-Siedel method, as opposed to the direct solution illustrated by the Crout matrix inversion.

The problem of fixing the values of just the right number of variables in order to leave the number of remaining variables exactly equal to the number of equations has been the subject of articles by Gilliland and Reed(40) and lately by Kwauk(64). Using the nomenclature and technique of Kwauk, it will now be shown that the non-ideal stage absorber problem is a completely specified one.

Kwauk has defined an element as "a single stage equipment, such as a flash drum, a total condenser, a theoretical plate, etc." For any element, the number of variables available for process specification, N_a^e, is equal to the total number of variables, N_v^e, minus the number of conditions inherent to the system, N_c^e, minus the number of normally fixed variables, N_x^e.

$$N_a^e = N_v^e - N_c^e - N_x^e \qquad (204)$$

The phase rule states that for one phase or for two or more in equilibrium,

$$N = C + 2 - \Phi \qquad (205)$$

that is, the number of degrees of freedom, N, is equal to the number of independent components, C, plus 2, minus the number of phases, Φ. The degrees of freedom are "intensive" ones, and to them may be added one more, an "extensive" one, the rate of flow. Therefore, either for one phase or for two phases in equilibrium, where the flow rate of either phase may be varied independently, the number of variables is C + 2. In consideration of any element, one may introduce yet one more variable, the heat gain or loss to the surroundings.

Kwauk, in discussing the theoretical plate, states that there are C + 2 variables associated with each of the streams entering the plate, C + 2 with the two equilibrium phases leaving, and one more with the heat transfer aspect, for a total of 3C + 7.

$$N_v^e = (2)(C + 2) + (C + 2) + 1 = 3C + 7 \qquad (206)$$

The inherent conditions are C material balances and one heat balance for all streams, so

$$N_c^e = C + 1 \qquad (207)$$

The normally fixed variables are the compositions and flow rates of the two entering streams, the pressure, and the heat exchange with the surroundings, so

$$N_x^e = (2)(C + 2) + 1 + 1 = 2C + 6 \qquad (208)$$

Therefore,

$$N_a^e = (3C + 7) - (C + 1) - (2C + 6) = 0 \tag{209}$$

and the theoretical plate just described is invariant.

Let us now consider the non-ideal stage. In place of the two equilibrium phases leaving the plate, we now have two which are not in equilibrium and

$$N_v^e = (4)(C + 2) + 1 = 4C + 9 \tag{210}$$

As before, inherent conditions include C material balances and one heat balance, but there are others also. The C + 2 variables associated with a single stream consist of C - 1 compositions, pressure, temperature, and total flow rate, or (equivalently) C component flow rates, pressure, and temperature. The reason that C + 2 variables define a two-phase equilibrium system, even though either stream alone has C + 2 variables associated with it, is that the condition of equilibrium implies C + 2 additional restrictions: C mass transfer equilibrium relations, equal temperatures in both phases, and equal pressures. Returning to the non-ideal stage, we introduce an additional C + 2 inherent conditions: C mass transfer rate or non-equilibrium relations, a heat transfer equation relating temperatures in the two phases, and again the requirement that pressures in the two phases be equal. Therefore,

$$N_c^e = (C + 1) + (C + 2) = 2C + 3 \tag{211}$$

As before,

$$N_x^e = 2C + 6 \tag{212}$$

and so the single non-ideal stage is also an invariant system.

$$N_a^e = (4C + 9) - (2C + 3) - (2C + 6) = 0 \tag{213}$$

Proceeding now with Kwauk's analysis of a multiplate contactor, we note that the total number of variables associated with a system of n elements is 1 (for the option of deciding the value of n) plus n times the number of independent variables associated with each element. Now

$$N_i^e = N_v^e - N_c^e = (4C + 9) - (2C + 3) = 2C + 6 \qquad (214)$$

and so

$$N_v^E = 1 + (n)(2C + 6) = 2nC + 6n + 1 \qquad (215)$$

and the capital E used as a superscript signifies a complex element or system of elements. The inherent conditions are summarized by the notion of interstreams. If plate m is neither the top nor the bottom plate of the column, then the two feed streams to plate m are themselves the product streams of other plates. To avoid double counting of the variables associated with these interstreams, we recognize these restrictions as inherent conditions.

$$N_c^E = (2)(n - 1)(C + 2) = 2nC - 2C + 4n - 4 \qquad (216)$$

The normally fixed variables are the properties of the feed streams, the pressure on each plate (assumed constant throughout the column in our case), the heat transfer with the surroundings on each plate, and the total number of plates.

$$N_x^E = (2)(C + 2) + n + n + 1 = 2C + 2n + 5 \qquad (217)$$

Therefore,

$$N_a^E = (2nC + 6n + 1) - (2nC - 2C + 4n - 4) - (2C + 2n + 5) = 0 \qquad (218)$$

and the non-ideal stage absorber is proved to be invariant or completely specified.

B. The Iterative Solution

The set of equations characterizing conditions in an absorber may be thought of as a system of n non-linear equations in the variables x_1 through x_n with x_j the general variable. The equations 1 through n may be solved for variables 1 through n respectively to give another set of equations

$$x_j = f_j(x_1, x_2, \ldots, x_n) \qquad (j = 1, 2, \ldots, n) \tag{219}$$

Two general methods exist for the iterative solution of this set of equations--the total step and the single step. In the total step procedure, when k is any iteration,

$$(x_j)_{k+1} = f_j[(x_1)_k, (x_2)_k, \ldots, (x_n)_k] \tag{220}$$

In the single step procedure,

$$(x_j)_{k+1} = f_j[(x_1)_{k+1}, \ldots, (x_{j-1})_{k+1}, (x_j)_k, \ldots, (x_n)_k] \tag{221}$$

If the set $(x_j)_k$ is considered a vector, then for the total-step procedure,

$$\vec{x}_{k+1} = \vec{T}\, x_k \tag{222}$$

and for the single-step procedure,

$$\vec{x}_{k+1} = T\, (\vec{x}_{k+1}, \vec{x}_k) \tag{223}$$

where "T" means "a transformation of". In the case of linear equations, the above procedures will be recognized as the Jacobi and the Gauss-Siedel methods, respectively.

Collatz$^{(23)}$ has investigated iterative solution of non-linear equations and has developed sufficient conditions for convergence of total- and single-step methods. Let the set of equations (219) have continuous partial derivatives in the region F, and let α_{jr} be the maximum absolute value of the partial derivative of f_j with respect to each of the variables r.

$$\alpha_{jr} = \max_F \left| \frac{\partial f_j}{\partial x_r} \right| \tag{224}$$

These α_{jr} may be considered to form a matrix. Now if

$$k = \max_j \sum_{r=1}^{n} \alpha_{jr} \tag{225}$$

and k is less than 1, the "row sum" criterion is met and the sequence (220) or (221) will be a convergent one. If

$$k = \max_r \sum_{j=1}^{n} \alpha_{jr} \tag{226}$$

and k is less than 1, the "column sum" criterion is met and the sequence likewise converges.

One further criterion, and the most important for our purposes, applies only to single-step procedures. Let

$$\beta_1 = \sum_{s=1}^{n} \alpha_{1s} \tag{227}$$

and

$$\beta_j = \sum_{s=1}^{j-1} \alpha_{js}\beta_s + \sum_{s=j}^{n} \alpha_{js} \tag{228}$$

Now if k is the maximum value of β_j and is less than 1, the single-step procedure is convergent.

Unfortunately, the proofs given by Collatz cannot be applied directly to the absorber problem because the condition of continuous partial derivatives cannot be met. The region F must include all possible values taken on by the variables during the iterative solution, not just the ones which may be expected in operation of the equipment. Two of the most frequent sources of discontinuity in the partial derivatives are negative quantities of certain components (which may cause a total stream to become negative and thus abruptly reverse the signs of all mole fractions) and the exceeding of bounds in the correlations of various physical properties.

Examination of Equations (224) through (228) will produce some valuable principles even though the equations themselves may not be applicable. First, the set of equations should be arranged so that all the partial derivatives are as small as possible. (The equivalent statement in the case of a set of linear equations is that one should order the equations to produce a large main diagonal in the matrix of coefficients.) Secondly, if one has equations with large α_{jr}, he should put them toward the end of the list, so that as many of the α_{jr} as possible may be multiplied by β_j less than 1. Further, if one has equations which involve only a few of the variables, they should be placed in the list in such a way that as many as possible of the α_{jr} fall below the main diagonal of the matrix of α_{jr}.

The "natural" sequence of equations used in a plate-to-plate calculation will usually satisfy the second and third principles. One usually does not have machine storage enough to store two sets of values for each of the variables involved, and so one begins at one end of the column and proceeds from one plate to the next, using values calculated on plate m as a basis for the evaluation of the variables on plate m+1, etc.

C. Experience with the Iterative Solution

As explained previously, the iterative solution of the absorption column is carried out by (1) assuming the properties of the rich oil stream, L_1, (2) performing a plate-to-plate calculation upward through the column until the stream V_m corresponding to the lean gas, V_n, is reached, (3) calculating the properties of V_n by overall material and energy balance with L_1, (4) comparing corresponding properties of V_m and V_n, which should ultimately be equal, of course, and (5) on the basis of this comparison, revising the estimate of the properties of L_1.

The most mathematically straightforward method of revising the properties of L_1 would be by material and energy balance with V_m. For example,

$$(\ell_{1,i})_{k+1} = v_{0,i} + \ell_{n+1,i} - (v_{m,i})_k \tag{229}$$

This method has been found to be grossly unstable for the lighter components. For nitrogen in a typical column, ℓ_1 might be on the order of 0.0008 moles/sec and v_m about 0.21 moles/sec. A small percentage change of ℓ_1 might result in only a small percentage change in v_m, but the absolute change of v_m relative to the size of ℓ_1, and hence the partial derivative of v_m with respect to ℓ_1, would be quite large. This "direct substitution" method was found to be unsuitable.

The percentage change of v_m caused by perturbation of ℓ_1 was found to be the key to forcing convergence of the iterative sequence. The revision

$$(\ell_{1,i})_{k+1} = [(\ell_{1,i})_k][\frac{(v_{n,i})_k}{(v_{m,i})_k}] \tag{230}$$

made simultaneously to all components, was successful with a simplified three-plate column. For longer columns, the formula was

$$(\ell_{1,i})_{k+1} = [(\ell_{1,i})_k][\frac{(v_{n,i})_k}{(v_{m,i})_k}]^{(\frac{g_i}{m^2})} \qquad (231)$$

for those components whose net rate of flow was upward (the lighter components) and

$$(\ell_{1,i})_{k+1} = [(\ell_{1,i})_k][\frac{(\ell_{n+1,i})}{(\ell_{m+1,i})_k}]^{(\frac{g_i}{m^2})} \qquad (232)$$

for those whose net flow was downward (the heavier components). This choice resulted in the more stable of the two possible ratios being used, i.e., the one involving larger numbers. The divisor in the exponent, m^2, was chosen in order to produce a greater correction in the first few iterations, when the calculation proceeded only part-way up the column.

The parameters g_i in the exponents were determined experimentally, and the following set was found to be satisfactory for all problems run: 0.2 for the non-hydrocarbon gases and methane, 0.5 for hexane through decane, and 1.0 for ethylene through n-pentane and the absorber oils.

At this point, a procedure had been developed which was stable and convergent but quite slow. A thousand iterations might have been required for the solution of a difficult problem, and the need for some method of speeding convergence was evident.

D. The Aitken "Delta-Squared" Method

Aitken's Δ^2 method has been adequately discussed elsewhere(49,56), and so no detailed description of it will be given here. If one has a convergent function in one variable

$$x_{k+1} = f(x_k) \tag{233}$$

and the sequence of approximations x_{k-1}, x_k, x_{k+1} to the root x, then rather than use the value x_{k+1} as the argument for the next iteration, one may speed up the convergence by using an extrapolated value $\bar{x}_{k+1}$ defined

$$\bar{x}_{k+1} = \frac{(x_{k+1})(x_{k-1}) - (x_k)^2}{x_{k+1} - (2)(x_k) + x_{k-1}} = x_{k+1} - \frac{(x_{k+1} - x_k)^2}{x_{k+1} - (2)(x_k) + x_{k-1}}$$

$$= x_{k+1} - \frac{(\Delta x_k)^2}{\Delta^2 x_{k-1}} \tag{234}$$

The extrapolation may be applied every other iteration to give the sequence $\bar{x}_{k-3}$, x_{k-2}, $\bar{x}_{k-1}$, x_k, $\bar{x}_{k+1}$, ..., the bar indicating an argument obtained by extrapolation.

It was found that the Δ^2 process could be applied to each of the sequences of values of $\ell_{1,i}$ in spite of the fact that a system of simultaneous equations was involved, provided that certain precautions were taken. The use of the extrapolation on all $\ell_{1,i}$ at once would cause a disruption of the slow, smooth convergence, and certain of the $\ell_{1,i}$ would begin an accelerating approach to the final values. It was found necessary to delay the next application of the Δ^2 method to any of the variables until the acceleration had ceased for all, and then apply the extrapolation once more to all the variables at once. Eight or ten iterations usually occurred between applications of the Δ^2 method, and so it was not particularly useful even though it did speed up convergence somewhat.

The difficulty encountered with an increasing absolute value of the first difference of the sequence of $\ell_{1,i}$ can be readily understood from an examination of the "symmetrical" form of Equation (234). The quantities x_{k-1} and x_{k+1} are interchangeable, and the extrapolation is made in the direction of decreasing absolute value of the first difference.

E. Wegstein's Method

Recently, Wegstein(92) described a technique which, when applied to an iterative procedure, accelerates the rate of convergence if the iteration converges and very frequently results in convergence of otherwise divergent iterations.

Suppose that we have the iterative sequence

$$x_{k+1} = f(x_k) \tag{233}$$

and that

$$-1 < f'(x) < 0 \tag{235}$$

in the vicinity of the root, causing convergence in an oscillating manner. In order to change the rate of convergence, the successive values of x_k must be changed. We denote this by

$$\bar{x}_{k+1} = (q)(x_k) + (1 - q)(x_{k+1}) \tag{236}$$

where

x_k is the argument used in iteration k+1

x_{k+1} is the value of $f(x_k)$ produced by that iteration

$\bar{x}_{k+1}$ is the value to replace x_{k+1} as the argument of iteration k+2

q is determined anew for each iteration.

Let the convergence be as shown in Figure 12.

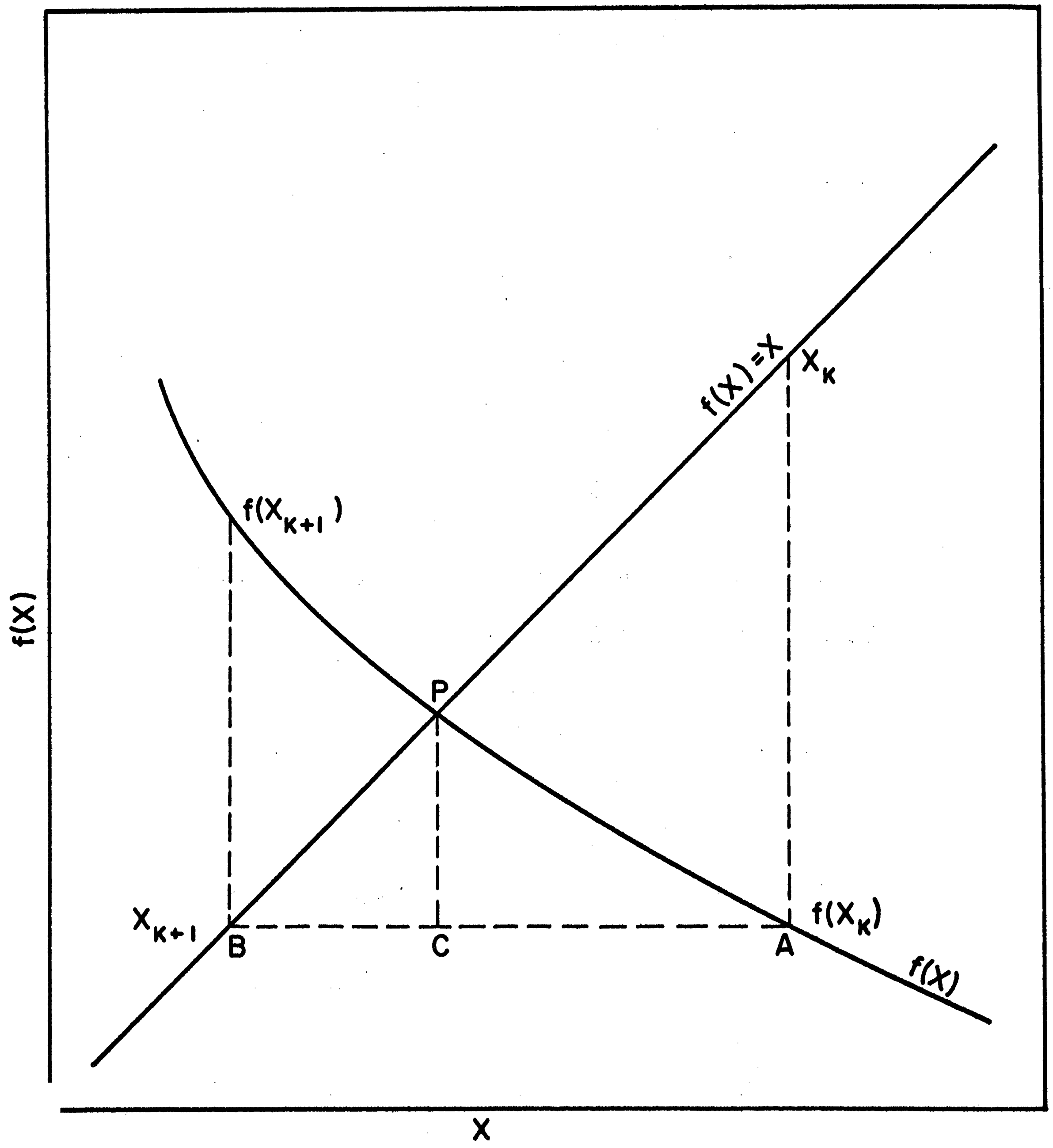


Figure 12. The Wegstein Method

The ideal value of q is such that $\bar{x}_{k+1}$ would equal the abscissa of point C; i.e., we would like to have

$$\frac{q}{1 - q} = \frac{\overline{BC}}{\overline{CA}} \tag{237}$$

To get an approximation to q, we note that $\overline{PC} = \overline{BC}$ and $\overline{PC}/\overline{CA} = - w$, where, by the Mean Value theorem, w is the value of f'(x) at some point between P and A. Thus

$$\frac{q}{1 - q} = - w \tag{238}$$

and

$$q = \frac{w}{w - 1} \tag{239}$$

Since a more convenient method is lacking, w can be approximated by a suitable difference quotient

$$w = \frac{f(x_k) - f(x_{k-1})}{x_k - x_{k-1}} = \frac{x_{k+1} - x_k}{x_k - x_{k-1}} \tag{240}$$

At this point, the method is equivalent to the Aitken Δ^2 method, which may easily be proved. Beginning with Equations (236) and (239),

$$\bar{x}_{k+1} = \left(\frac{w}{w - 1}\right)(x_k) + \left(\frac{-1}{w - 1}\right)(x_{k+1}) \tag{241}$$

$$\bar{x}_{k+1} = \frac{(x_{k+1} - x_k)(x_k - x_{k-1})(x_k)}{(x_k - x_{k-1})(x_{k+1} - x_k - x_k + x_{k-1})} - \frac{(x_k - x_{k-1})(x_{k+1})}{(x_{k+1} - x_k - x_k + x_{k-1})} =$$

$$\frac{(x_{k+1} - x_k)(x_k)}{\Delta^2 x_{k-1}} - \frac{(x_k - x_{k-1})(x_{k+1})}{\Delta^2 x_{k-1}} = \frac{(x_{k+1})(x_{k-1}) - (x_k)^2}{\Delta^2 x_{k-1}}$$

(242)

A variation of Equations (236) and (240) results in the Wegstein method.

$$\bar{x}_{k+1} = (q)(\bar{x}_k) + (1 - q)(x_{k+1}) \tag{243}$$

$$w = \frac{x_{k+1} - x_k}{\bar{x}_k - \bar{x}_{k-1}} \tag{244}$$

Whereas the Δ^2 procedure may be used (at most) every other iteration, we now have a procedure which may be used every iteration after the first. (On the second iteration, it is equivalent to the Δ^2 method.) Its increased utility may be rationalized from this fact and also from the fact that the Wegstein method produces an extrapolation based on four previous values, rather than three.

The Wegstein procedure was applied independently to each sequence ..., $(\ell_{1,i})_{k-1}$, $(\ell_{1,i})_k$, $(\ell_{1,i})_{k+1}$, ... for each component i and was found to accelerate convergence by a factor of 15 or 20 over the basic, slowly convergent sequence. The greatest improvement occurred during the initial phases, when the values of $\ell_{1,i}$ were relatively distant from their converged values. In order to avoid difficulties caused by round-off error in the calculation of very small second differences, (1) the successive values of $\ell_{1,i}$ were required to satisfy the condition

$$0.9 < \frac{(\bar{\ell}_{1,i})_{k+1}}{(\ell_{1,i})_{k+1}} < 1.1 \tag{195}$$

and (2) use of the extrapolation method was discontinued for each variable when the error in that variable had been reduced within allowable limits. The success of this very naive use of the extrapolation method on a system of perhaps twelve or fifteen variables can be credited to the fact that the dependence of the variables on one another is quite small, that is,

$$\frac{\partial f_j(x_1, x_2, \ldots, x_n)}{\partial x_r} \ll \frac{\partial f_j(x_1, \ldots, x_n)}{\partial x_j} \quad (j \neq r) \tag{245}$$

VII. RESULTS

Following are results obtained in the investigation of five different columns, the material being arranged in the chronological order of the work. Where pairs of values occur in the tables, the top line is the computed value; the bottom line, the value with which comparison is made, usually the test value. The solid dots on the figures are computed values; the circled points, test results. Various other symbols--short arrows, triangles, dashed lines, and asterisks--occur on the figures. Their significance is explained under Analysis of Results.

On the average, fifty iterations of the column calculation loop were required for the solution of each of the problems. Machine time varied between 45 minutes and an hour.

A. An Ideal Stage Column

During the early stages of the investigation, a test was made to determine if setting E_q and E_{MV} of all components equal to 1.00 would produce a reasonably close approximation of an ideal stage calculation, that is, if the non-ideal stage calculation would reduce to the logical limiting case. Examination of Equation (89) shows, of course, that the calculation will be <u>identically</u> an ideal stage one only if the vapor stream rate does not change.

$$v_m = (y_m)(V_m) = V_{m-1} \, [y_{m-1} + E_{MV} \, (Kx_m - y_{m-1})] \qquad (89)$$

A test problem involving a three-plate ideal stage absorber at 100 psia was devised, and the problem was solved using the ideal stage, IBM 650 program developed by Norman(76). The IBM 704 non-ideal stage program was then modified to use efficiencies of 1.00 and simplified correlations of enthalpies and K values in order to approximate the correlations used in the Norman program insofar as was convenient. A comparison of the results is given in Table 10.

B. Column A

The Phillips Petroleum Company donated a set of test data for a 20-plate, bubble cap column operating at 232 psia. Plate detail drawings indicated that the column diameter was 6.0 ft, plate spacing 27 in., length of the liquid path 3.39 ft, and fractional cross-section for vapor flow 0.768. The column was assumed to operate adiabatically. The "mineral seal oil" fraction had a molecular weight of 223.

A comparison of machine computation results with the test data is given in Tables 11 and 12, and in Figure 13. Computed plate efficiencies appear in Figure 14. The values of y_0 upon which the machine calculation was based appear in Table 11. Reference to Figure 13 will show that in some cases they are not the same as any of the test analysis points. Apparently these values of y_0 were chosen as representing average values or most reliable estimates. The mole fractions of nitrogen, methane, and ethane in the rich oil appearing as test data were actually values calculated by the Phillips people. They assumed that (1) the rich oil was a bubble point liquid and (2) the ratios $(y^*_{1,CH_4}/y^*_{1,N_2})$ and $(y^*_{1,CH_4}/y^*_{1,C_2H_6})$ were the same as the ratios $(y_{0,CH_4}/y_{0,N_2})$ and $(y_{0,CH_4}/y_{0,C_2H_6})$, respectively, i.e., the mole fraction ratios in a vapor stream in equilibrium with the rich oil were equal to those same ratios in the rich gas. If the K values used had been those which the N.G.A.A. data would predict, the mole fractions of nitrogen, methane, and ethane in the rich oil would have been approximately 0.0030, 0.0607, and 0.0298 instead of 0.0014, 0.0458, and 0.0276.

C. Column B

A data set contributed by "X" Petroleum Company (name withheld by request) contained results obtained with a 27-plate, Koch Kaskade-type column operating at 740 psia. Inside diameter was 4.5 ft, plate spacing 26 in., and the Kaskade plates were estimated to give an equivalent liquid path of 4.5 in., weir height of 2.25 in., and a fractional column cross-section for vapor flow of 0.390. The plate efficiency subroutine is intended for bubble cap plates only, but the data set was used because it was one of the few which included compositions of internal streams.

The unit was actually a combined accumulator and absorber, and the properties of the vapor stream entering the absorber were obtained by mass balance around the accumulator. The volumetric flow rate, API gravity, A.S.T.M. distillation, and temperature of the lean oil were furnished, and the composition and temperature of the rich oil. Two components listed as "156 M.W." and "170 M.W." were combined as absorber oil 1. The "absorption oil" fraction of the lean oil, designated absorber oil 2, was estimated to have a molecular weight of 210; the entire lean oil, a molecular weight of 190. (The lean oil had a 10% - 90% slope of 1.2°F per percent, volumetric average boiling point of 483°F, and gravity of 41.3°API. The 80% - 98% fraction distilled between 513°F and 609°F, and its gravity was 39.5°API.) With these estimates, the remaining properties of the lean oil and the rich oil were calculated by overall column material balance.

Results of the initial Column B run are given in Tables 13 and 14 and Figures 15 and 16. Significance of the short arrows in Figure 15 and the small triangles in Figure 16 will be explained under Analysis of Results.

When it became apparent that the estimate of lean oil composition had contained excessive amounts of certain of the rich gas components (n-butane through hexane), another run was made using a well-stripped lean oil. This lean oil contained only 0.001 mole fraction of hexane and heptane. Results are given in Tables 15 and 16 and Figure 17.

Since Column B operated at the highest temperatures of any of the columns investigated, a third run was made to demonstrate the effect of an intercooler. The intercooler was placed above the 10th plate (just above the hottest part of the column) and produced a 10°F temperature change. Results are presented in Tables 17 and 18 and Figure 17. In Table 17, the comparison is of the machine-computed results with and without the intercooler. Because of machine time limitations, computation was discontinued at a point where mass balance convergence had been obtained for an assumed rich oil temperature which was still a bit too high. The computed lean oil temperature was 1.57°F above the given value, and it was known from previous experience with this column that lowering the assumed rich oil temperature by about half this amount would lower the lean oil temperature by the required 1.57°F and the temperatures of intermediate streams proportionately. The original results are found in Table 18, but the revised temperatures are plotted in Figure 17 in the interest of presenting an orderly picture.

D. Column C

A set of test data was obtained through the courtesy of the N.G.A.A. Absorption Committee. The 30-plate, bubble cap column operated at 1475 psia, the highest pressure investigated. Column diameter was 5.5 ft, plate spacing 2.0 ft, length of liquid path 3.0 ft, and weir height 3.0 in. Heat loss by convection and radiation was estimated to be 60 Btu/ft^2 hr. Molecular weight of the absorber oil component was estimated to be 207 (molecular weight of the total lean oil stream was given as 205).

A rather severe degree of instability was experienced in the machine computation, showing up most strongly in the various quantities of carbon dioxide. It is probable that this component did not cause the instability, but merely reflected it in the greatest degree because of its high volatility and low concentrations. The program was modified to omit application of the Wegstein extrapolation to carbon dioxide, and the calculation then converged slowly and with no further difficulty. Results are given in Tables 19 and 20 and Figure 18.

E. Column D

An absorber data set designated as Unit 3 of the N.G.A.A. Low Pressure Data was investigated in an attempt to predict the value of C_q, the empirical constant in the heat transfer efficiency equation. (This aspect will be discussed under Analysis of Results.) The column operated at 400 psia, was 5.0 ft in diameter, had plate spacing of 2.0 ft, liquid path of 2.917 ft, weir height of 1-7/8 in., and a fractional cross-section for vapor flow of 0.687. Molecular weight of the absorber oil was 207, and this was the only column investigated whose lean oil consisted entirely of the absorber oil component. The original data set specified 0.012 mole fraction of air in the rich gas and 0.013 in the lean gas. This small amount was eliminated in the interest of expediting convergence of the iterative calculation, and the remaining mole fractions were normalized. Results are given in Tables 21 and 22 and Figure 19.

TABLE 10

RESULTS FOR AN IDEAL STAGE COLUMN

Property	Rich Gas	Plate 1	Plate 2	Plate 3	Lean Oil
V_m (moles/sec)	0.6000	0.5911	0.5855	0.5683	--
	0.6000	0.5902	0.5846	0.5670	--
L_m (moles/sec)	--	0.1517	0.1428	0.1372	0.1200
	--	0.1530	0.1433	0.1376	0.1200
t_m (°F)	80.00	101.19	103.36	100.49	90.00
	80.00	101.20	103.39	100.88	90.00
y_m (methane)	0.9000	0.9131	0.9216	0.9413	--
	0.9000	0.9143	0.9230	0.9435	--
(n-butane)	0.0900	0.0851	0.0774	0.0577	--
	0.0900	0.0842	0.0761	0.0557	--
(heptane)	0.0100	0.0018	0.0010	0.0009	--
	0.0100	0.0013	0.0007	0.0007	--
(abs. oil)	-0-	10^{-5}	10^{-5}	10^{-5}	--
	-0-	-0-	-0-	-0-	--
x_m (methane)	--	0.0331	0.0334	0.0340	-0-
	--	0.0329	0.0331	0.0339	-0-
(n-butane)	--	0.1476	0.1308	0.0998	0.0100
	--	0.1541	0.1348	0.1023	0.0100
(heptane)	--	0.0677	0.0373	0.0354	0.0400
	--	0.0679	0.0363	0.0349	0.0400
(abs. oil)	--	0.7516	0.7986	0.8308	0.9500
	--	0.7451	0.7958	0.8289	0.9500
L_m/V_m ratio	--	0.2567	0.2438	0.2414	--
	--	0.2598	0.2458	0.2431	--
Bub. Pt. of L_m	--	105.33	106.07	106.76	--
Dew Pt. of V_m	--	101.90	103.80	101.44	--

Fractional recovery of	methane	n-butane	heptane
	0.0093	0.3924	0.9120
	0.0093	0.4145	0.9325

In each pair of values: top line-value by non-ideal stage calculation,
bottom line-value by ideal stage calculation.

TABLE 11

COMPONENT RESULTS FOR COLUMN A

Component	y_0	x_{n+1}	y_n	x_1	Rec.	Avg. E_{MV}
Nitrogen	0.1540	0	0.1604	0.0030	0.0037	0.0012
	0.1540	0	0.1615	0.0014*	--	--
Methane	0.7211	0	0.7423	0.0585	0.0157	0.0046
	0.7211	0	0.7434	0.0458*	0.0130	--
Ethane	0.0650	0	0.0622	0.0283	0.0842	0.0214
	0.0650	0	0.0621	0.0276*	0.0853	--
Propane	0.0375	0	0.0289	0.0509	0.2626	0.0562
	0.0375	0	0.0289	0.0510	0.2621	--
Isobutane	0.0045	0	0.0022	0.0123	0.5296	0.0987
	0.0045	0	0.0021	0.0129	0.5532	--
n-Butane	0.0104	0.00011	0.0036	0.0363	0.6729	0.1192
	0.0104	0.00011	0.0016	0.0462	0.8528	--
Pentane	0.0047	0.00251	0.0003	0.0246	0.9339	0.2083
	0.0047	0.00251	0.0004	0.0244	0.9186	--
Hexane +	0.0028	0.00087	0.00001	0.0151	0.9957	0.2810
(Heptane)	0.0028	0.00087	--	0.0152	1.0	--
Abs. Oil	0	0.99651	0.00001	0.7709	--	0.2554
	0	0.99651	--	0.7755	--	--

* Estimated values.

In each pair of values: top line-computed value,
bottom line-test value.

TABLE 12

PLATE RESULTS FOR COLUMN A

Plate	V_m	t_{V_m}	L_m	t_{L_m}	Bub. Pt. L_m	Dew Pt. V_m	E_q	Conv. Pres.
L. Oil	--	--	0.2044	67.00	--	--	--	--
	--	--	0.2044	67.00	--	--	--	--
20	1.3068	74.19	0.2095	68.87	995.85	77.42	0.1338	7125.
	1.3094	72.00	--	--	--	--	--	--
19	1.3119	75.01	0.2148	70.44	791.71	77.24	0.1453	7576.
18	1.3172	75.79	0.2196	71.85	597.37	77.66	0.1571	7564.
	--	--	--	76.00	--	--	--	--
17	1.3220	76.52	0.2240	73.18	404.85	78.06	0.1684	7561.
16	1.3264	77.20	0.2280	74.40	251.41	78.41	0.1793	7552.
15	1.3304	77.81	0.2315	75.51	189.59	78.70	0.1897	7545.
14	1.3339	78.35	0.2347	76.50	156.40	78.91	0.1996	7537.
	--	--	--	80.00	--	--	--	--
13	1.3371	78.81	0.2375	77.39	135.71	79.03	0.2089	7530.
12	1.3399	79.18	0.2401	78.18	121.85	79.05	0.2177	7521.
11	1.3425	79.46	0.2424	79.14	112.20	78.93	0.2260	7516.
10	1.3448	79.56	0.2445	79.70	105.33	78.53	0.2337	7507.
	--	--	--	80.00	--	--	--	--
9	1.3469	79.52	0.2464	80.14	100.37	77.89	0.2411	7498.
8	1.3488	79.32	0.2483	80.47	96.77	77.96	0.2484	7488.
7	1.3507	78.93	0.2501	80.67	94.14	76.76	0.2557	7476.
6	1.3525	78.34	0.2520	80.74	92.24	75.06	0.2632	7464.
5	1.3544	77.48	0.2539	80.64	90.88	72.68	0.2712	7448.
4	1.3563	76.30	0.2560	80.77	90.00	69.37	0.2798	7433.
	--	--	--	83.00	--	--	--	--
3	1.3584	74.56	0.2583	80.28	89.43	64.70	0.2891	7411.

TABLE 12

PLATE RESULTS FOR COLUMN A (CONT'D)

Plate	V_m	tV_m	L_m	tL_m	Bub.Pt. L_m	Dew Pt. V_m	E_q	Conv. Pres.
2	1.3607	72.24	0.2610	79.48	89.10	57.81	0.2998	7383.
	--	--	--	83.00	--	--	--	--
1	1.3634	69.14	0.2642	78.26	88.97	48.64	0.3124	7347.
	--	--	0.2627	80.00	--	--	--	--
R.Gas	1.3666	65.00	--	--	--	--	--	--
	1.3666	65.00	--	--	--	--	--	--

In each pair of values: top line-computed value,
bottom line-test value.

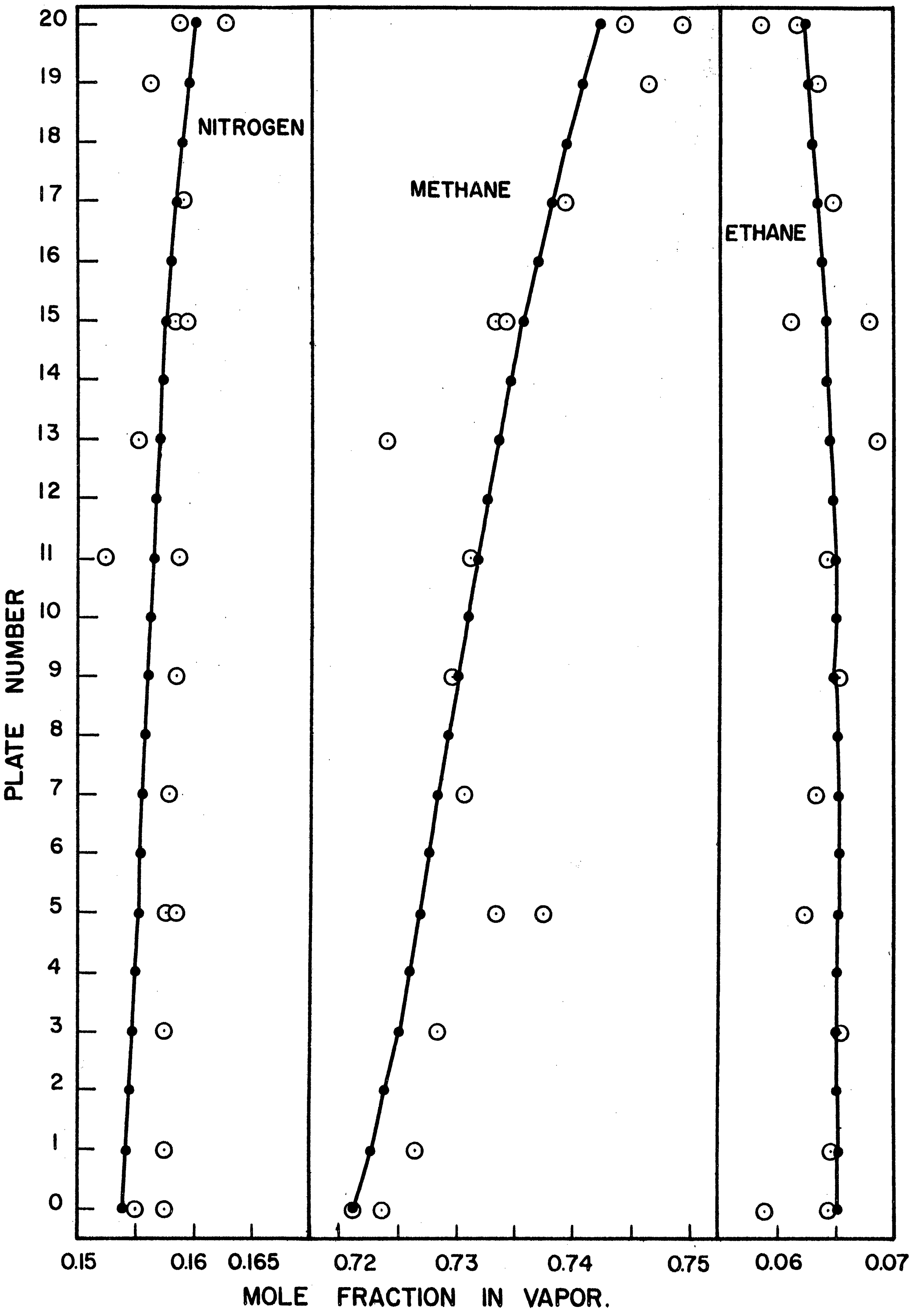


Figure 13-a. Results for Column A

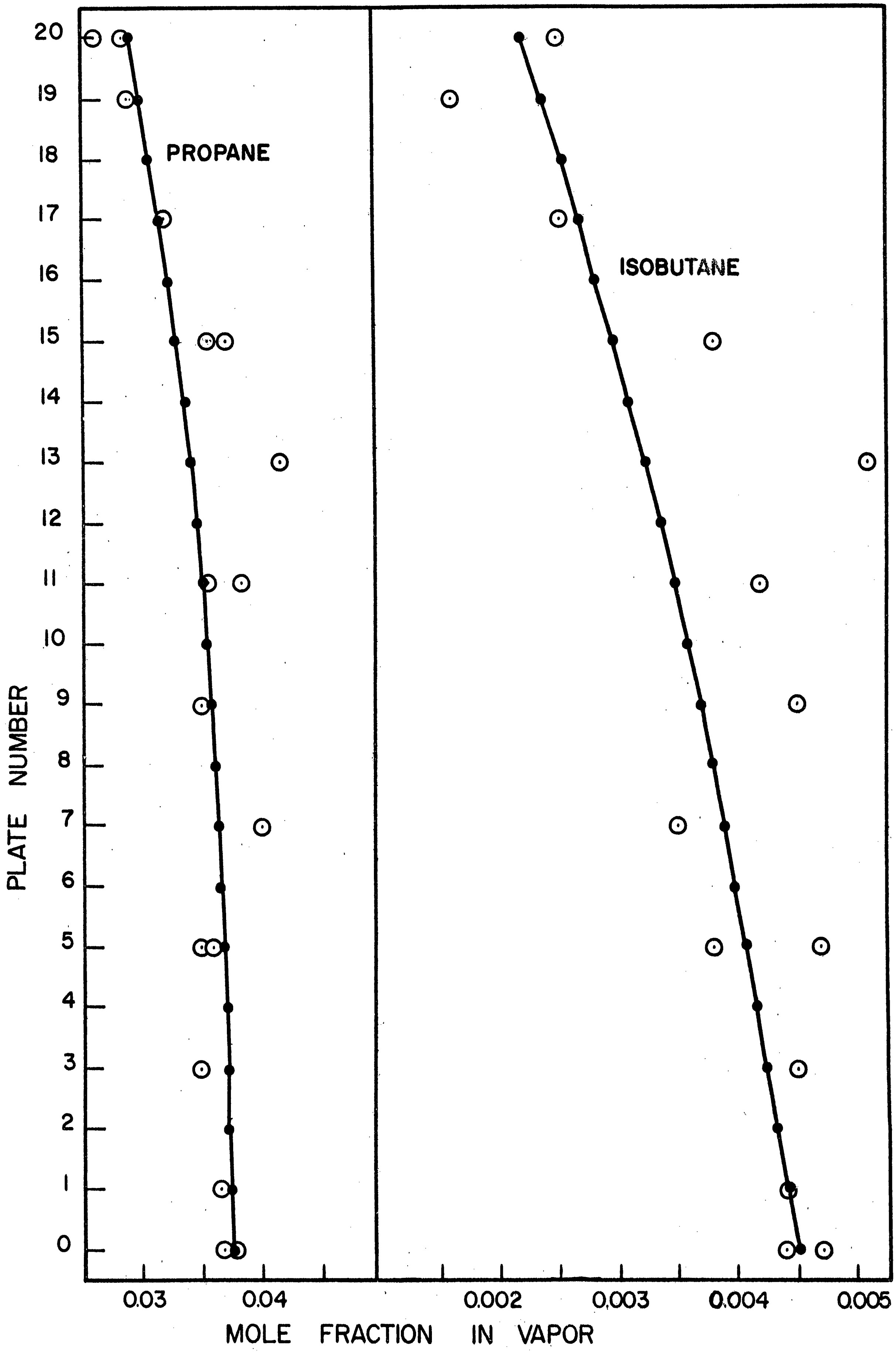


Figure 13-b. Results for Column A

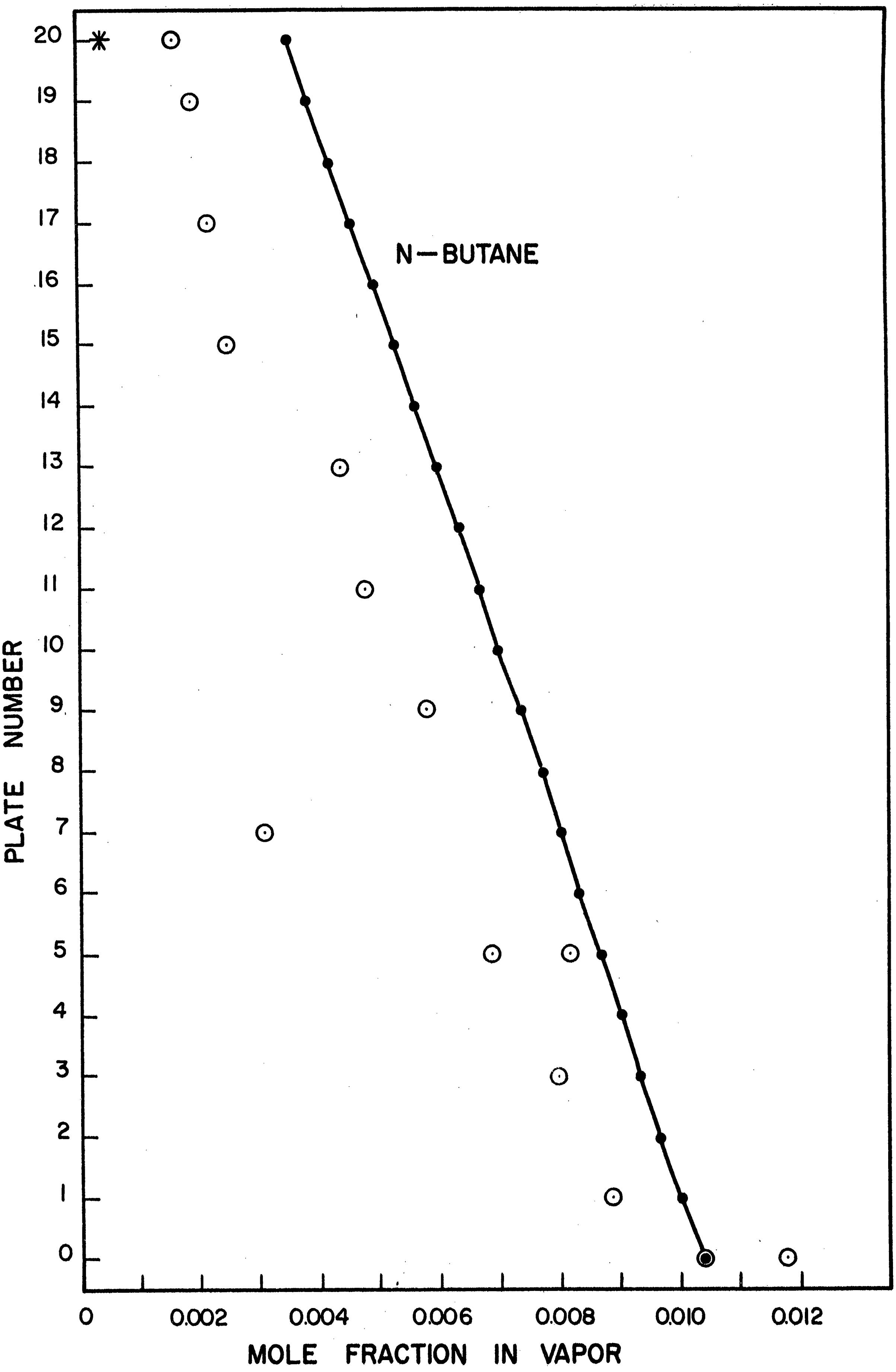


Figure 13-c. Results for Column A

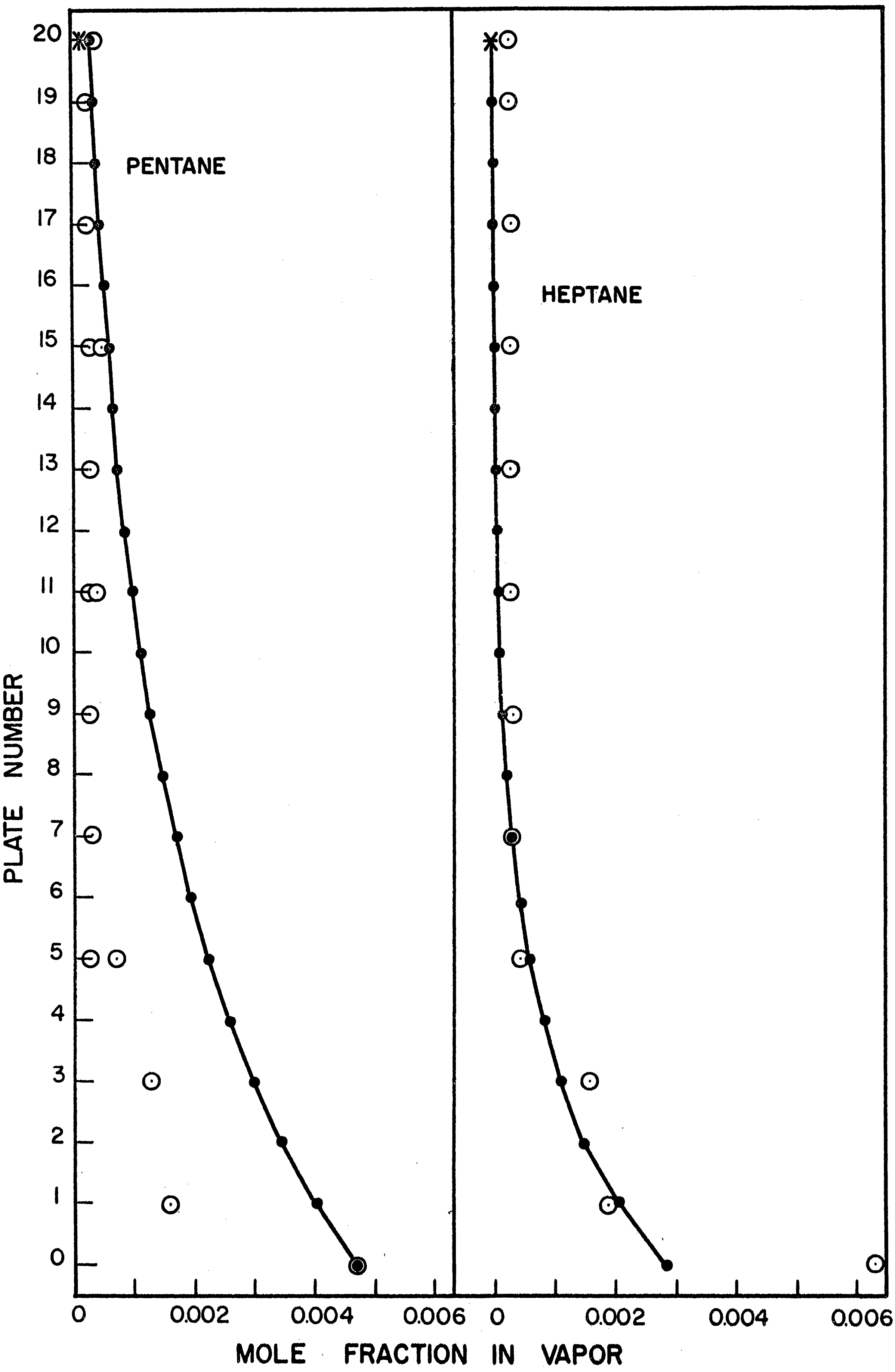


Figure 13-d. Results for Column A

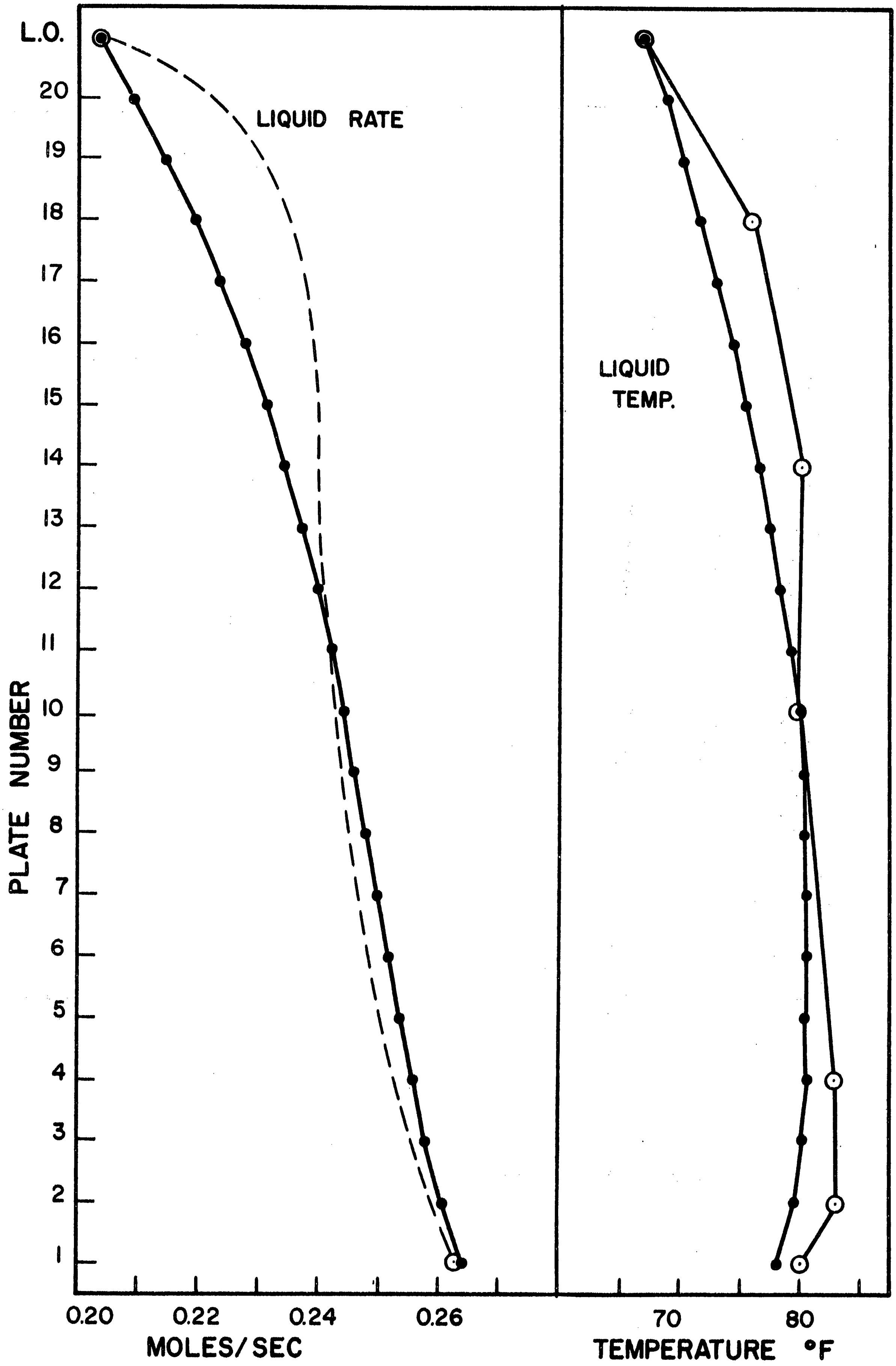


Figure 13-e. Results for Column A

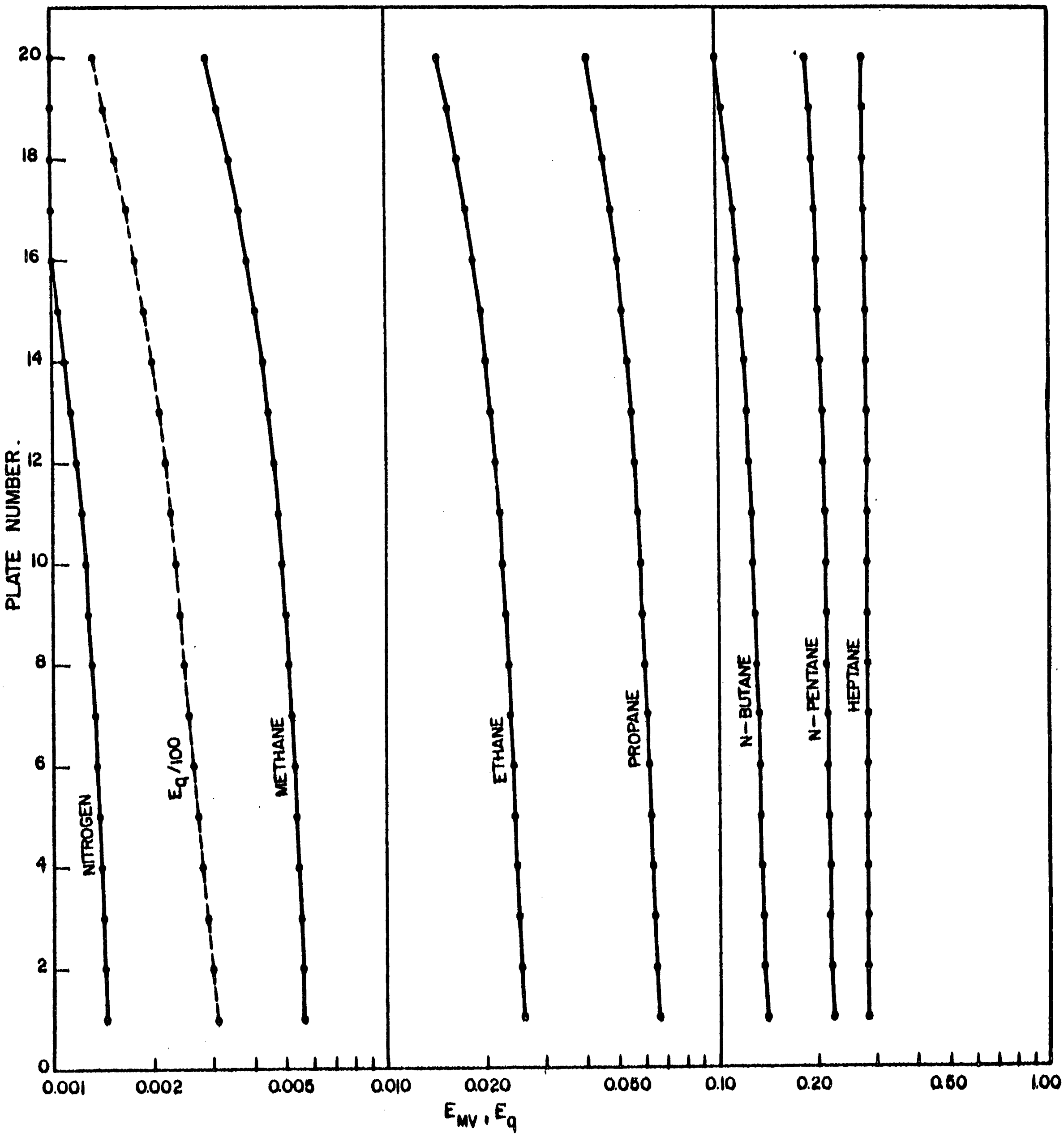


Figure 14. Plate Efficiencies in Column A

TABLE 13

COMPONENT RESULTS FOR COLUMN B

Component	y_0	x_{n+1}	y_n	x_1	Rec.	Avg. E_{MV}
Nitrogen	0.0410	0	0.0466	0.00204	0.0194	0.0030
	0.0410	0	0.0536	--	--	--
Methane	0.8026	0	0.8610	0.15201	0.0739	0.0105
	0.8026	0	0.8915	0.11638	0.0325	--
Ethane	0.0723	0	0.0595	0.05360	0.2894	0.0360
	0.0723	0	0.0442	0.05314	0.4674	--
Propane	0.0597	0	0.0269	0.09352	0.6115	0.0707
	0.0597	0	0.0092	0.08060	0.8654	--
Isobutane	0.0059	0	0.0012	0.01255	0.8302	0.1020
	0.0059	0	0.0007	0.01581	0.9091	--
n-Butane	0.0135	0.0123	0.0033	0.03534	0.7909	0.1187
	0.0135	0.0123	0.0005	0.04400	0.9682	--
Isopentane	0.0016	0.0080	0.0006	0.00784	0.6458	0.1518
	0.0016	0.0080	0.0001	0.00952	0.9333	--
n-Pentane	0.0014	0.0110	0.0007	0.00919	0.5689	0.1637
	0.0014	0.0110	0.0001	0.01124	0.9231	--
Hexane	0.0004	0.0093	0.0002	0.00651	0.4552	0.1921
	0.0004	0.0093	0.0001	0.00743	0.7500	--
Heptane	0.0016	0.0010	0.00002	0.00471	0.9918	0.2070
	0.0016	0.0010	--	0.00057	1	--
Octane	0	0.0017	0.00001	0.00109	--	0.2111
	0	0.0017	--	0.00114	--	--
Nonane	0	0.0169	0.00002	0.01093	--	0.2096
	0	0.0169	--	0.01181	--	--
Decane	0	0.0287	0.00002	0.01860	--	0.2063
	0	0.0287	--	0.02000	--	--
Abs. Oil 1	0	0.1573	0.00007	0.10204	--	0.2009
	0	0.1573	--	0.10838	--	--
Abs. Oil 2	0	0.7538	--	0.49003	--	0.1906
	0	0.7538	--	0.52058	--	--

In each pair of values: top line - computed value,
bottom line - test value.

TABLE 14

PLATE RESULTS FOR COLUMN B

Plate	V_m	tV_m	L_m	tL_m	Bub.Pt. L_m	Dew Pt. V_m	E_q	Conv. Pres.
L.Oil	--	--	0.2365	103.00	--	--	--	--
	--	--	0.2365	103.00	--	--	--	--
27	0.8049	109.12	0.2423	104.33	--	127.81	0.0772	4809.
	0.8121	112.00	--	--	--	--	--	--
26	0.8107	109.52	0.2486	105.17	969.67	119.18	0.0812	6391.
25	0.8170	109.91	0.2547	106.00	909.69	117.50	0.0858	6820.
24	0.8231	110.28	0.2608	106.83	822.22	117.09	0.0907	6910.
	--	--	--	108.00	--	--	--	--
23	0.8291	110.62	0.2666	107.62	708.17	116.94	0.0955	6899.
22	0.8350	110.94	0.2723	108.39	646.17	116.79	0.1003	6888.
21	0.8407	111.22	0.2778	109.11	598.48	116.62	0.1050	6877.
20	0.8462	111.47	0.2832	109.82	555.87	116.44	0.1097	6866.
19	0.8516	111.67	0.2883	110.50	514.75	116.22	0.1143	6855.
18	0.8567	111.82	0.2933	111.14	471.29	115.96	0.1188	6842.
	--	--	--	117.00	--	--	--	--
17	0.8617	111.92	0.2981	111.75	422.18	115.63	0.1232	6831.
16	0.8665	111.94	0.3028	112.31	369.22	115.23	0.1274	6818.
15	0.8712	111.89	0.3073	112.83	319.40	114.73	0.1316	6805.
14	0.8757	111.74	0.3116	113.29	279.89	114.11	0.1356	6792.
13	0.8800	111.50	0.3158	113.71	250.71	113.33	0.1396	6778.
12	0.8842	111.14	0.3199	114.07	229.09	112.36	0.1434	6764.
	--	--	--	118.00	--	--	--	--
11	0.8883	110.65	0.3239	114.36	212.64	111.16	0.1471	6750.
10	0.8923	110.01	0.3278	114.58	199.86	109.66	0.1508	6735.
9	0.8962	109.20	0.3317	114.71	189.70	107.77	0.1544	6719.

TABLE 14

PLATE RESULTS FOR COLUMN B (CONT'D)

Plate	V_m	t_{V_m}	L_m	t_{L_m}	Bub.Pt. L_m	Dew Pt. V_m	E_q	Conv. Pres.
8	0.9001	108.20	0.3355	114.76	181.50	105.40	0.1579	6702.
7	0.9039	106.97	0.3393	114.81	174.84	102.41	0.1611	6685.
6	0.9077	105.46	0.3432	114.62	169.37	98.57	0.1645	6666.
	--	--	--	116.00	--	--	--	--
5	0.9116	103.66	0.3470	114.42	164.86	93.69	0.1676	6647.
4	0.9154	101.49	0.3510	113.93	161.13	87.38	0.1710	6625.
3	0.9194	98.92	0.3551	113.47	158.06	79.63	0.1740	6603.
2	0.9235	95.86	0.3594	112.62	155.55	75.45	0.1772	6577.
1	0.9278	92.25	0.3640	111.53	153.50	69.97	0.1805	6549.
	--	--	0.3568	114.00	--	--	--	--
R.Gas	0.9324	88.00	--	--	--	--	--	--
	0.9324	88.00	--	--	--	--	--	--

In each pair of values: top line - computed value,
bottom line - test value.

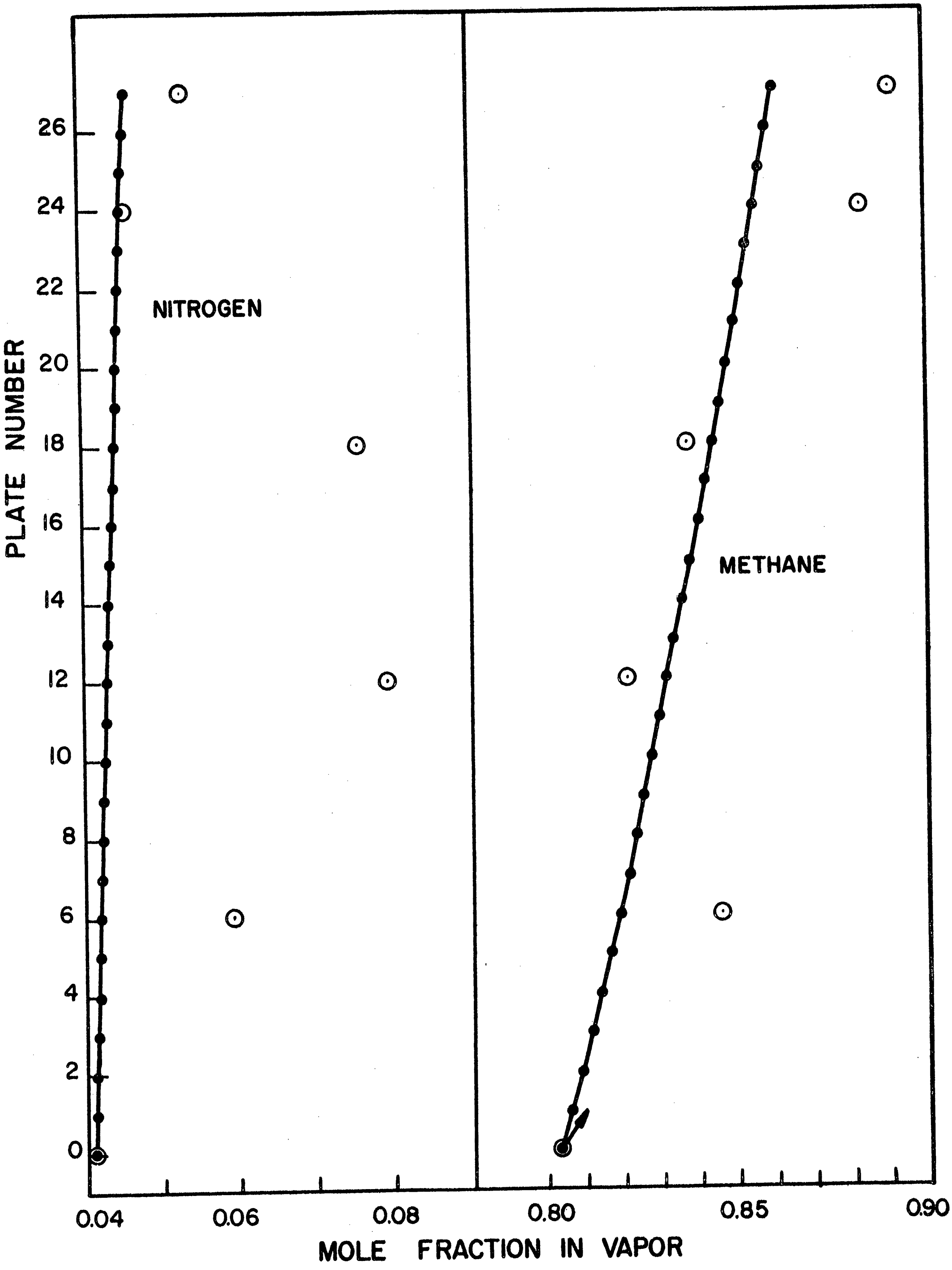


Figure 15-a. Results for Column B

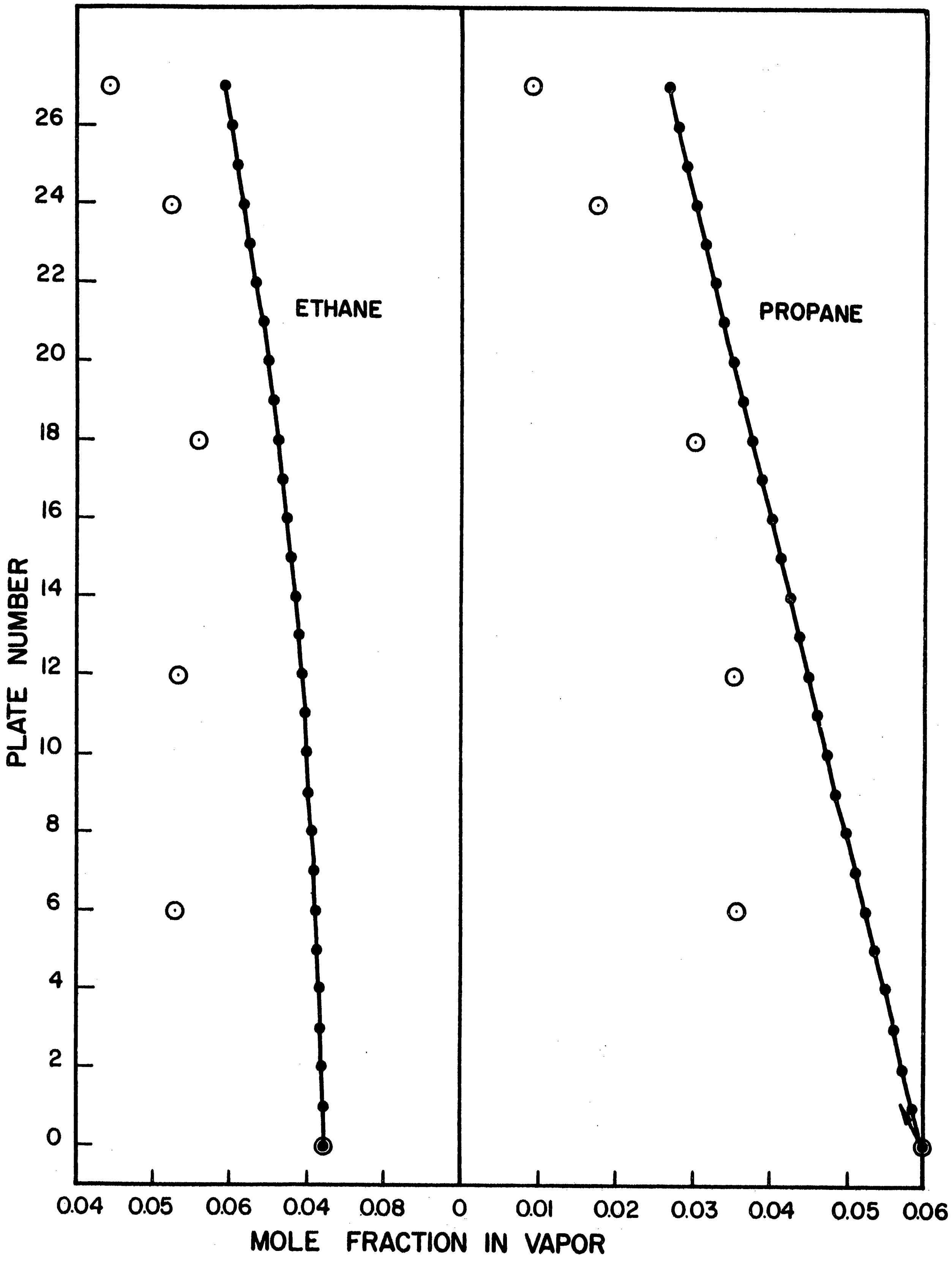


Figure 15-b. Results for Column B

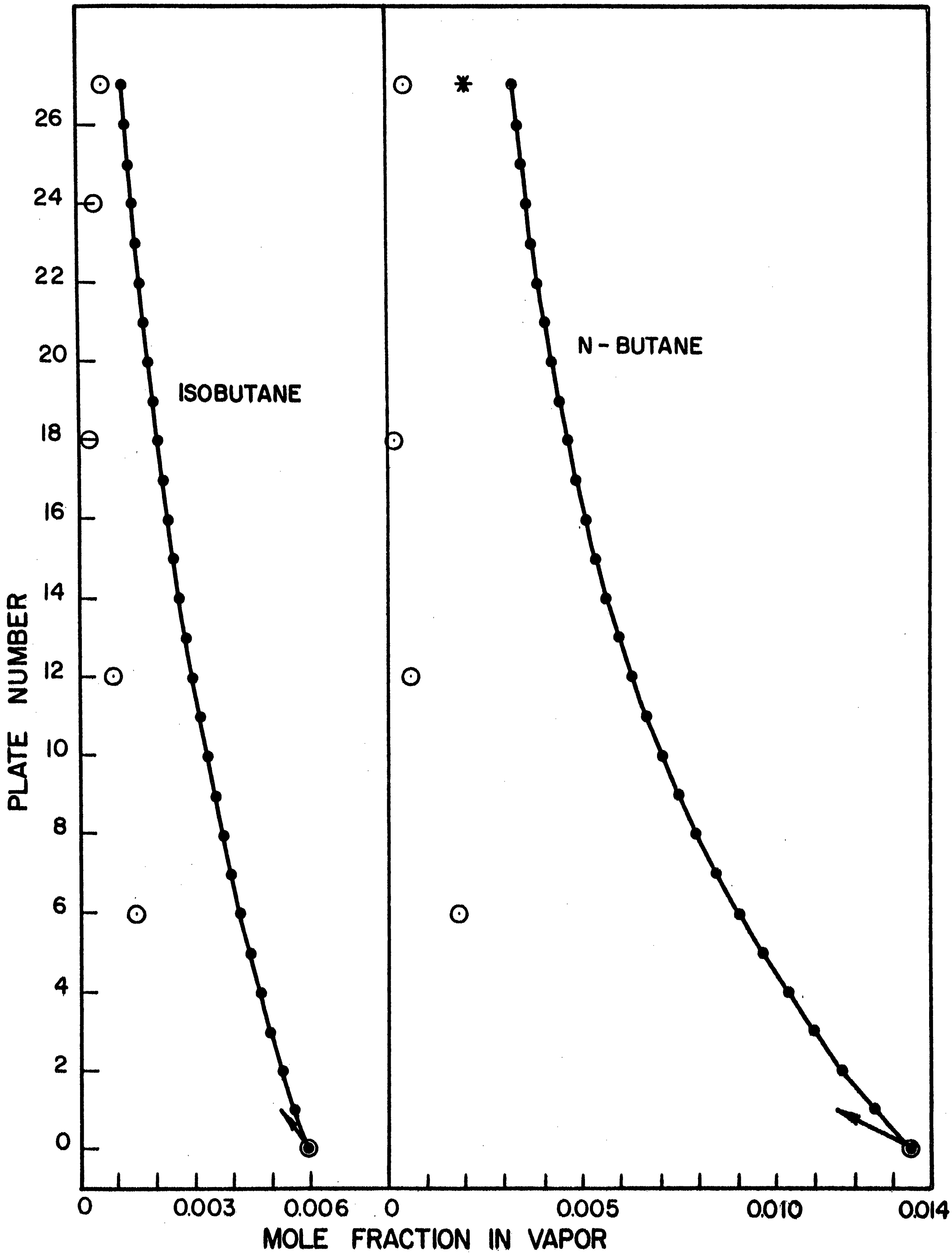


Figure 15-c. Results for Column B

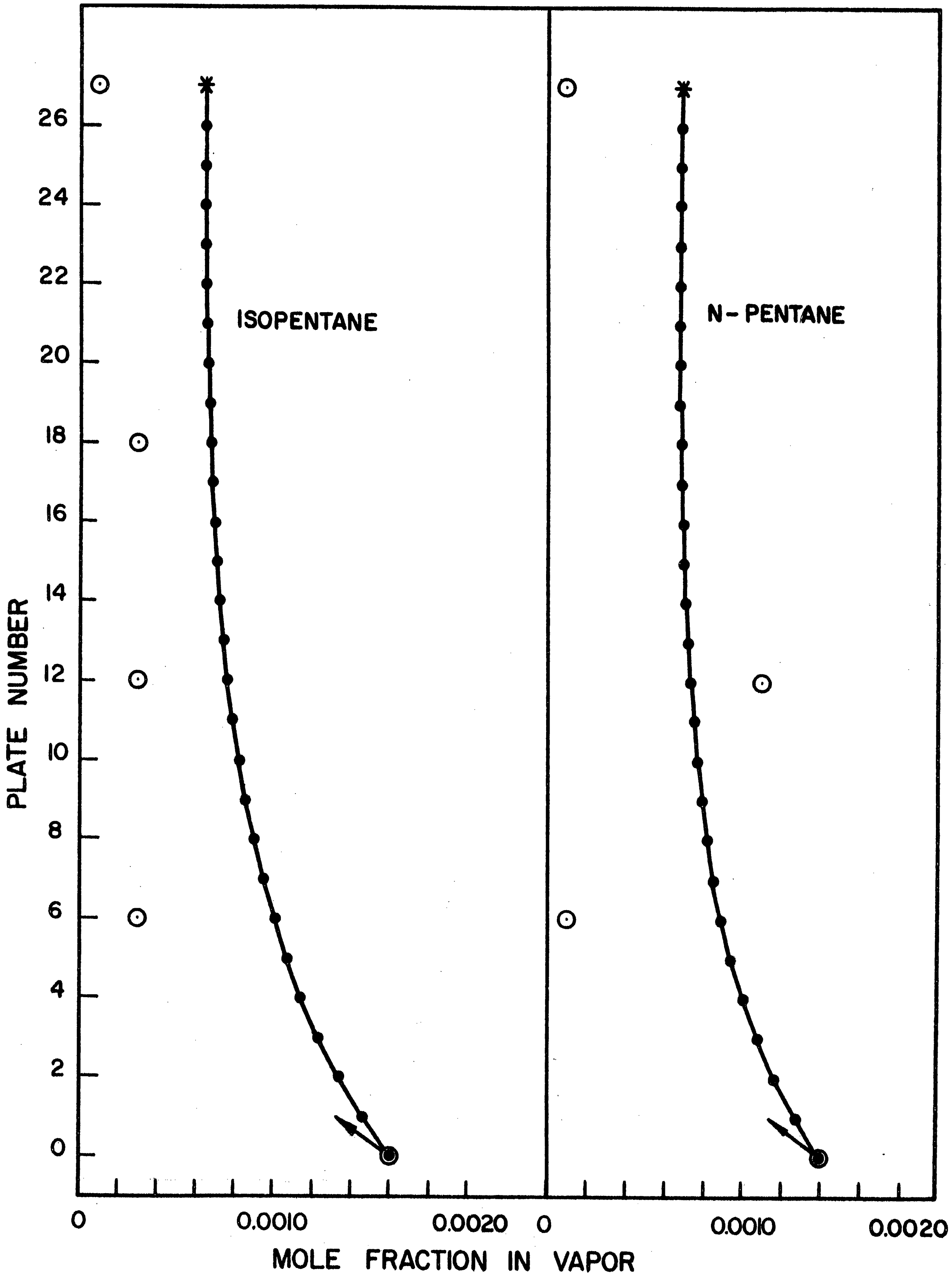


Figure 15-d. Results for Column B

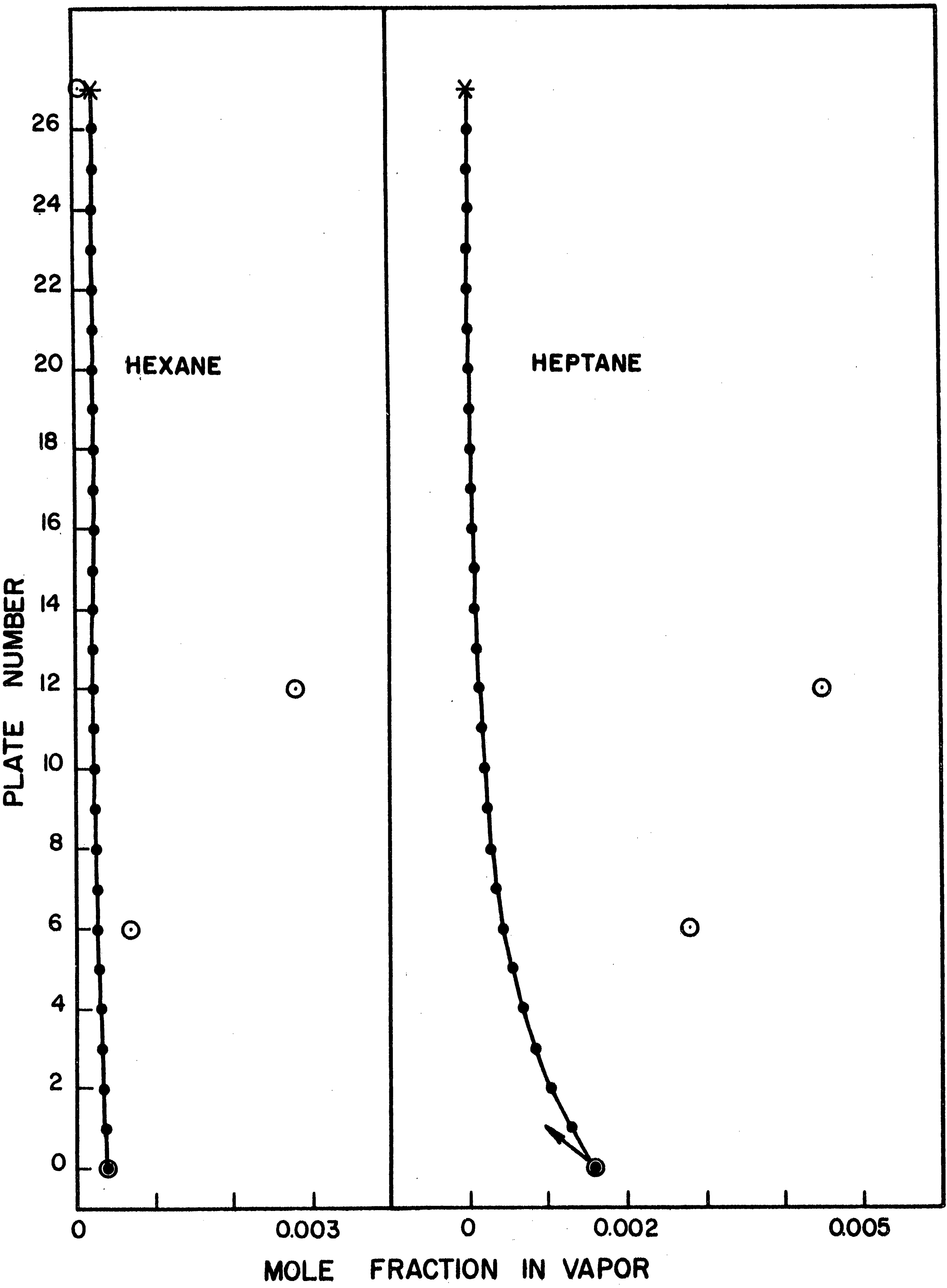


Figure 15-e. Results for Column B

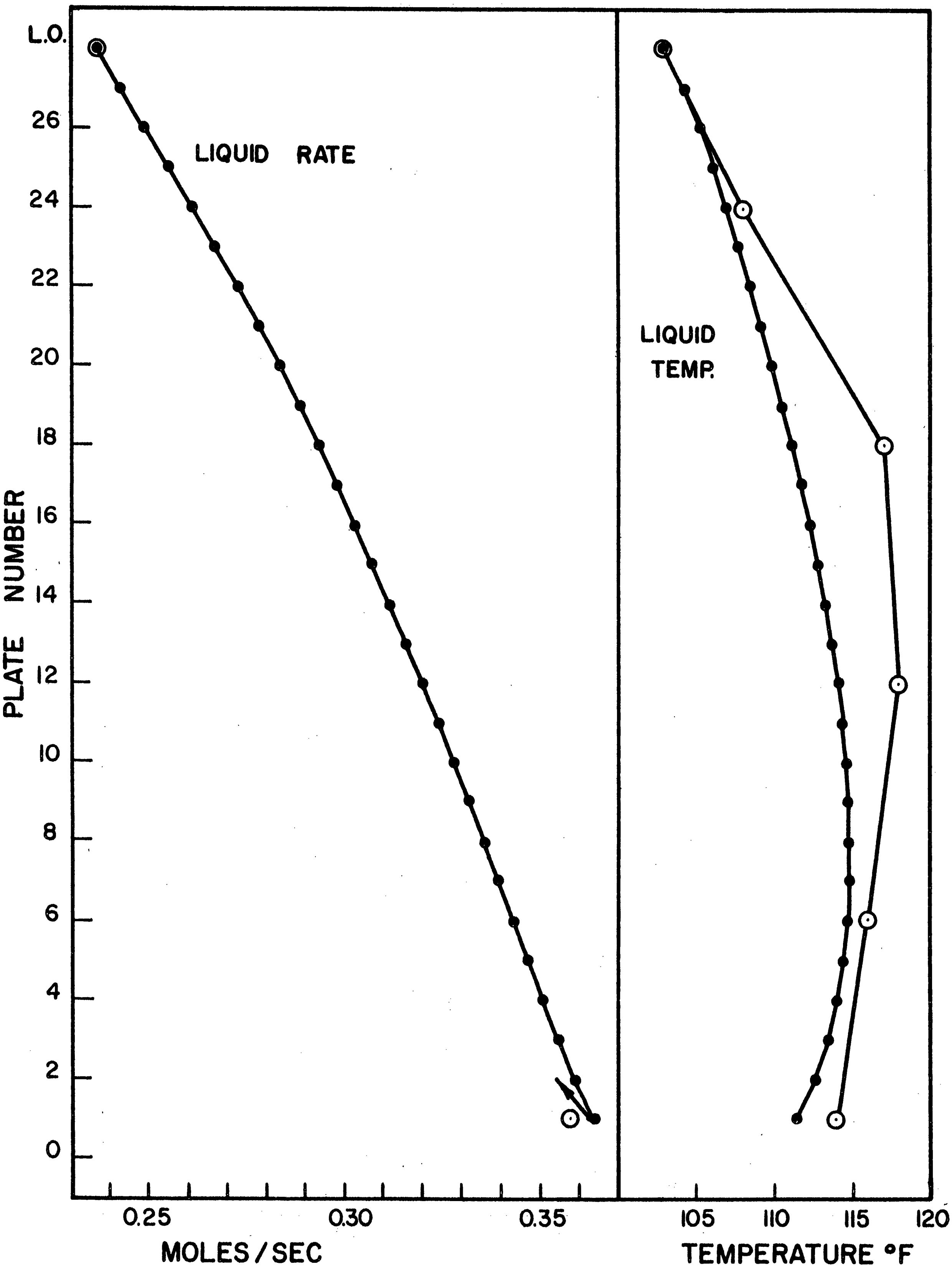


Figure 15-f. Results for Column B

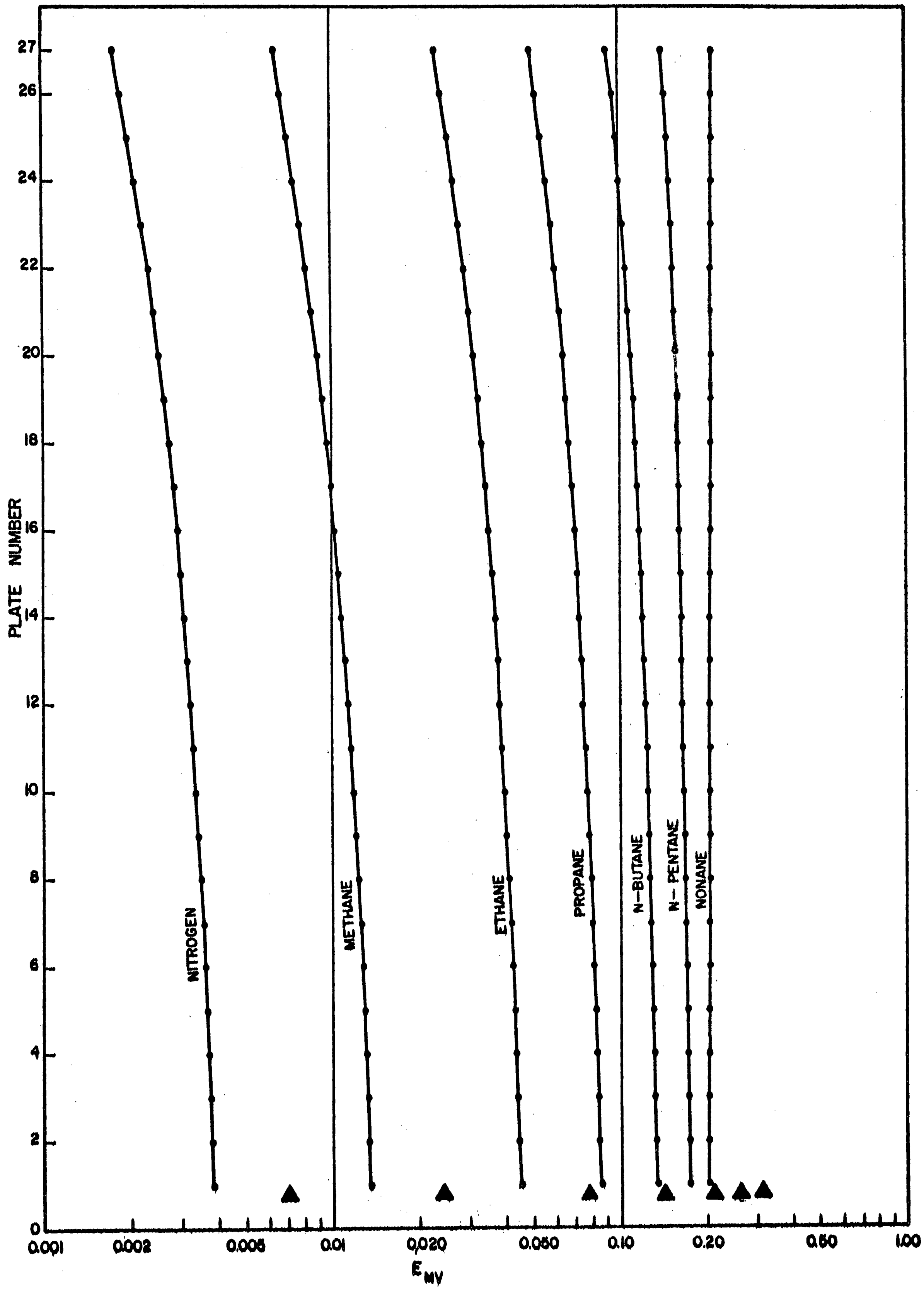


Figure 16. Plate Efficiencies in Column B

TABLE 15

COMPONENT RESULTS FOR COLUMN B WITH WELL-STRIPPED LEAN OIL

Component	y_0	x_{n+1}	y_n	x_1	Rec.
Nitrogen	0.0410	0	0.0467	0.00204	0.0196
	0.0410	0	0.0536	--	--
Methane	0.8026	0	0.8630	0.15079	0.0737
	0.8026	0	0.8915	0.11638	0.0325
Ethane	0.0723	0	0.0598	0.05289	0.2869
	0.0723	0	0.0442	0.05314	0.4674
Propane	0.0597	0	0.0275	0.09191	0.6038
	0.0597	0	0.0092	0.08000	0.8654
Isobutane	0.0059	0	0.0012	0.01238	0.8229
	0.0059	0	0.0007	0.01581	0.9091
n-Butane	0.0135	0	0.0017	0.03066	0.8905
	0.0135	0	0.0005	0.04400	0.9682
Isopentane	0.0016	0	0.00006	0.00395	0.9688
	0.0016	0	0.0001	0.00952	0.9333
n-Pentane	0.0014	0	0.00003	0.00350	0.9804
	0.0014	0	0.0001	0.01124	0.9231
Hexane	0.0004	0.0010	0.00003	0.00161	0.9408
	0.0004	0.0010	0.0001	0.00743	0.7500
Heptane	0.0016	0.0010	--	0.00470	0.9992
	0.0016	0.0010	--	0.00057	1
Octane	0	0.0017	0.00001	0.00108	
	0	0.0017	--	0.00114	
Nonane	0	0.0169	0.00003	0.01087	
	0	0.0169	--	0.01181	
Decane	0	0.0287	0.00002	0.01851	
	0	0.0287	--	0.02000	
Abs. Oil 1	0	0.1573	0.00004	0.10166	
	0	0.1573	--	0.10838	
Abs. Oil 2	0	0.7934	--	0.51343	
	0	0.7934	--	0.52058	

In each pair of values: top line - computed value,
bottom line - test value.

TABLE 16

PLATE RESULTS FOR COLUMN B WITH WELL-STRIPPED LEAN OIL

Plate	V_m	t_{V_m}	L_m	t_{L_m}	Conv.Pres.
L.Oil	--	--	0.2365	103.00	--
	--	--	0.2365	103.00	--
27	0.8078	108.76	0.2469	104.09	7031.
	0.8121	112.00	--	--	--
26	0.8136	109.17	0.2526	104.89	7021.
25	0.8194	109.56	0.2583	105.67	7011.
24	0.8250	109.95	0.2638	106.46	7002.
	--	--	--	108.00	--
23	0.8305	110.31	0.2692	107.22	6991.
22	0.8359	110.65	0.2745	107.96	6981.
21	0.8412	110.96	0.2796	108.68	6970.
20	0.8464	111.24	0.2846	109.37	6959.
19	0.8514	111.48	0.2895	110.04	6947.
18	0.8563	111.67	0.2943	110.68	6935.
	--	--	--	117.00	--
17	0.8610	111.81	0.2989	111.29	6924.
16	0.8656	111.89	0.3034	111.86	6911.
15	0.8701	111.89	0.3077	112.40	6898.
14	0.8745	111.81	0.3120	112.88	6885.
13	0.8787	111.64	0.3161	113.33	6871.
12	0.8829	111.35	0.3202	113.72	6858.
	--	--	--	118.00	--
11	0.8870	110.94	0.3242	114.06	6842.
10	0.8910	110.37	0.3282	114.32	6827.
9	0.8949	109.63	0.3321	114.53	6811.

TABLE 16

PLATE RESULTS FOR COLUMN B WITH WELL-STRIPPED LEAN OIL (CONT'D)

Plate	V_m	t_{V_m}	L_m	t_{L_m}	Conv.Pres.
8	0.8988	108.68	0.3360	114.62	6794.
7	0.9027	107.50	0.3399	114.61	6776.
6	0.9066 --	106.04 --	0.3438 --	114.47 116.00	6757. --
5	0.9106	104.27	0.3479	114.18	6736.
4	0.9146	102.12	0.3520	113.83	6714.
3	0.9188	99.51	0.3563	113.50	6690.
2	0.9231	96.34	0.3608	112.64	6664.
1	0.9276 --	92.54 --	0.3656 0.3568	111.50 114.00	6634. --
R.Gas	0.9324 0.9324	88.00 88.00	-- --	-- --	-- --

In each pair of values: top line - computed value,
bottom line - test value.

TABLE 17

COMPONENT RESULTS FOR COLUMN B WITH WELL-STRIPPED LEAN OIL AND INTERCOOLER*

Component	y_0	x_{n+1}	y_n	x_1	Rec.
Nitrogen	0.0410	0	0.0467	0.00204	0.0196
	0.0410	0	0.0467	0.00204	0.0196
Methane	0.8026	0	0.8642	0.15068	0.0739
	0.8026	0	0.8630	0.15079	0.0737
Ethane	0.0723	0	0.0594	0.05389	0.2934
	0.0723	0	0.0598	0.05289	0.2869
Propane	0.0597	0	0.0267	0.09331	0.6152
	0.0597	0	0.0275	0.09191	0.6038
Isobutane	0.0059	0	0.0012	0.01244	0.8300
	0.0059	0	0.0012	0.01238	0.8229
n-Butane	0.0135	0	0.0016	0.03071	0.8954
	0.0135	0	0.0017	0.03066	0.8905
Isopentane	0.0016	0	0.00006	0.00394	0.9702
	0.0016	0	0.00006	0.00395	0.9688
n-Pentane	0.0014	0	0.00003	0.00349	0.9812
	0.0014	0	0.00003	0.00350	0.9804
Hexane	0.0004	0.0010	0.00003	0.00159	0.9339
	0.0004	0.0010	0.00003	0.00161	0.9408
Heptane	0.0016	0.0010	0.00001	0.00468	0.9916
	0.0016	0.0010	--	0.00470	0.9992
Octane	0	0.0017	0.00001	0.00108	
	0	0.0017	0.00001	0.00108	
Nonane	0	0.0169	0.00003	0.01083	
	0	0.0169	0.00003	0.01087	
Decane	0	0.0287	0.00002	0.01845	
	0	0.0287	0.00002	0.01851	
Abs. Oil 1	0	0.1573	0.00004	0.10129	
	0	0.1573	0.00004	0.10166	
Abs. Oil 2	0	0.7934	--	0.51156	
	0	0.7934	--	0.51343	

* Figures on the second lines are computed values without intercooler.

TABLE 18

PLATE RESULTS FOR COLUMN B WITH WELL-STRIPPED LEAN OIL AND INTERCOOLER

Plate	V_m	t_{V_m}	L_m	t_{L_m}	Conv.Pres.
L.Oil	--	--	0.2365	103.00	--
27	0.8019	107.96	0.2406	105.43	--
26	0.8060	108.17	0.2466	106.12	5853.
25	0.8120	108.35	0.2524	106.81	6651.
24	0.8178	108.50	0.2582	107.49	6961.
23	0.8236	108.60	0.2638	108.12	7002.
22	0.8292	108.65	0.2693	108.73	6990.
21	0.8347	108.64	0.2746	109.29	6980.
20	0.8400	108.56	0.2798	109.80	6968.
19	0.8452	108.41	0.2848	110.29	6956.
18	0.8503	108.17	0.2897	110.72	6944.
17	0.8552	107.82	0.2945	111.10	6932.
16	0.8599	107.36	0.2991	111.42	6919.
15	0.8645	106.76	0.3036	111.67	6905.
14	0.8690	106.02	0.3080	111.85	6891.
13	0.8734	105.09	0.3123	111.94	6876.
12	0.8777	103.98	0.3165	111.94	6861.
11	0.8819	102.63	0.3206	111.86	6845.
10	0.8860	101.02	0.3250	102.40	6780.
9	0.8904	100.79	0.3294	102.92	6766.
8	0.8948	100.42	0.3338	103.35	6749.
7	0.8992	99.88	0.3382	103.72	6731.

TABLE 18

PLATE RESULTS FOR COLUMN B WITH WELL-STRIPPED LEAN OIL AND INTERCOOLER (CONT'D)

Plate	V_m	t_{V_m}	L_m	t_{L_m}	Conv.Pres.
6	0.9036	99.15	0.3427	104.02	6712.
5	0.9081	98.20	0.3472	104.21	6692.
4	0.9127	96.98	0.3519	104.38	6670.
3	0.9173	95.44	0.3567	104.63	6648.
2	0.9221	93.45	0.3617	104.43	6622.
1	0.9271	91.00	0.3670	104.04	6594.
R.Gas	0.9324	88.00	--	--	--

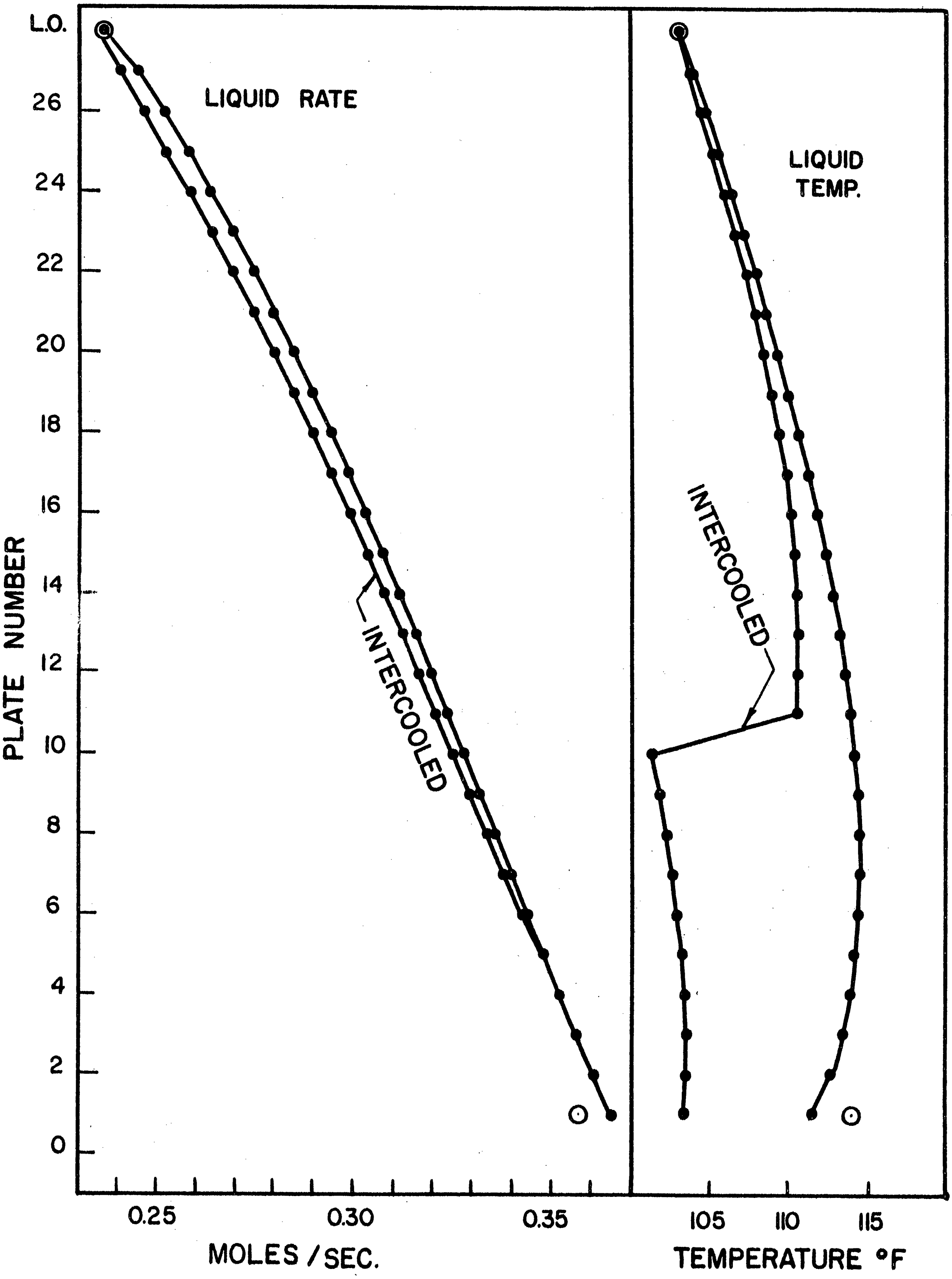


Figure 17. Results for Column B with Well-Stripped Lean Oil

TABLE 19

COMPONENT RESULTS FOR COLUMN C

Component	y_0	x_{n+1}	y_n	x_1	Rec.	Avg. E_{MV}
Methane	0.8471	0	0.9039	0.2941	0.0925	0.0280
	0.8471	0	0.9083	0.2383	0.0826	--
Ethane	0.0737	0.0040	0.0619	0.0807	0.2854	0.0700
	0.0737	0.0040	0.0616	0.0833	0.2850	--
Propane	0.0383	0.0010	0.0198	0.0812	0.5614	0.1078
	0.0383	0.0010	0.0172	0.0901	0.6158	--
Isobutane	0.0060	0.0020	0.0017	0.0180	0.7601	0.1359
	0.0060	0.0020	0.0005	0.0221	0.9287	--
n-Butane	0.0116	0.0020	0.0019	0.0382	0.8572	0.1519
	0.0116	0.0020	0.0001	0.0441	0.9926	--
Pentane + (Hexane)	0.0123	0.0040	0.00015	0.0474	0.9897	0.2221
	0.0123	0.0040	0.0003	0.0806	0.9791	--
Abs. Oil	0	0.9870	0.00002	0.4328	--	0.2284
	0	0.9870	0	0.4415	--	--
Carbon Dioxide	0.0110	0	0.0106	0.0075	0.1828	0.0526
	0.0110	0	0.0120	--	--	--

In each pair of values; top line - computed value,
bottom line - test value.

TABLE 20

PLATE RESULTS FOR COLUMN C

Plate	V_m	t_{V_m}	L_m	t_{L_m}	Bub.Pt. L_m	Dew Pt. V_m	E_q	Conv. Pres.
L.Oil	--	--	0.1592	81.00	--	--	--	
	--	--	0.1592	81.00	--	--	--	--
30	1.1764	94.86	0.1863	82.79	996.32	100.24	0.0992	7258.
	1.1662	94.00	--	--	--	--	--	--
29	1.1863	96.19	0.1964	85.33	975.88	100.67	0.1148	7213.
	--	--	--	94.00	--	--	--	--
28	1.1963	97.60	0.2064	87.90	954.32	101.08	0.1316	7180.
27	1.2063	99.07	0.2163	90.46	787.89	101.51	0.1494	7153.
	--	--	--	102.00	--	--	--	--
26	1.2162	100.59	0.2260	92.98	649.49	101.96	0.1679	7130.
25	1.2259	102.12	0.2353	95.44	560.77	102.43	0.1867	7107.
	--	--	--	106.00	--	--	--	--
24	1.2353	103.66	0.2442	97.80	473.40	102.90	0.2054	7087.
23	1.2441	105.17	0.2525	100.06	353.06	103.37	0.2239	7067.
	--	--	--	108.00	--	--	--	--
22	1.2524	106.65	0.2603	102.19	260.40	103.81	0.2418	7047.
21	1.2602	108.07	0.2674	104.19	216.89	104.21	0.2588	7028.
	--	--	--	109.00	--	--	--	--
20	1.2674	109.43	0.2740	106.06	191.87	104.56	0.2750	7009.
19	1.2739	110.71	0.2800	107.79	175.47	104.81	0.2901	6991.
	--	--	--	110.00	--	--	--	--
18	1.2799	111.90	0.2855	109.38	164.02	104.96	0.3042	6974.
17	1.2854	113.00	0.2905	110.84	155.73	104.98	0.3173	6956.
	--	--	--	111.00	--	--	--	--
16	1.2904	114.01	0.2951	112.17	149.54	104.83	0.3294	6938.
15	1.2950	114.91	0.2993	113.38	144.92	104.47	0.3404	6921.
	--	--	--	112.00	--	--	--	--
14	1.2992	115.70	0.3032	114.45	141.46	103.85	0.3505	6904.

TABLE 20

PLATE RESULTS FOR COLUMN C (CONT'D)

Plate	V_m	t_{V_m}	L_m	t_{L_m}	Bub.Pt. L_m	Dew Pt. V_m	E_q	Conv. Pres.
13	1.3032	116.37	0.3069	115.71	138.94	110.16	0.3595	6888.
	--	--	--	112.50	--	--	--	--
12	1.3068	116.74	0.3103	116.42	137.09	109.30	0.3676	6869.
11	1.3102	116.93	0.3137	116.96	135.76	108.00	0.3749	6849.
	--	--	--	113.50	--	--	--	--
10	1.3136	116.91	0.3170	117.33	134.86	106.15	0.3815	6828.
9	1.3169	116.66	0.3204	117.50	134.31	103.58	0.3874	6805.
	--	--	--	113.00	--	--	--	--
8	1.3203	116.13	0.3239	117.44	134.06	100.09	0.3928	6779.
7	1.3238	115.28	0.3276	117.14	134.08	95.42	0.3975	6750.
	--	--	--	113.00	--	--	--	--
6	1.3275	114.05	0.3317	116.54	134.34	89.29	0.4015	6717.
5	1.3316	112.37	0.3362	115.61	134.85	81.58	0.4049	6678.
	--	--	--	112.50	--	--	--	--
4	1.3361	110.18	0.3414	114.28	135.62	72.84	0.4075	6633.
3	1.3413	107.35	0.3474	112.48	136.70	65.11	0.4093	6579.
	--	--	--	111.00	--	--	--	--
2	1.3474	103.80	0.3546	110.14	138.12	64.41	0.4100	6516.
1	1.3545	99.39	0.3631	107.17	139.99	66.41	0.4094	6439.
	--	--	0.3561	104.00	--	--	--	--
R.Gas	1.3630	94.00	--	--	--	--	--	--
	1.3630	94.00	--	--	--	--	--	--

In each pair of values: top line - computed value,
bottom line - test value.

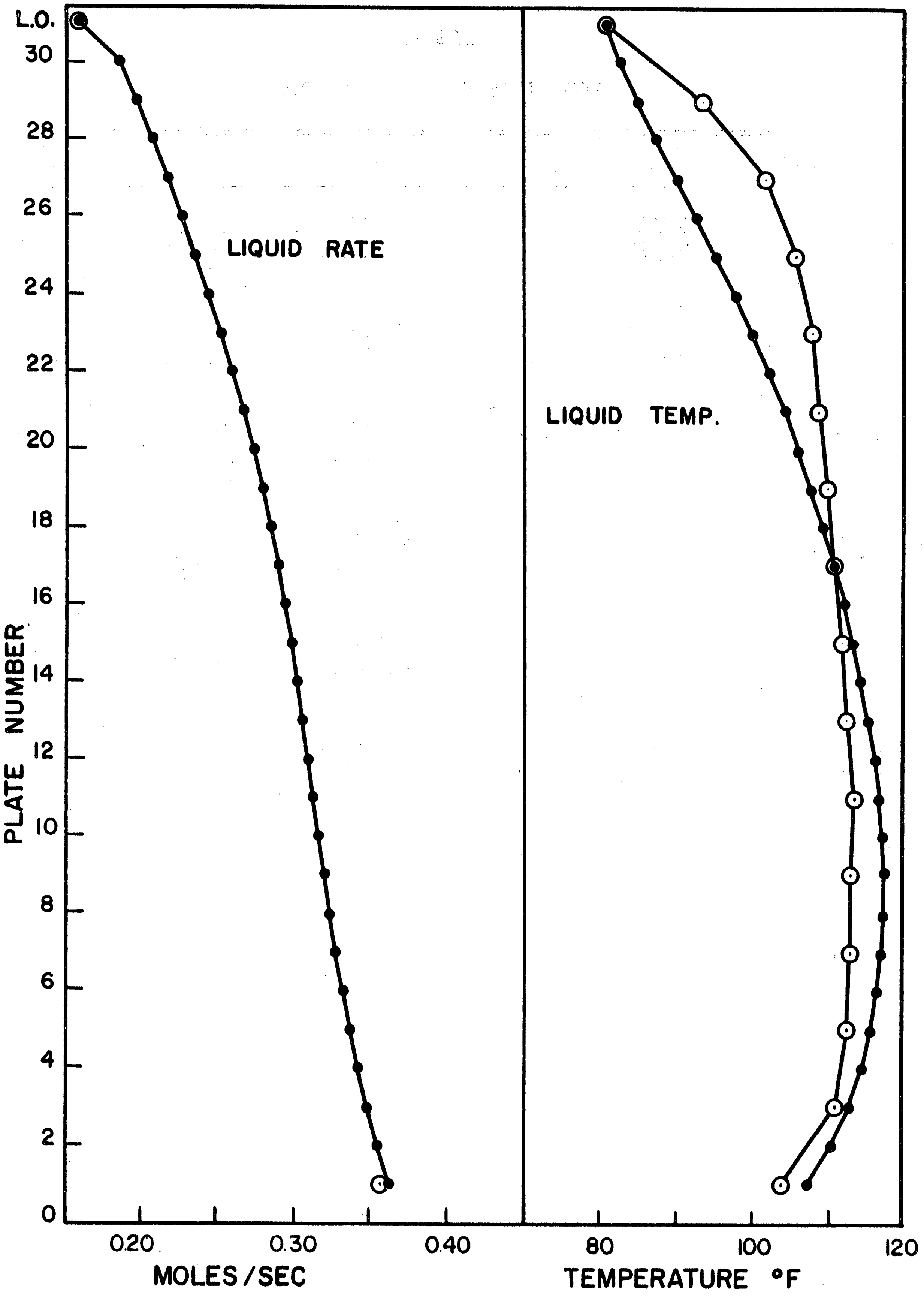


Figure 18. Results for Column C

TABLE 21

COMPONENT RESULTS FOR COLUMN D

Component	y_0	x_{n+1}	y_n	x_1	Rec.
Methane	0.7529	0	0.81254	0.0946	0.0382
	0.7529	0	0.81413	0.0850	0.0344
Ethane	0.0564	0	0.05192	0.0334	0.1796
	0.0564	0	0.05448	0.0253	0.1371
Propane	0.0505	0	0.02883	0.0817	0.4912
	0.0505	0	0.02740	0.0854	0.5159
Isobutane	0.0092	0	0.00200	0.0244	0.8064
	0.0092	0	0.00046	0.0288	0.9555
n-Butane	0.0181	0	0.00214	0.0533	0.8945
	0.0181	0	0.00009	0.0591	0.9947
Pentanes + (Hexane)	0.0127	0	0.00003	0.0417	0.9981
	0.0127	0	0.00010	0.0412	0.9924
Abs. Oil	0	1.0000	--	0.6426	--
	0	1.0000	0	0.6471	--
Carbon Dioxide	0.1002	0	0.10280	0.0282	0.0856
	0.1002	0	0.10334	0.0260	0.0781

TABLE 22

PLATE RESULTS FOR COLUMN D

Plate	V_m	t_{V_m}	L_m	t_{L_m}	E_q	Conv.Pres.
L.Oil	--	--	0.1895	71.00	--	--
	--	--	0.1895	71.00	--	--
24	0.8664	81.47	0.1947	73.70	0.1174	6346.
	0.8690	78.00	--	76.00	--	--
23	0.8716	82.50	0.2014	75.44	0.1289	6626.
22	0.8782	83.55	0.2078	77.14	0.1406	6666.
21	0.8846	84.60	0.2138	78.79	0.1524	6672.
20	0.8906	85.64	0.2194	80.38	0.1642	6668.
	--	--	--	89.00	--	--
19	0.8963	86.67	0.2248	81.92	0.1759	6658.
18	0.9016	87.68	0.2297	83.40	0.1874	6645.
17	0.9066	88.67	0.2343	84.82	0.1987	6630.
16	0.9112	89.63	0.2386	86.17	0.2098	6614.
	--	--	--	94.00	--	--
15	0.9155	90.55	0.2426	87.47	0.2208	6597.
14	0.9195	91.42	0.2464	88.71	0.2315	6579.
13	0.9232	92.24	0.2499	89.89	0.2421	6560.
12	0.9268	92.99	0.2532	91.01	0.2525	6541.
	--	--	--	93.00	--	--
11	0.9301	93.66	0.2564	92.07	0.2630	6520.
10	0.9332	94.23	0.2594	93.34	0.2730	6502.
9	0.9363	94.56	0.2624	94.26	0.2834	6480.
8	0.9393	94.68	0.2654	95.07	0.2941	6457.
	--	--	--	95.00	--	--
7	0.9423	94.52	0.2685	95.75	0.3052	6431.

TABLE 22

PLATE RESULTS FOR COLUMN D (CONT'D)

Plate	V_m	t_{V_m}	L_m	t_{L_m}	E_q	Conv.Pres.
6	0.9453	93.99	0.2717	96.25	0.3169	6402.
5	0.9486	92.94	0.2752	96.53	0.3295	6369.
4	0.9520	91.17	0.2790	96.46	0.3432	6330.
	--	--	--	98.00	--	--
3	0.9559	88.40	0.2835	95.88	0.3584	6283.
2	0.9603	84.23	0.2888	94.52	0.3751	6222.
1	0.9656	78.06	0.2953	92.00	0.3937	6143.
	--	--	0.2926	92.00	--	--
R.Gas	0.9721	69.00	--	--	--	--
	0.9721	69.00	--	--	--	--

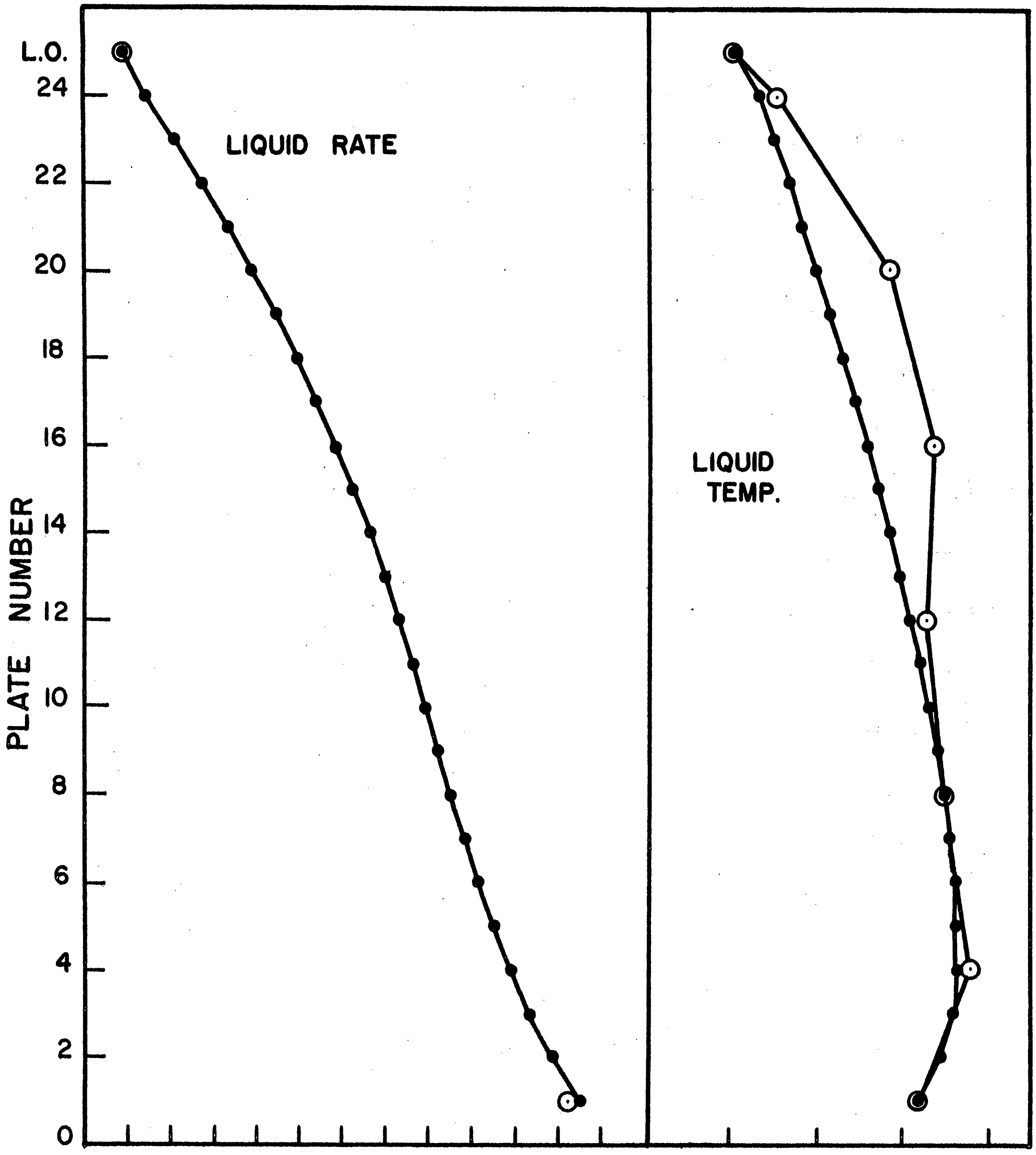


Figure 19. Results for Column D

VIII. ANALYSIS OF RESULTS

A. The Ideal Stage Calculation

The results, although not in particularly close agreement with those of the "legitimate" ideal stage calculation, do seem to indicate that no serious discrepancies exist. Some measure of the program's inability to produce equilibrium streams may be gathered from examination of the computed bubble and dew points.

Sources of the disagreement, in probable order of importance, are (1) the mass transfer relationship used in the writer's program (see the discussion under Results--An Ideal Stage Column), (2) the different ways in which enthalpies and K values were correlated in the two programs, and (3) the fact that neither set of results represents a true or completely converged solution of the equations involved. Both contain truncation and round-off error within "reasonable" limits specified by the user.

B. Recovery of Components

Probably the most striking thing common to the results for all four non-ideal stage columns is the discrepancy between computed and test recoveries of the medium-volatility components of the rich gas. The most likely causes of this error are (1) the approximation of using V_{m-1} in place of $\overline{V}$ in the mass transfer expressions,

$$v_m = v_{m-1} + (E_{MV})(V_{m-1}Kx_m - v_{m-1}) \qquad (89)$$

(2) the use of plate efficiencies which are too low, and (3) the estimation of lean oil compositions (in some cases) which contain excessive

amounts of some components of the rich gas. These three possibilities will be discussed in order.

C. The Average Vapor Flow Rate

The bottom plate of Column B (where the vapor flow rate changes most rapidly) was selected as the basis for a short hand calculation to demonstrate the justifiability of using V_{m-1} in place of $\overline{V}$ (some average of V_{m-1} and V_m) in the mass transfer equations. In Table 23, V_0 and y_0 are the input flow rate and composition to plate 1, and V_1 and y_1 are the corresponding quantities leaving the plate as calculated by the machine. The arithmetic average of V_0 and V_1 is $\overline{V}$, and when $\overline{V}$ is used in the mass transfer expressions, V_1' and y_1' result. The difference in all cases is quite small, amounting to about 0.0044% for V_1 and V_1'.

D. The Effect of Plate Efficiency

In absorbers, plate efficiency and number of plates are critical only for the "key" component and those immediately adjacent to it in volatility. The key component is defined as the one whose average absorption factor is closest to 1.00, or equivalently, the one whose operating line is most nearly parallel to its equilibrium line. In Column A, n-butane, the key, has a K value of 0.21 at 80°F, and the L/V ratio on plate 10 (the middle of the column) is 0.182. Figure 20 illustrates the case for propane, n-butane, and pentane. Note the rapid change of propane concentrations near the top of the column where the driving force is greatest, the opposite effect with pentane, the almost uniform change for n-butane, and the fact that the curve in the operating lines reflects

TABLE 23

THE EFFECTS OF AVERAGE VAPOR RATE AND PLATE EFFICIENCY

Component	y_0	E_{MV}	y_1	y_1'	* y_1''
Nitrogen	0.0410	0.003862	0.041191	0.041193	0.041387
Methane	0.8026	0.013544	0.805711	0.805722	0.808874
Ethane	0.0723	0.045267	0.072169	0.072165	0.072029
Propane	0.0597	0.086171	0.058380	0.058374	0.057034
Isobutane	0.0059	0.118339	0.005568	0.005567	0.005231
n-Butane	0.0135	0.135166	0.012573	0.012572	0.011595
Isopentane	0.0016	0.164772	0.001459	0.001459	0.001316
n-Pentane	0.0014	0.175153	0.001276	0.001276	0.001150
Hexane	0.0004	0.196579	0.000363	0.000363	0.000325
Heptane	0.0016	0.206374	0.001288	0.001288	0.000973
Octane	0	0.207433	0.000001	0.000001	0.000002
Nonane	0	0.204857	0.000005	0.000005	0.000009
Decane	0.	0.201063	0.000003	0.000003	0.000007
Abs. Oil 1	0	0.195577	0.000007	0.000007	0.000014
Abs. Oil 2	0	0.185291	0.000005	0.000005	0.000011

$V_0 = 0.932400$

$V_1 = 0.927834$

$\overline{V} = 0.930117$

$V_1' = 0.927793$

* $V_1'' = 0.923186$

* y_1'' and V_1'' were computed using values of E_{MV} twice as large as those used in computing y_1, y_1', V_1, and V_1'.

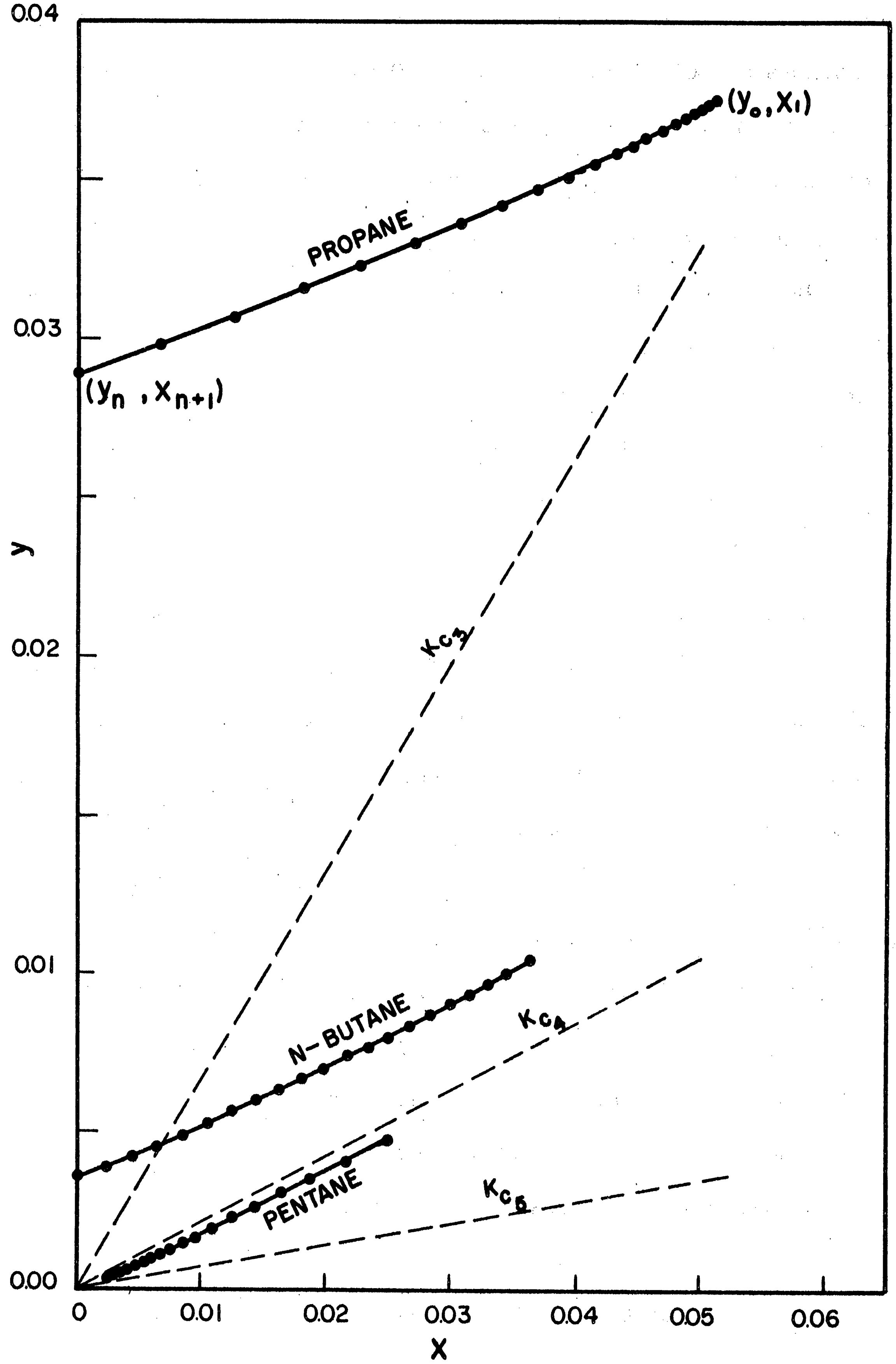


Figure 20. Operating and Equilibrium Lines

the decrease of L/V ratios as m increases. The equilibrium lines represent K values at 80°F, 232 psia, and 5000 psia convergence pressure. Components much lighter than the key component usually reach a concentration in the rich oil which is nearly in equilibrium with the rich gas, i.e., the "pinch" or zone of diminished driving force occurs in the lower part of the column; components much heavier than the key reach a concentration in the lean gas nearly in equilibrium with the lean oil, i.e., the pinch is in the upper part of the column. This latter case is illustrated by pentane in Column A, Figure 13-D, whose computed absorption is much slower than the test results indicate but almost as complete.

In both Columns A and B, vapor composition test data for lighter components in the internal streams scatter too badly to indicate anything except trends. Data on the medium-volatility components show that they are absorbed out of the vapor stream much more quickly than the machine computation predicts. A liquid rate curve prepared by the Phillips people from material balance calculations (shown dotted because it is derived rather than primary data) has a much more pronounced "S" shape than the one computed by the machine and shown in Figure 13-E.

Returning to Table 23, the values V_1'' and y_1'' were computed by hand using values of E_{MV} twice as large as the machine-computed ones. The difference in this case is significant, and the short arrows on Figure 15 show that the use of larger plate efficiencies would produce computed concentration profiles much more nearly in accord with the test data.

The importance of plate efficiency to the key component and neighboring ones is illustrated in Column A by the fact that the discrepancy between computed and test recoveries is greatest for n-butane and less serious for isobutane and pentane. In Column B with well-stripped lean oil, the keys are propane and isobutane, and here again the discrepancies are greatest for the keys, less serious for those close to the keys. Similar situations hold in Columns C and D.

E. The Effect of Lean Oil Composition

When the results for Column B showed large discrepancies between computed and test recoveries of components heavier than the keys, a well-stripped lean oil was substituted in order to determine the effect of the lean oil composition. As expected, recovery was markedly increased and exceeded the test recoveries in most cases.

The fact that lean gas concentrations of heavier components approach equilibrium with the liquid from the top plate is illustrated by the asterisks in Figures 13 and 15, which show the equilibrium compositions. Approach to equilibrium is only a contributing factor to the low recovery of n-butane in Columns A and B, however. In the high-pressure Column C, the key component was isobutane; the concentrations of ethane, propane, isobutane, n-butane, and hexane in the lean oil were 0.06115, 0.01958, 0.001649, 0.001936, and 0.000147, respectively; the vapor mole fractions which would have been in equilibrium with the lean oil were 0.01021, 0.00254, 0.000424, 0.000416, and 0.000120; and the actual lean gas concentrations, found in Table 19, were 0.0619, 0.0198, 0.0017, 0.0019, and 0.00015. Thus, it appears that only the recovery of hexane (which was satisfactory) was influenced significantly by the lean oil composition. The lean oil to Column D was completely stripped.

F. The Effect of Intercooling

Examination of Table 17, which compares machine computation results of Column B (well-stripped lean oil) with and without an intercooler, indicates that the effect of the intercooler was about what might have been expected. The lowered temperatures caused lower K values and greater recoveries of all rich gas components except nitrogen (unchanged), hexane, and heptane. Recoveries of the key and adjacent components were increased the most.

G. Convergence Pressure

Convergence pressure is computed from liquid compositions and is a function of temperature and the boiling points of the effective light and heavy components. The light component effective boiling point is influenced most strongly by the mole fractions of the lightest components in the liquid, as Equation (175) indicates; a similar statement holds for the effective heavy component. In the range of conditions found in gas absorbers, an increase in the heavy component boiling point or a decrease in the light component boiling point will raise the convergence pressure. The effect of system temperature is variable and depends on the values of the other two variables, but it is small and should not be significant over the small temperature ranges found in absorbers.

The convergence pressure profiles of all columns seem to follow approximately the same pattern. They increase slowly from the bottom of the column to a plate either at the top or near the top and then (in the latter case) decrease rather abruptly. Flow rates of the heavy components of the lean oil are almost constant in the liquid streams throughout a column. Since L_m decreases as m increases, mole fractions of the heavy components increase, the heavy component effective boiling point increases, and this would seem to explain the slow rise of p_k as m increases. Mole fractions of the lightest components decrease slowly as m increases until the top few plates are reached, at which point they drop off to zero in the lean oil stream. (The degree of approach to convergence acceptable to the machine may even permit very small negative mole fractions of nitrogen or methane in L_n or L_{n-1}.) This sudden disappearance of light components raises the light component effective boiling point and probably accounts for those decreases of convergence pressure which do occur. Excluding the top and bottom plates, the percentage changes of p_k do not exceed 10% through any of the columns.

H. Dew Points and Bubble Points

The dew points and bubble points computed for Columns A, B, and C show the trends that might be expected of them. The lean oil enters the column well-stripped of light and medium-volatility components. The liquid stream has extremely high bubble point temperatures at the top of the column, the temperatures drop as the liquid flows downward absorbing material from the vapor stream, and the bubble point temperatures near the bottom approach the liquid stream temperatures. The dew point of the vapor stream rises slightly as the stream proceeds up the column. The vapor loses its heavier components, but very small amounts of the heaviest components of the absorber oil are vaporized. These small quantities, because of their extremely low K values, are sufficient to increase the dew point temperature.

A curious anomaly arises in the computation of dew point temperatures in that they become higher than the vapor stream temperatures in the upper parts of the columns. This condition, if it were found in test data, might be considered an indication that the vapor contained entrained liquid, but the machine program is not equipped to detect or predict entrainment. In view of the high sensitivity of the dew point calculation to heavy components in the vapor stream, this inversion of dew point temperature and vapor stream temperature must be considered a computational phenomenon with no physical significance.

I. Heat Transfer Efficiency

In all four columns investigated, the heat transfer efficiencies decrease markedly as m, the plate number, increases. The lower efficiencies on the upper plates result in (1) less curvature in the graphs of computed liquid temperatures than in those of the measured temperatures, and (2) higher computed lean gas temperatures than the test data contain. The importance of the one exception to the second stated general result, Column B, may be discounted somewhat by the facts that the computed temperatures are generally low in that column and the lean oil rate is only an estimated value. The two effects mentioned above would seem to be consequences of the lowered heat exchange rates computed for the upper parts of the columns.

The variations of the E_q values produce one worthwhile result, however. The liquid temperature profiles computed for the lower parts of the columns have shapes in fairly good agreement with those plotted from test data; the maximum liquid temperatures occur reasonably close to the test data locations, for instance, and this agreement would seem to be desirable since absorption of the most valuable components takes place in these regions. The values of C_q for Columns A, B, and C were adjusted to make the computed differences between t_L (maximum) and t_{L_1} approximately equal to the differences which existed in the actual columns. The value of C_q for Column D was predicted with the same objective in mind.

The effect of using a constant value of E_q is illustrated by Figure 21, which shows the test data liquid temperature profile, the final computed one, and the results obtained with various constant values of E_q, all for Column A. The arithmetic average of the twenty computed values of E_q is 0.2260. The temperature profiles obtained with E_q of 0.2 and 0.3 agree well with test values on the upper plates of the column, but agreement is poor on the middle plates, and the maximum temperatures occur too high in the column. The poor results obtained with E_q of 0.8 show that values approaching 1.00 (usually tacitly assumed) are not suitable, at least not with the machine program used.

The shapes of the test liquid temperature curves seem to indicate that E_q, if it is a valid measure of heat transfer at all, must have large values at the top and bottom of a column and somewhat smaller values in between. This observation leads one to two statements made earlier: (1) The "S" shapes of the liquid flow rate curves indicate that more absorption takes place in the upper and lower sections of the columns than in the middle. (2) The heat transfer efficiency expression was derived without reference to the effect of mass transfer on heat transfer.

The cause of the decrease in E_q with increase of m is easily understood from examination of Equation (101).

$$E_q = C_q \Sigma_i (y_i \; E_{MV,i})(Le)_i^{2/3} \qquad (101)$$

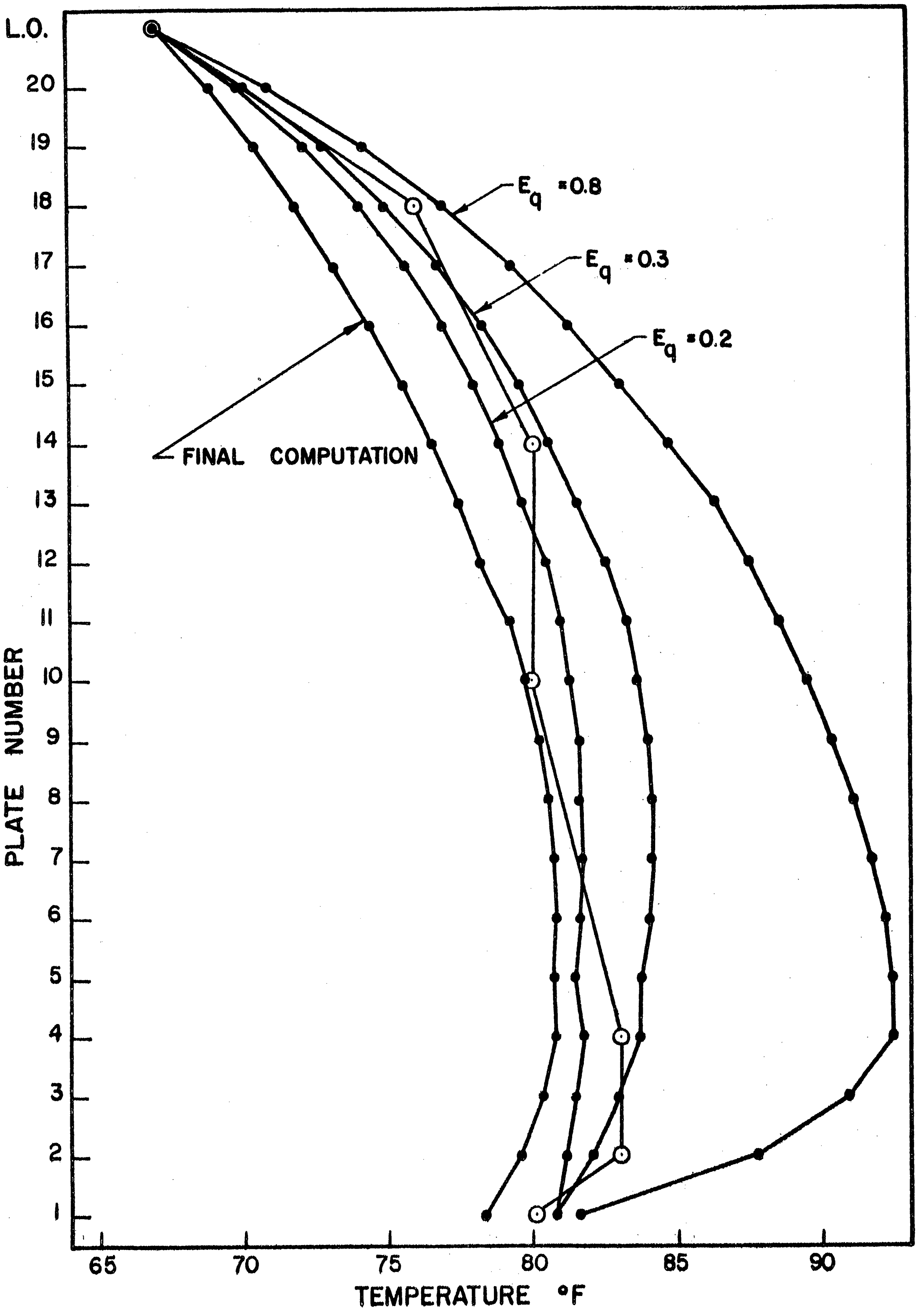


Figure 21. **Variation in Temperature Profiles**

The plate efficiencies of nitrogen and methane are much lower than those of the heavier components. As the vapor stream proceeds up the column, the heavier constituents are absorbed and the mole fractions of nitrogen and methane increase. Since methane is the principal constituent of all the vapor streams, E_q follows the trend of E_{MV} of methane quite closely, as shown by the plot of E_q on Figure 14. E_q is plotted as $E_q/100$ in order to avoid cluttering the right side of the figure and to juxtapose it to the methane curve. This transformation (on a logarithmic scale) changes position but neither shape nor orientation.

J. Prediction of the Heat Transfer Efficiency Factor

After three columns had been investigated with values of C_q adjusted to give the desired liquid temperature profiles, a study was made to determine if a value of C_q might be accurately predicted for a fourth absorber, Column D. Table 24 presents the various quantities involved.

The arithmetic average values of E_q were computed and compared to the ratios of L_{n+1}/V_0 in Columns A, B, and C. The product of these two quantities was found to be very nearly a constant, the average value being 0.348. Using 0.35 as the constant and the known L_{n+1}/V_0 ratio of Column D, 0.195, $\overline{E_q}$ was estimated to be 0.179. The implication here is not that such a simple empirical relationship adequately describes the functional dependence of $\overline{E_q}$, merely that lack of knowledge and scarcity of data points make a simple function necessary.

In an attempt to correlate C_q and $\overline{E_q}$, the quotients $C_q/\overline{E_q}$ were computed and plotted as the large dots in Figure 22. The quantity $C_q/\overline{E_q}$ is inversely proportional to the quantity which would be produced

TABLE 24

PREDICTION OF THE FACTOR C_q

Column	A	D	B	C
Pressure	232 psia	400 psia	740 psia	1475 psia
L_{n+1}/V_0	0.156	0.195	0.254	0.117
Avg. temp. $\bar{t}$	81.0°F	85.0°F	110.5°F	102.5°F
C_q	24	17	9	9
Avg. E_q	0.2260	0.179	0.1328	0.3030
$(L/V)(\overline{E_q})$	0.0352	0.035	0.0337	0.0354
$C_q/\overline{E_q}$	106.2	96	67.8	29.7
Δt	19.0	15.0	-10.5	-2.5
$\Delta(C_q/\overline{E_q})$	-7.6	-6.0	4.6	1.0
% change	-7.16	-6.25	6.78	3.37
New $C_q/\overline{E_q}$	98.6	90.0	72.4	30.7

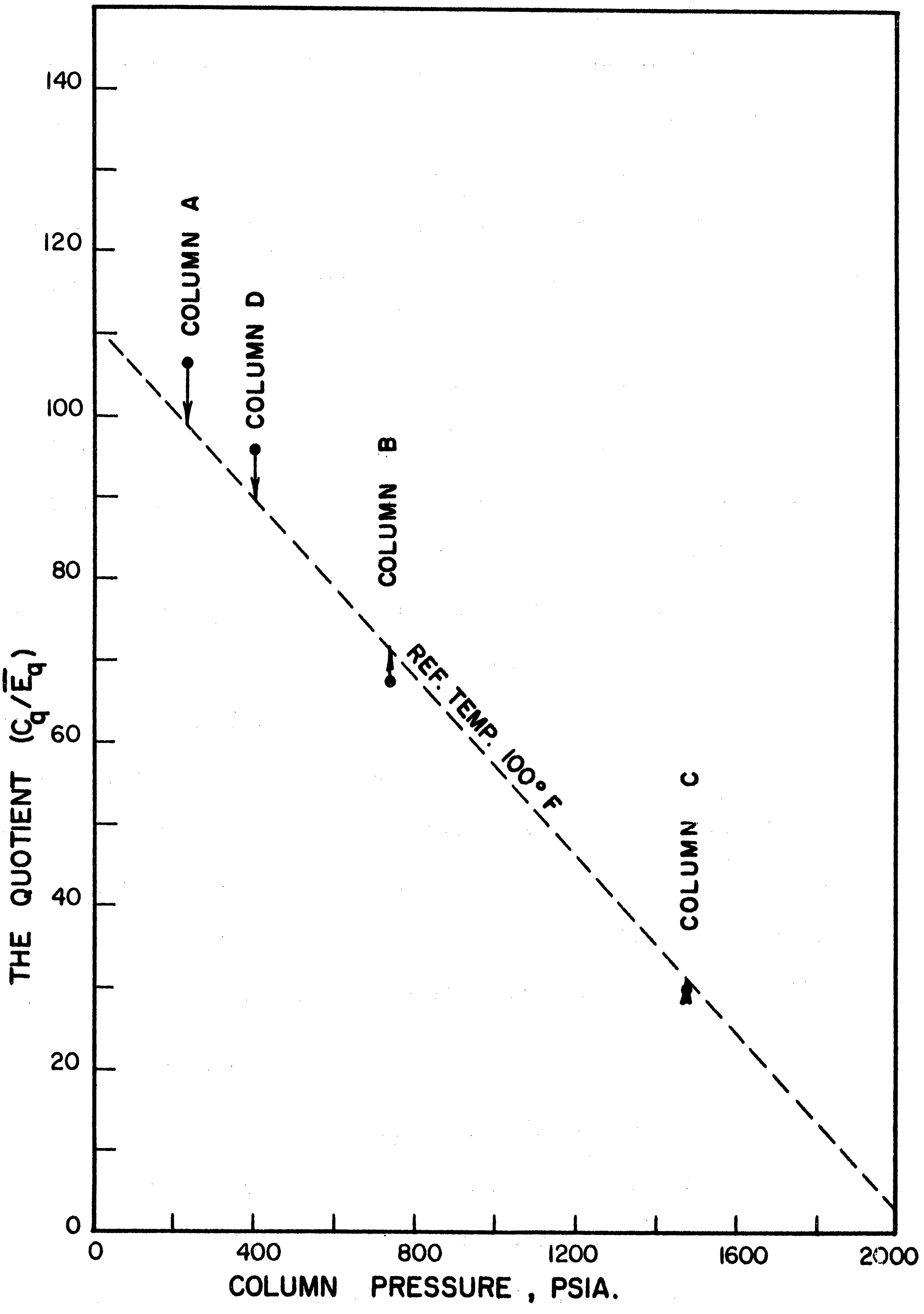


Figure 22. Prediction of the Factor C_q

by the mass transfer-heat transfer analogy without use of a factor C_q. In lesser degree, it is inversely proportional to E_{MV} of methane and, in turn, proportional to the K value of methane. The "average temperatures", $\bar{t}$, of the columns were computed as the arithmetic averages of t_{V_0} and t_{L_1} plus 15°F and were compared to an arbitrary reference, 100°F. If $\bar{t}$ of Column A, for instance, were 100°F instead of 81°F, it is reasonable to assume that the K value and E_{MV} of methane would be larger and C_q and $C_q/\overline{E_q}$ smaller. The points representing the three columns were moved by distances proportional to ($\bar{t}$ - 100°F) to produce three points lying in a straight line, and the short arrows indicate these displacements. There is, of course, no particular reason why the points should lie on a straight line; the percentage changes of the quotients necessary to produce this convenience are not large, however.

Reading a corrected quotient of 90.0 for Column D and carrying out the above procedure in reverse produced a value of 17 for C_q. The machine computation gave a liquid temperature profile which conformed to the test results (in the lower half of the absorber) more closely than that of any other column. On the other hand, the arithmetic average of computed heat transfer efficiencies was 0.248 instead of 0.179 as had been predicted.

K. Estimation of Plate Efficiencies

As mentioned in the section The Effect of Plate Efficiency, it appears that the computed plate efficiencies in all columns were too low. Those in Column B were particularly low because of the equivalent bubble cap plate properties estimated for the Kaskade plates. When the properties of a typical bubble cap plate were used instead, as in the sample plate efficiency calculation, Table 1, the efficiencies for the bottom plate shown as triangles in Figure 16 were computed. Components are in the same order as they occur on the curves.

By comparison with the large amount of work which has been done on the subject of predicting plate efficiencies, the few brief remarks made here are little more than conjecture. It would seem that the most likely reasons for the high computed values of vapor and liquid phase resistances and low plate efficiencies are the following:

(1) A factor involving m, the "slope of the equilibrium curve", is used to convert N_L, the number of liquid phase mass transfer units, to the vapor phase basis. This is inherently an inaccurate procedure for light components (where the liquid phase resistance is the larger of the two), but the same basis must be used for all components. Furthermore, m is an ambiguous quantity in a system of more than two components, and its approximation by the K value is still a further source of error. The large K values of nitrogen and methane produce extremely small plate efficiencies. Unfortunately test analyses of vapor streams show the most scatter in the concentrations of light components (see Figures 13-A and 15-A), and no conclusions may be drawn from them.

(2) Liquid phase resistances in the hydrocarbon systems were compared to those of the reference system (air-water-carbon dioxide) by using the square roots of the ratios of Schmidt numbers. In the sample calculation, Table 1, these comparison factors always lie between 0.67 and 1.38. In comparing vapor phase resistances with the reference system (air-water-ammonia), the square roots of the ratios of vapor diffusivities were used, and these factors were in the range 8.7 to 15.5.

This represents quite a large increase of vapor phase resistance due to change of system, probably too large an increase to be an accurate estimate. Had the ratios of Schmidt numbers been used, the range would have been 1.27 to 2.26, and hindsight indicates that this would have been the more cautious comparison, even though, as discussed under Engineering Concepts, there is no conclusive evidence to dictate the use of one comparison in preference to the other.

(3) A third source of error lies in the fact that the plate efficiency procedure takes no account of plate size or configuration, other than to specify bubble cap plates. Properties of the reference systems were determined in laboratory-size apparatus, and it is doubtful that these data can be extrapolated to large columns without adjustment.

IX. CONCLUSIONS

(1) The non-ideal stage calculation appears to be a very useful tool for those seeking better ways of understanding, analyzing, and predicting the operating conditions of vapor-liquid stage contacting devices. The calculation, as presented here, contains many assumptions, none of which is less reasonable than those embodied in the ideal stage calculation. Some of these assumptions--driving forces or potentials proportional to mole fractions, constant liquid composition, the use of an "average" vapor rate in one term of the mass transfer expression--might be eliminated if one had more complete knowledge of the systems involved and were willing to undertake the additional computation necessary.

(2) The utility of the computer procedure is demonstrated by its ability to duplicate, at least in an approximate way, the conditions on each actual plate and the general trends and effects found in operating absorption columns. Greatest discrepancies between computed and test results occur in the fractional recoveries of key components and the liquid temperature profiles. The cause of these deficiencies appears to be inaccurate values of E_{MV} and E_q.

(3) The Murphree plate efficiency, as employed in the mass transfer relations developed here, is a very useful characterization of the behavior of the various components in stage-wise separation processes. It is not suitable for plate-to-plate calculations in absorbers when used <u>as originally defined</u>.

(4) Prediction of Murphree plate efficiencies from separate phase resistances apparently has found more favor than the more patently

empirical procedures. In the present work, the two most difficult aspects of the procedure are relating resistances or numbers of transfer units in different systems, and accounting for the effect of changing column size or configuration.

(5) The heat transfer or "vapor temperature" efficiency expression used in this investigation is a suitable concept per se. Its theoretical basis, an equation for heat transfer in the absence of mass transfer, appears to be as strong as the basis for the Murphree plate efficiency. The fact remains (and this applies equally to the use of E_q and E_{MV}) that heat transfer and mass transfer do not occur independently, and their interaction must ultimately be learned.

(6) Better methods of predicting the heat transfer efficiency, E_q, must be found. Perhaps more astute use of the Colburn analogy, such as applying it to both phases separately and then combining resistances, will provide the needed improvement. Alternatively, empirical correlation based on test data may be satisfactory.

(7) The inherent computational instability of either the bottom-up or the top-down plate-to-plate calculation of absorbers has been mitigated by an iterative procedure based on the reduction of relative, rather than absolute errors. The Wegstein extrapolation procedure has been successful in speeding up the otherwise slow convergence of the iterative solution.

(8) The vapor and liquid enthalpy correlations employed in this investigation are somewhat more complicated and at least potentially more complete and accurate than those generally used in hand calculation or on intermediate-size computers. The computation done so far does not

constitute a complete test of the correlations, but an estimate of their worth may be obtained from the usually favorable comparison of test and computed values of flow rates and temperatures of the exit streams from the absorbers.

(9) In view of the small percentage change of convergence pressure found throughout each of the absorbers investigated, the use of a constant value of p_k appears to be in order.

(10) For industrial use, machine computation time might be reduced by a factor of five through the use of constant values of plate efficiency, heat transfer efficiency, and convergence pressure. Present accuracy in the prediction of E_{MV} and E_q does not justify the added expense of computing these efficiencies for each plate (on each iteration of the column calculation) except in research work.

X. APPENDIX - MACHINE UTILIZATION

A. Description of Machine and System

The IBM 704 Electronic Data Processing Machine

The IBM 704 is a large-scale, high-speed electronic calculator controlled by an internally stored program of the single address type(57). The machine executes instructions at an average rate of about 10,000 per second on engineering-type problems, and operates parallel in the binary number system. The machine installed at the General Motors Technical Center contains 8,192 magnetic core storage registers, 8,192 units of storage on four logical high-speed magnetic drums, and eight magnetic tape units, each with 2400 feet of tape.

The Input-Output System

The General Motors Research I/O system is a method of integrating the 704 main frame, attached equipment, peripheral equipment, coordinators, and programmers into an efficient, smoothly-functioning group. Objectives of the system are(36):

> "(1) Minimizing input-output time by utilizing magnetic tape as the input-output medium.
>
> (2) Tying together of many jobs to be run as a multi-job entity in order to reduce machine time costs.
>
> (3) Reducing programmer effort and time required to process a job through the check-out stage into the production stage.
>
> (4) Simplifying operating procedures so that machine operators need not be trained specifically for each job and programmers need not be present.
>
> (5) Standardizing procedures relative to layout and programming for greater staff efficiency.
>
> (6) Providing the programmer with input, output, and debugging routines without the usual storage liability."

In order to use the I/O system, the programmer must relinquish use of locations $(0 - 299)_{10}$ in core storage, tapes 1, 2, 3, and 7, logical drum number 1, and all sense switches. For all except the very longest problems, the cost of using the I/O system is more than repaid by the advantages.

CRUTCH

An adjunct to the I/O system is a group of subroutines called CRUTCH, occupying locations $(7000 - 8191)_{10}$ of core storage. CRUTCH contains the common functional subroutines of exponential, logarithm, square root, etc., plus several subroutines used in transfer of instructions or data between the various storage media of the machine.

Operation of the System

The sequence of events involved in making a machine run under control of the I/O system is as follows: (1) The input deck, containing program, data, etc., in proper order is delivered to the 704 coordinator. (2) The coordinator prepares the BCD input tape, utilizing the peripheral card reader and tape unit. (3) The BCD input tape, comprising one or more machine runs together with suitable control flags, is delivered to the machine operator. (4) The 704, in input-translation phase, translates instructions and data into the binary mode, prepares the binary input tape, and automatically enters the compute phase. (5) The I/O system, in compute phase, brings the programs, one at a time, into core, brings in CRUTCH if indicated, and transfers control to the programs. The programs write output on the binary output tape and return control to the system when finished. When all programs have been run, the 704 automatically enters the next phase. (6) During output-translation phase, the binary output tape is translated and written on the BCD output tape, which is then dismounted and taken to the peripheral room. (7) The BCD output tape is printed on the peripheral printer, and the results are returned to the originators of the machine runs.

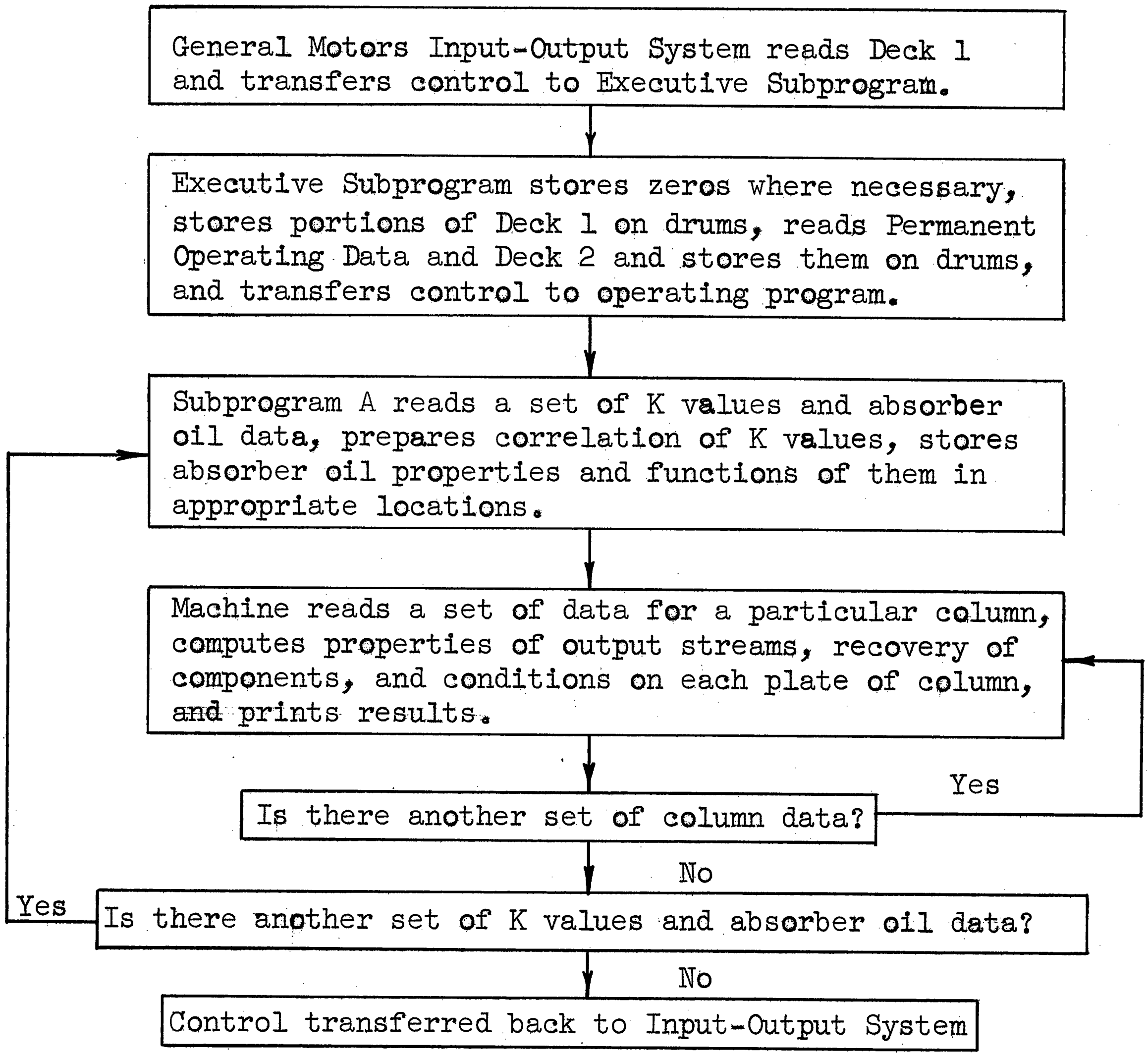
B. Machine Run Procedure

Figure 23 illustrates the control sequence for a typical production run. The contents of Decks 1 and 2 are given in Table 25. The composition of the input deck for a machine run is the following:

(1) "A" Record - A single blue card containing information required by the I/O system. Column 63 contains an 11 or minus punch, the signal that CRUTCH is to be brought into core just before transferring control to the program.

(2) Deck 1 - Manilla-colored column binary program cards with identification numbers U00Z5001 through U00Z5146, the last card of which is an "END" or transition card and is the signal for transfer of control to the Executive subprogram.

(3) Permanent Operating Data - Green class 2 (specified field, floating point decimal) data cards, containing the following data: molecular weights, normal boiling points, critical temperatures, critical pressures, cube roots of kinematic viscosities at 60°F, cube roots of kinematic viscosities at 200°F, specific gravities, molecular volumes to the 0.6 power, molecular volumes to the 1/3 power, vapor diffusivity constants, ideal gas enthalpy coefficients, Beattie-Bridgeman constants, and pressure correction constants. Identification numbers are B67E4001



General Motors Input-Output System reads Deck 1 and transfers control to Executive Subprogram.

Executive Subprogram stores zeros where necessary, stores portions of Deck 1 on drums, reads Permanent Operating Data and Deck 2 and stores them on drums, and transfers control to operating program.

Subprogram A reads a set of K values and absorber oil data, prepares correlation of K values, stores absorber oil properties and functions of them in appropriate locations.

Machine reads a set of data for a particular column, computes properties of output streams, recovery of components, and conditions on each plate of column, and prints results.

Is there another set of column data?

Is there another set of K values and absorber oil data?

Control transferred back to Input-Output System

Figure 23. Machine Run Procedure.

TABLE 25

COMPOSITION OF PROGRAM DECKS

Block	Title/Purpose	Symbol	Locations
1-E	Executive Subprogram	E	5030-6999
1-C	Plate-to-Plate Calculation Subprogram	C	0360-1877
1-D	Output Subprogram	D	2150-2404
1-R	Plate Efficiency Subroutine	PLEFF	2410-2936
1-S	Vapor Density Subroutine	VDENS	2940-3278
1-U	Vapor Diffusivity Subroutine	VDIFF	3280-3456
1-V	Liquid Diffusivity Subroutine	LDIFF	3460-3574
1-X	Heat Transfer Efficiency Subroutine	HTEFF	3595-3793
1-Y	Thermal Conductivity Subroutine	TCOND	3795-3923
1-N	Dew Point, Bubble Point Subroutine	DEWPT BUBPT	3925-4156
1-P	Convergence Pressure Subroutine	CONVP	4160-4499
1-Q	K Value Subroutine	KVALU	4505-4774
1-T	Liquid Density Subroutine	LDENS	4780-4874
1-W	Liquid Viscosity Subroutine	LVISC	4880-5025
2-A	Data Conversion Subprogram	A	0360-1424
2-B	Initial Approximation Subprogram	B	1425-2409
2-F	Stream Temperature (Vapor or Liquid) Subroutine	VTEMP LTEMP	2410-2578
2-G	Vapor Enthalpy Subroutine	VAPEN	2580-2658
2-H	Liquid Enthalpy Subroutine	LIQEN	2660-2765
2-J	Ideal Gas Enthalpy Subroutine	IDGAS	2895-2993

TABLE 25

COMPOSITION OF PROGRAM DECKS (CONT'D)

Block	Title/Purpose	Symbol	Locations
2-K	Pressure Correction	PCORR	2995-3596
2-L	Heat of Vaporization Subroutine	HVAPN	3600-3686
2-M	Enthalpy Change of Subcooled Liquid Subroutine	SUBCL	3740-3906
CRUTCH	Transfer instructions or data from magnetic tape into core memory	GOREAD	7050-7078
		READOV	0252
		READTR	0253
CRUTCH	Transfer instructions or data between core and magnetic tape or drums	DRMTAP	7282-7321
CRUTCH	Print output	GODUMP	7187-7255
		NODUMP	7187-7255
		WRITER	7112-7186
		REMARK	7094-7111
CRUTCH	Exponential	GMEXP1	7418-7490
CRUTCH	Natural Logarithm	GMLOG1	7365-7417
CRUTCH	Square Root	GMSQT2	7342-7364
CRUTCH	Turn off accumulator overflow, multiplier-quotient overflow, divide check, and tape check triggers	TRGOFF	7088-7093
CRUTCH	Space printer to top of next page	EJECT1	7322-7338
CRUTCH	Space printer to top of next 1/6 page	EJECT6	7322-7338

through B67E4159. Cards B67E4118 and B67E4159 have a minus punch in column 1 to indicate returns from the READOV subroutine.

(4) Deck 2 - Manilla column binary program cards with identification numbers U00Z6001 through U00Z6112. The last card is a transition card returning control from the READTR subroutine to the Executive subprogram.

(5) K Value and Absorber Oil Data - Green class 2 data cards with identification numbers in the series U00Z5---. K values must be given for every component appearing in following column data sets. One or two absorber oil components must be specified. The last card contains a minus punch in column 1. One or more sets, each followed by one or more sets of column data, may appear.

(6) Column Data - Green class 6 (variable field; octal, fixed point decimal, floating point decimal) data cards with identification numbers in the series U00Z6---. One or more sets may be used with each set of K value and absorber oil data. The last card of the last set contains a plus punch (12) in column 1; last cards of all other sets contain a minus punch in column 1.

C. Programming and Coding Policy

Assembly

The SHARE Assembly Program (SAP), originally written by the United Aircraft Corporation and subsequently modified by the Data Processing Group, General Motors Research Staff, was used in coding and assembly of the problem. The program consisted of two decks, each containing several "blocks" of coding. Each block was a separate subprogram or subroutine and was distinguished by its own alphabetic character in column 76 of each of the decimal symbolic program cards.

Transfer of Control

Transfer between subprograms was made by the direct, unconditional transfer instruction (TRA). Transfer between subprograms and subroutines or between two subroutines was accomplished by the Transfer and Set Index (TSX) instruction, which is the standard method of transfer to subroutines.

Subroutine Conventions

The program was arranged in blocks, called subprograms or subroutines, in an attempt to facilitate the checking out, modification, and replacement of portions of the program. Because of the size of the program, a rigid set of conventions had to be devised and followed in order to avoid confusion in the use of subroutines. These rules were as follows:

(1) Index register 4 was used in the calling sequence of all subroutines. (This is a SHARE convention.)

(2) The machine had to store the contents of index register 4 before executing a TSX instruction, but the subroutine to which the machine transferred was required to store the contents of index registers 1 and 2 and to replace them before the return transfer.

(3) Index register 1 was usually used for handling the 25 components; index register 2, for counting iterations around a loop.

(4) All iterative procedures had a counting arrangement, even if there were other exits from the loop, in order to insure that an exit would eventually be made.

(5) If data were to be used or treated by more than one subprogram or subroutine, they were stored in block E (Executive Subprogram). Otherwise, they were stored in the block using them.

(6) The calling sequence of a subroutine contained all information that the subroutine (and any other subroutines which it employed) required for its operation. No exchange of information between blocks, other than by means of a calling sequence, was allowed.

(7) Blocks of data, such as a group of 25 mole fractions, were designated by the first address, e.g., x_m. If a subroutine required incremented addresses for an indexed instruction, e.g., $x_m + 25$, the subroutine incremented it.

(8) If a subroutine returned one or two items of information, they were placed in the accumulator and the multiplier-quotient registers before the return. Otherwise, the calling sequence specified the first location of the block in which the data were to be stored.

(9) If the indication that a certain function or piece of information occurring in a group of locations had not been calculated was to be zero, the subroutine first stored zeros in all locations of the group, then filled the appropriate ones.

(10) Subroutines checked input data for reasonableness and gave an error or off-range return if indicated.

(11) In the event an error occurred in a subroutine, the subroutine gave an indication of it with a remark or dump, but the parent program took necessary corrective action if possible.

(12) All subroutines (except library subroutines not written by the author) performed formal initiating and terminating procedures.

The initiating procedure included (1) storing contents of accumulator, multiplier-quotient register, and index registers, (2) transferring information to calling sequences of other subroutines, (3) incrementing and storing addresses furnished by the calling sequence, and (4) executing TRGOFF. The terminating procedure included (1) checking error triggers and giving an error return if indicated, (2) restoring contents of index registers, (3) loading answers into the accumulator and multiplier-quotient registers (if applicable), and (4) returning to the parent subroutine or subprogram.

D. User's Instructions

The term "user" is used in place of "operator", which occurs in most discussions of this type, in recognition of the roles which various persons play in the operation of the I/O system. The program operates entirely within the system, so neither the coordinator nor the machine operator need have any knowledge of the problem. These instructions are for the person who desires to use the program to solve a problem. Knowledge of the IBM 704 and the I/O system, which may be obtained from References (36) and (57), is assumed.

Machine Storage

In the following discussion, all locations will be given in the decimal number system. In the analysis of a word or storage unit, the octal representation will be used.

Components

The order of components is (1) hydrogen, (2) nitrogen, (3) methane, (4) ethylene, (5) ethane, (6) propylene, (7) propane, (8) isobutane,

(9) n-butane, (10) isopentane, (11) n-pentane, (12) hexane, (13) heptane, (14) octane, (15) nonane, (16) decane, (17) 1st absorber oil component, (18) 2nd absorber oil component, (19) carbon monoxide, (20) oxygen, (21) carbon dioxide, (22) hydrogen sulfide, (23) water vapor, (24) and (25) not used. If there is one absorber oil component, it should be the first; if there are two, the less volatile should be the second. The order or identity of components should be changed only with extreme care and a complete knowledge of the program.

K Values

Class 2, five-digit data cards have been found most convenient for loading K data, but actually any applicable type card may be used to load the indicated data into the proper locations. All numbers are in floating point form.

Location	Datum
5979	Pressure (psia) of K value correlation
5980	t_1 in K correlation (0°F)
5981	t_2 (100°F)
....	
5988	t_9 (800°F)
5989	1st (lower) convergence pressure, p_{k1}
5990	2nd (higher convergence pressure, p_{k2}
5991	$K_{1,1}$ (component 1 at t_1) at p_{k1}
5992	$K_{2,1}$ (component 1 at t_2)
....	
5999	$K_{9,1}$ (component 1 at t_9) at p_{k1}
6000	$K_{1,2}$ (component 2 at t_1)
....	

Location	Datum
6008	$K_{9,2}$
....	
6215	$K_{9,25}$ (component 25 at t_9) at p_{k1}
6216	$K_{1,1}$ (component 1 at t_1) at p_{k2}
....	
6440	$K_{9,25}$ at p_{k2}

The temperature range 0°F to 800°F was found necessary for computing bubble points of lean oils. The program is flexible, however, and any temperature range above 0°F may be used, provided only that the temperatures t_1 through t_9 be equally spaced. K values need be given only for the components that appear in the column data sets which follow. The program writes over the original data, so a complete set must be given each time.

Absorber Oil Data

A complete set of data must be given for each absorber oil component used; only one need be used in any problem, however. All numbers are in floating point form.

Location	Datum
6441	Molecular weight of 1st absorber oil
6442	Normal boiling point in °F
6443	Critical temperature in °F
6444	Critical pressure in psia
6445	Kinematic viscosity at 60°F
6446	Kinematic viscosity at 200°F

Location	Datum
6447	Specific gravity (or API gravity with negative sign)
6448	Heat of vaporization at 77°F in Btu/lb mole
6449	Molecular weight of 2nd absorber oil
....	
6456	Heat of vaporization of 2nd absorber oil

The last card of the absorber oil data must have a minus punch in column 1.

Column Data

Class 6 data cards have been found most convenient for loading column data, but again any appropriate data card type may be used. Numbers are in floating point decimal form unless specified otherwise.

Location	Datum
6459	Column identification number (octal)
6460	Rich gas dimension code flag (octal)
6461	Lean oil dimension code flag (octal)
6462	Column dimension code flag (octal)
6463	Computation code flag (octal)
6464	Number of actual plates (fixed decimal)
6465	Quantity of rich gas
6466	Thermal energy indication of rich gas
6467	Quantity of lean oil
6468	Thermal energy indication of lean oil
6469	Composition of component 1 in rich gas
6470	Composition of component 2 in rich gas
....	

Location	Datum
6493	Composition of component 25 in rich gas
6494	Composition of component 1 in lean oil
....	
6518	Composition of component 25 in lean oil
6519	Column pressure in psia
6520	Column diameter in ft
6521	Plate spacing
6522	Length of liquid path across plate in ft
6523	Weir height
6524	Heat loss by convection and radiation
6525	Fraction of column cross section for vapor flow
6526	1st side stream cooling (intercooling) data (octal)
....	
6535	10th side stream cooling (intercooling) data (octal)
6536	Initial estimate mole fraction of component 1 in lean gas, or initial estimate fractional recovery of component 1
6537	Initial estimate... component 2...
....	
6560	Initial estimate... component 25...
6561	Initial estimate mole fraction of component 1 in rich oil
....	
6585	Initial estimate... component 25...
6695	Initial estimate temperature of lean gas in °F
6749	Initial estimate temperature of rich oil in °F

Data need not be loaded into locations 6526 - 6585, 6695, and 6749 unless specified by code flags.

Code Flags

A code flag is a twelve-digit octal number. The left-most digit, together with the sign, which may be omitted if positive, is called the prefix (P); the next five digits are the decrement (D); the next one, the tag (T); and the right-most five, the address (A). The significance of the various code flags is given below.

Flag	Code	Meaning
Gas	P = 1	Thermal energy indication given by temperature in °F
	P = 2	Energy indication is enthalpy in Btu/lb
	P = 4	Energy indication is enthalpy in Btu/lb mole
	D = 1	Composition in mole fraction
	D = 2	Composition in weight fraction
	T = 1	Unit time is one second
	T = 2	Unit time is one hour
	T = 4	Unit time is one day
	A = 1	Quantity of stream in moles/unit time
	A = 2	Quantity of stream in SCF/unit time
	A = 4	Quantity of stream in lb/unit time
Oil	Same as Rich Gas Dimension Code Flag	
Column	P = 1	All column dimensions in ft
	P = 2	Weir height and plate spacing in in., others in ft
	D = 1	No intercooling
	D = 2	Intercooling in Btu/unit time
	D = 4	Intercooling given by temperature change in °F
	T = 1	Unit time is one second
	T = 2	Unit time is one hour
	T = 4	Unit time is one day

Flag	Code	Meaning
Column	A = 1	No convection and radiation heat loss
	A = 2	Heat loss in Btu/unit time for whole column
	A = 4	Heat loss in Btu/ft^2 (unit time)
Compute	P = 1	Machine is to compute initial estimate of outlet compositions and temperatures
	P = 2	Initial estimate of outlet compositions and temperatures is given
	P = 4	Initial estimate of fractional recoveries of components is given
	D	Maximum number of complete column iterations
	T = 1	Print final results and column summary on last iteration only
	T = 2	Print column summary after each iteration and complete plate results on last iteration
	T = 4	Print complete plate results and column summary on each iteration

At the conclusion of a column run, the machine will have changed input data into the standard units of the program--moles, mole fractions, feet, seconds, and °F. The output stream compositions will be loaded into locations 6536 through 6585, the temperatures will be in locations 6695 and 6749, and the prefix of the Computation Code Flag will be +2. Table 26 contains a typical set of column data.

Dumps

Dumps in the 306-- series, originally diagnostic, have been left in operation to give a running account of progress at the end of each column iteration (every 30 to 60 seconds, usually). Numbers in locations 1126 - 1150 are the values of r_1 of the various components; locations 6692 - 6716 contain values of $\overline{\ell}_{1,i}$ for the next iteration;

TABLE 26

A TYPICAL SET OF COLUMN DATA

Addr.*	Opn.	Data	Identification
6459	OCT	001005001001	U00E6701
6460	OCT	100001400001	U00E6702
6461	OCT	100001400001	U00E6703
6462	OCT	100001100001	U00E6704
6463	OCT	200024200000	U00E6705
6464	DEC	24	U00E6706
6465	DEC	83992.,69.,16375.,71.	U00E6707
6469	DEC	0,0,.7529,0,.0564,0,.0505,.0092,.0181,0,0,.0127,0,0,0,0	U00E6708
	DEC	0,0,0,0,.1002,0,0,0,0	U00E6709
6494	DEC	0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,1.,0	U00E6710
	DEC	0,0,0,0,0,0,0	U00E6711
6519	DEC	400.,5.,2.,2.917,.1562,0,.687	U00E6712
6536	DEC	0,0,.81413,0,.05448,0,.0274,.00046,.00009,0,0,.0001	U00E6713
	DEC	0,0,0,0,.00001,0,0,0,.10334,0,0,0,0	U00E6714
6561	DEC	0,0,.085,0,.0253,0,.0854,.0288,.0591,0,0,.0412	U00E6715
	DEC	0,0,0,0,.6471,0,0,0,.026,0,0,0,0	U00E6716
6695	DEC	78.	U00E6717
6749	DEC	92.	U00E6718

* A series of numbers loads sequentially.

location 675 contains the value of $t_{L_{m+1}}$ on the last iteration where m was the highest plate reached. Thus, if a machine error or other difficulty should interrupt computation, the series of dumps will give the minimum information necessary for restarting the problem.

Dump 105 gives the initial estimate of the outlet compositions; dump 106, the initial estimate of recoveries. Any other dumps indicate trouble and should contain information sufficient for diagnosis.

Timing

A column of 20 plates containing 12 components will require about 30 seconds per iteration. Iteration time is roughly proportional to the number of plates and the number of components. About 50 to 100 iterations will be required for convergence, depending upon how good the initial approximation is. It is advisable to make one or two test runs of short duration to insure that the program is working properly.

Convergence Ratio Exponents

The parameters g_i used in the equations

$$(\ell_{1,i})_{k+1} = (\ell_{1,i})_k \, (r_i)^{\left(\frac{g_i}{m^2}\right)} \tag{190}$$

were determined experimentally and found to be suitable for all problems investigated. It is quite possible, however, that they will not produce convergence for some future problems. The parameters are found in locations 479 - 503 of deck 1 and may be changed by override cards. It is recommended that the parameters be reduced by factors of 2 until a successful set is found. Examination of the 306-- series of dumps will show which parameters need to be changed.

Heat Transfer Efficiency Constant

A value of C_q to be used in a given column calculation may be estimated by the method discussed under Analysis of Results, Prediction of the Heat Transfer Efficiency Factor.

E. Subroutine Specifications

All subroutines are restricted to floating point arguments. Contents of index registers 1 and 2 will be restored. SHARE assembly program (SAP) symbolic notation is used in calling sequences, i.e., (Location, Prefix, Address, Tag, Decrement). TRGOFF is executed at the beginning of each subroutine, and if divide check, accumulator overflow, or multiplier-quotient overflow is detected, an error dump and error return will be given. Access to the table of physical properties is assumed.

Plate Efficiency (PLEFF)

Purpose: Given temperature, pressure, compositions of vapor and liquid streams, flow rates, and dimensions of the bubble cap plates; compute the Murphree plate efficiency, E_{MV}, for each component.

Restrictions: E_{MV} are restricted to the range 0.001 to 1.2.

Method: N_G and N_L, based on systems air-water-ammonia and air-water-carbon dioxide, are combined to give N_{OG}. E_p and E_{MV} are computed from the separate phase resistances.

Calling sequence: (t_{L_m} in AC, p in MQ)

```
d        TSX     PLEFF,4
d + 1    PZE     Addr of x_{m,1} ,0, Addr of y_{m-1,1}
```

d + 2 PZE Addr of $K_{m,1}$, 0, Addr for $E_{MV,1}$

d + 3 Value of L_m

d + 4 Value of V_{m-1}

d + 5 Error return

d + 6 Normal return (E_{MV} stored where specified)

Storage required: Instructions-- 250, data-- 252, erasable-- 25.

Other subroutines used: VDENS, LDENS, VDIFF, LDIFF, LVISC, GMSQT2, GMLOG1, GMEXP1, TRGOFF, NODUMP.

Vapor Density (VDENS)

Purpose: Given temperature, pressure, and composition of a vapor mixture, compute its density in lb moles/ft^3.

Restrictions: Mole fractions smaller than 0.001 are ignored.

Method: The volume-explicit form of the Beattie-Bridgeman equation is used(12). Constants for pure components are combined according to methods of Beattie, Stockmayer, and Ingersoll(14).

Calling sequence: (t_V in AC, p in MQ)

d TSX VDENS,4

d + 1 PZE Addr of $y_{m-1,1}$

d + 2 Error return

d + 3 Normal return (ρ_V in AC)

Storage required: Instructions-- 156, data-- 163, erasable-- 20.

Other subroutines used: TRGOFF, NODUMP.

Liquid Density (LDENS)

Purpose: Given temperature and composition of a liquid mixture, compute its density.

Restrictions: Mole fractions smaller than 0.001 are ignored.

Method: Density at 60°F is computed as a summation based on pure component densities. Temperature correction is made.

Calling sequence: (t_L in AC)

```
    d       TSX    LDENS,4
    d + 1   PZE    Addr of x_{m,1}
    d + 2   Error return
    d + 3   Normal return (ρ_L in lb/ft^3 in AC, ρ_L in lb moles/ft^3 in MQ)
```

Storage required: Instructions-- 73, data-- 12, erasable-- 10.

Other subroutines used: TRGOFF, NODUMP.

Vapor Diffusivity (VDIFF)

Purpose: Given temperature, pressure, composition of a vapor stream, and the composition of an adjacent liquid stream, compute the vapor phase diffusivity of each component that appears in either the vapor or the liquid. Units are ft^2/sec.

Restrictions: The correlation is based on the components hydrogen, nitrogen, and the hydrocarbons methane through absorber oil.

Method: Diffusivities of binaries are computed by Gilliland's formula(39). Diffusivities of components in the multicomponent mixture are computed from those of binaries by Wilke's formula(93).

Calling sequence: (t_V in AC, p in MQ)

```
    d       TSX    VDIFF,4
```

d + 1 PZE Addr of $y_{m-1,1}$, 0, Addr for $D_{G,1}$

d + 2 PZE Addr of $x_{m,1}$

d + 3 Error return

d + 4 Normal return (D_G stored where specified)

Storage required: Instructions-- 120, data-- 30, erasable-- 25.

Other subroutines used: GMSQT2, TRGOFF, NODUMP.

Liquid Diffusivity (LDIFF)

Purpose: Given temperature, viscosity, and composition of a liquid mixture, compute the diffusivity of each component in ft^2/sec.

Restrictions: None.

Method: Diffusivities are computed by the method of Wilke and Chang(94).

Calling sequence: (t_L in AC, μ_L in MQ)

d TSX LDIFF,4

d + 1 PZE Addr of $x_{m,1}$, 0, Addr for $D_{L,1}$

d + 2 Error return

d + 3 Normal return (D_L where specified)

Storage Required: Instructions-- 72, data-- 8, erasable-- 35.

Other subroutines used: GMSQT2, TRGOFF, NODUMP.

Liquid Viscosity (LVISC)

Purpose: Given temperature, pressure, density, and composition of a liquid mixture, compute its viscosity in lb/ft sec.

Restrictions: None.

Method: Kinematic viscosities of pure components at 60°F and 200°F are combined according to the formula of Kendall(59). Temperature dependence is expressed according to Cornelissen and Waterman(24). Further correction is made for pressure.

Calling sequence: (t_L in AC, p in MQ)

d	TSX	LVISC,4
d + 1	Value of liquid density	
d + 2	PZE	Addr of $x_{m,1}$
d + 3	Error return	
d + 4	Normal return (μ_L in AC)	

Storage required: Instructions-- 108, data-- 23, erasable-- 15.

Other subroutines used: GMLOG1, GMEXP1, TRGOFF, NODUMP.

Heat Transfer Efficiency (HTEFF)

Purpose: Given temperature, pressure, composition and density of a vapor phase, and individual component Murphree plate efficiencies, compute the heat transfer efficiency.

Restrictions: E_q is restricted to the range 0.05 to 1.0.

Method: Specific heat of the vapor phase and vapor thermal conductivities of all components are computed. Efficiency is estimated by the summation

$$E_q = C_q \sum_i y_{m,i} \left(\frac{k_i}{c_p \rho_V D_{G,i}}\right)^{2/3} \tag{246}$$

Calling sequence: (t in AC, p in MQ)

d	TSX	HTEFF,4
d + 1	PZE	Addr of $y_{m,1}$, 0, Addr of $E_{MV,1}$
d + 2	PZE	Addr of $D_{G,1}$
d + 3	Value of vapor density	

d + 4 Error return

d + 5 Normal return (E_q in AC)

Storage required: Instructions-- 117, data-- 66, erasable-- 15.

Other subroutines used: VAPEN, TCOND, GMLOG1, GMEXP1, TRGOFF, NODUMP.

Thermal Conductivity (TCOND)

Purpose: Given temperature and composition of a vapor mixture, compute thermal conductivity of all components appearing. Units are Btu/sec ft °F.

Restrictions: None.

Method: Values at 32°F are stored. Temperature dependence is computed according to the Sutherland equation.

Calling sequence: (t_V in AC)

```
    d        TSX    TCOND,4
    d + 1    PZE    Addr of y_m,1 , 0, Addr for k_1
    d + 2    Error return
    d + 3    Normal return (k_i where specified)
```

Storage required: Instructions-- 63, data-- 56, erasable-- 10.

Other subroutines used: TRGOFF, NODUMP.

Stream Temperature (VTEMP or LTEMP)

Purpose: Given the molal enthalpy and composition of a vapor or liquid stream and the pressure, find the temperature.

Restrictions: Temperature must be in the range -100°F to 800°F. If outside the range, the bound exceeded is given and the off-range return is made.

Method: The Newton method is used to find a temperature corresponding to the molal enthalpy given.

Calling sequence: ($\underline{H}_V$ or $\underline{H}_L$ in AC, p in MQ)

d TSX VTEMP,4

d + 1 PZE Addr of $y_{m,1}$, 0, Addr of 1st approx. to t_V (or zero)

d + 2 Error return

d + 3 Off-range return (bound in AC)

d + 4 Normal return (t_V in AC)

The calling sequence for LTEMP is similar to the above.

Storage required: Instructions-- 140, data-- 14, erasable-- 15.

Other subroutines used: VAPEN (with VTEMP) or LIQEN and LIQSC (with LTEMP), TRGOFF, NODUMP.

Vapor Enthalpy (VAPEN)

Purpose: Given temperature, pressure, and composition of a vapor mixture, compute its enthalpy in Btu/lb mole.

Restrictions: If t_V is outside the range -100°F to 800°F, the exceeded bound is used instead of t_V and the off-range return is made.

Method: $\underline{H}_V$ is computed as the sum of $\underline{H}^o_{t_V}$ and $\Delta\underline{H}^{pc}_{t_V}$, the ideal gas enthalpy and the pressure correction to the ideal gas enthalpy at t_V, respectively.

Calling sequence: (t_V in AC, p in MQ)

d TSX VAPEN,4

d + 1 PZE Addr of $y_{m,1}$

d + 2 Error return

d + 3 Off-range return ($\underline{H}_V$ in AC)

d + 4 Normal return ($\underline{H}_V$ in AC)

Storage required: Instructions-- 60, data-- 9, erasable-- 10.

Other subroutines used: IDGAS, PCORR, TRGOFF, NODUMP.

Liquid Enthalpy (LIQEN, LIQSC)

Purpose: Given temperature, pressure, and composition of a liquid mixture, compute its enthalpy in Btu/lb mole.

Restrictions: If t_L is outside the range -100 °F to 800 °F, the exceeded bound is used instead of t_L and the off-range return is made.

Method: $\underline{H}_L$ is computed as the sum of $\underline{H}^o_{77}$, $\Delta\underline{H}^v_{77}$, and $\Delta\underline{H}^{sc}$, the ideal gas enthalpy at 77 °F, the isothermal heat of vaporization at 77 °F, and the enthalpy change of the subcooled liquid between 77 °F and t_L. If LIQSC (liquid enthalpy, short cut) is used, the machine computes a new value only of $\Delta\underline{H}^{sc}$, using the values of $\underline{H}^o_{77}$ and $\Delta\underline{H}^v_{77}$ determined in an earlier use of LIQEN.

Calling sequence: (t_L in AC, p in MQ)

d TSX LIQEN,4 (or LIQSC,4)
d + 1 PZE Addr of $x_{m,1}$
d + 2 Error return
d + 3 Off-range return ($\underline{H}_L$ in AC)
d + 4 Normal return ($\underline{H}_L$ in AC)

Storage required: Instructions-- 82, data-- 14, erasable-- 10.

Other subroutines used: IDGAS, HVAPN, SUBCL, TRGOFF, NODUMP.

Ideal Gas Enthalpy (IDGAS)

Purpose: Given temperature and composition of a vapor mixture, compute the ideal gas enthalpy in Btu/lb mole.

Restrictions: Mole fractions less than 0.001 are ignored.

Method: Enthalpies of pure components are computed by fifth-order polynomials and are then summed by mole fraction.

Calling sequence: (t_V in AC)

```
    d       TSX    IDGAS,4
    d + 1   PZE    Addr of y(m,1) or x(m,1)
    d + 2   Error return
    d + 3   Normal return (H° in AC)
```

Storage required: Instructions-- 76, data-- 8, erasable-- 15.

Other subroutines used: TRGOFF, NODUMP.

Pressure Correction (PCORR)

Purpose: Given temperature, pressure, and composition of a vapor mixture, compute the pressure correction to the ideal gas enthalpy in Btu/lb mole.

Restrictions: Parameters in the correlation are restricted to the following ranges: $0 \leqslant P_r \leqslant 2.0$, $0.3 \leqslant T_r \leqslant 3.0$, $0.3 \leqslant B_r \leqslant 2.2$. A parameter exceeding a bound is replaced by that bound. Mole fractions less than 0.001 are ignored.

Method: The partial molal pressure correction of each component is computed as a function of reduced temperature, reduced pressure, and reduced boiling point. Corrections are combined by mole fraction.

Calling sequence: (t_V in AC, p in MQ)

```
    d       TSX    PCORR,4
    d + 1   PZE    Addr of y(m,1)
```

d + 2 Error return

d + 3 Normal return ($\underline{\Delta H}^{pc}$ in AC)

Storage required: Instructions-- 187, data-- 395, erasable-- 20.

Other subroutines used: TRGOFF, NODUMP.

Heat of Vaporization (HVAPN)

Purpose: Given the composition of a liquid mixture, compute its isothermal heat of vaporization at 77°F in Btu/lb mole.

Restrictions: Mole fractions less than 0.001 are ignored.

Method: Partial molal heats of vaporization at 77°F are combined by mole fraction.

Calling sequence:

d TSX HVAPN,4

d + 1 PZE Addr of $x_{m,1}$

d + 2 Error return

d + 3 Normal return ($\underline{\Delta H}^{v}_{77}$ in AC)

Storage required: Instructions-- 52, data-- 30, erasable-- 5.

Other subroutines used: TRGOFF, NODUMP.

Enthalpy Change of Subcooled Liquid (SUBCL)

Purpose: Given t_1 and t_2 of a liquid mixture and its composition, compute the enthalpy change in heating or cooling from t_1 to t_2. Units are Btu/lb mole.

Restrictions: Mole fractions smaller than 0.001 are ignored.

Method: Specific heat at the average of t_1 and t_2 is computed by the formula of Fallon and Watson(33). Enthalpy change is computed as the product of specific heat, molecular weight, and temperature change.

Calling sequence: (t_1 in AC, t_2 in MQ)

```
     d        TSX     SUBCL,4
     d + 1    PZE     Addr of x_{m,1}
     d + 2    Error return
     d + 3    Normal return  (ΔH^{sc} in AC)
```

Storage required: Instructions-- 122, data-- 25, erasable-- 20.

Other subroutines used: TRGOFF, NODUMP.

K Value (KVALU)

Purpose: Given temperature, pressure, composition, and the natural logarithm of convergence pressure, compute the K value of every component appearing in the mixture.

Restrictions: Temperature is restricted to 1.5 times the range of the correlation. Convergence pressure must lie between the two on which K correlations are based. A variable exceeding a bound is replaced by that bound.

Method: The natural logarithm of K is computed as a function of temperature and pressure at each of the two convergence pressures used in the correlation. Interpolation of $\ell n(K)$ versus $\ell n(p_k)$ is performed. The subroutine contains its own exponential routine based on a formula of Hastings(47).

Calling sequence: (t in AC, p in MQ)

```
     d        TSX     KVALU,4
     d + 1    Value of ℓn(p_k)
```

d + 2 PZE Addr for K_1, 0, Addr of $x_{m,1}$ or $y_{m,1}$

d + 3 Error return

d + 4 Normal return (K values where specified)

Storage required: Instructions-- 167, data-- 88, erasable-- 20.

Other subroutines used: TRGOFF, NODUMP.

Convergence Pressure (CONVP)

Purpose: Given temperature and composition of a liquid mixture, compute the natural logarithm of its convergence pressure.

Restrictions: If hydrogen is present, the convergence pressure is immediately set equal to 20,000 psia. If there is no component lighter than ethylene, p_k of 1000 psia is used. Only hydrogen, nitrogen, and the hydrocarbons are used in the correlation.

Method: The natural logarithm of convergence pressure is computed according to the method of Lenoir and White(65).

Calling sequence: (t_L in AC)

d TSX CONVP,4

d + 1 PZE Addr of $x_{m,1}$

d + 2 Error return

d + 3 Normal return [$\ell n(p_k)$ in AC]

Storage required: Instructions-- 185, data-- 133, erasable-- 20.

Other subroutines used: TRGOFF, NODUMP.

Dew Point - Bubble Point (DEWPT - BUBPT)

Purpose: Given pressure, composition, and a first approximation to the temperature sought (optional), compute the dew point or bubble point temperature in °F.

Restrictions: Negative mole fractions are ignored.

Method: In DEWPT, a temperature is found which produces the equality

$$\sum_i \frac{y_i}{K_i} = 1 \tag{201}$$

In BUBPT, a temperature is found which produces the equality

$$\sum_i (x_i)(K_i) = 1 \tag{246}$$

The method of false position is used.

Calling sequence: (1st approx. of t_{dp} in AC, p in MQ)

```
     d       TSX    DEWPT,4
     d + 1   PZE    Addr of y_{m,1}, 0, Addr for K_1
     d + 2   Error return
     d + 3   Normal return (t_dp in AC)
```

The calling sequence for BUBPT is similar to the above.

Storage required: Instructions-- 174, data-- 47, erasable-- 10.

Other subroutines used: CONVP, KVALU, TRGOFF, NODUMP.

F. Availability of Program

A listing of the machine program requires approximately one hundred sheets of IBM 407 tabulator paper. A microfilm copy is in the possession of Professor J. T. Banchero, Department of Chemical and Metallurgical Engineering, University of Michigan. The machine program, as punched cards, is filed with the Data Processing Group, General Motors Research Staff, Detroit, Michigan

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XII. NOMENCLATURE

Capitals

A	A parameter used in evaluating the temperature dependence of η.
A_e, A'	Functions used in the Edmister effective absorption factor method.
A_{cs}	Cross-sectional area of the froth layer, ft^2.
$A_{j,i}$	Ideal gas enthalpy correlation coefficients.
$A_{m,i}$	Absorption factor of component i on plate m.
$A_{o,i}$	First constant for component i in the Beattie-Bridgeman equation of state.
^oAPI	API gravity of a liquid.
B	Bottoms stream flow rate from a fractionator, lb moles/sec.
B	A parameter used in evaluating the temperature dependence of η.
$B_{o,i}$	Second Beattie-Bridgeman constant of component i.
B_r	Reduced boiling point.
C	Number of components in a system.
C_q	Heat transfer efficiency factor.
C_s	Sutherland constant, °R.
D_G	Diffusion coefficient in the gas or vapor phase, ft^2/sec.
D_L	Diffusion coefficient in the liquid phase, ft^2/sec.
E_a	Absorption efficiency.
E_m	Enthalpy balance error on plate m.
E_{MV}	Murphree vapor plate efficiency.
E_p	Murphree vapor point efficiency.
E_q	Heat transfer efficiency.

F	"F" factor equal to $(u)(\rho_V)^{\frac{1}{2}}$, $(ft/sec)(lb/ft^3)^{\frac{1}{2}}$.
F	Empirical factor used in Norman's absorber program.
F	A multi-dimensional region.
F_{NL}	Liquid phase resistance factor.
F_{NV}	Vapor phase resistance factor.
H	Total enthalpy of a stream, Btu/sec.
$\underline{H}$	Molal enthalpy, Btu/lb mole.
$\overline{H}$	Partial molal enthalpy, Btu/lb mole.
K	Vapor-liquid equilibrium ratio.
K'	Characterization factor.
K_{OG}	Overall mass transfer coefficient based on the vapor phase.
L	Liquid flow rate, lb moles/sec.
M	Molecular weight.
N	Mass transfer rate, lb moles/sec.
N	Number of variables in a system (used with subscripts and superscripts).
N_G	Number of vapor phase transfer units.
N_{GH}	Number of overall heat transfer units based on the vapor phase.
N_L	Number of liquid phase transfer units.
N_{OG}	Number of overall mass transfer units based on the vapor phase.
Q	Heat transfer rate, Btu/sec.
R	Universal gas constant (various units).
R_i	Fractional recovery of component i in an absorber.
R_i	Feed plate mesh ratio of component i in a fractionator.
T	Temperature on the absolute scale, °R.

V	Vapor flow rate, lb moles/sec.
$\bar{V}$	Average vapor flow rate through the froth layer.
$\underline{V}$	Molal vapor volume, ft^3/lb mole.
$X_{m,i}$	Number of moles of component i in liquid stream L_m per mole of lean oil, L_{n+1}.
$Y_{m,i}$	Number of moles of component i in vapor stream V_m per mole of rich gas, V_0.

Lower Case

a	Surface area per unit volume of the froth layer, ft^2/ft^3.
a_i	Third Beattie-Bridgeman constant for component i.
$a_{j,i}$	Coefficients of the K value correlation for component i.
a, b	The two components of a binary mixture.
b_i	Flow rate of component i in the bottoms stream of a fractionator.
b_i	Fourth Beattie-Bridgeman constant for component i.
c_i	Fifth Beattie-Bridgeman constant for component i.
c_p	Specific heat at constant pressure, Btu/lb mole °F.
d	First instruction of a calling sequence.
f	Fugacity, atm.
f	Fanning friction factor.
f	A function
g_i	Emperical convergence promotion factor.
h	Heat transfer coefficient, Btu/sec ft^2 °F.
i	Any component of a mixture.
j_D	Colburn "j" factor for mass transfer (diffusion).
j_H	Colburn "j" factor for heat transfer.

k	Thermal conductivity, Btu/sec ft °F.
k_G	Mass transfer coefficient in the vapor phase, lb moles/sec ft^2 atm.
k_L	Mass transfer coefficient in the liquid phase.
ℓ_i	Flow rate of component i in a liquid stream, lb moles/sec.
m	The general plate of a column.
m	Slope of the equilibrium curve.
n	Number of variables in a system of equations.
n	Number of stages or "pools" on a plate.
n	Number of actual stages in a column.
n'	Number of theoretical or ideal stages in a column.
p	Pressure, psia.
p_j	Temperature function in the K value correlation.
p_k	Convergence pressure, psia.
q	A ratio occurring in the Wegstein extrapolation procedure.
r_i	Convergence ratio of component i.
t	Temperature, °F.
u	Vapor linear velocity, ft/sec.
v	Molecular volume, cm^3/g mole.
v_i	Flow rate of component i in a vapor stream, lb moles/sec.
w	Weir height, ft.
w_i	A ratio for component i occurring in the Wegstein procedure.
x	A variable.
x	Length of the liquid path on a bubble plate, ft.
x	Association factor.
x_i	Mole fraction of component i in a liquid mixture.

y_i	Mole fraction of component i in a vapor mixture.
z	Froth height on a plate, ft.
z_i	Mole fraction of component i in either a vapor or a liquid mixture.

Greek Letters

α, β	Functions of partial derivatives in a system of simultaneous, non-linear equations.
$\alpha,\beta,\gamma,\delta$	Coefficients in a polynomial series correlation for K values.
δ	Mass flux in a fractionator, lb moles/sec.
δ_s	Mass flux in an absorber, lb moles/sec.
δ_q	Heat flux in an absorber, Btu/sec.
Δ	An increment or difference.
η	Kinematic viscosity, centistokes.
θ	Residence time, sec.
Λ_m	Total holdup on plate m, lb moles
μ	Absolute viscosity, lb/ft sec.
ρ	Density, lb/ft^3 and lb $moles/ft^3$.
Σ	"The summation of ..."
Φ	Number of phases in a system.
φ	Froth density.
ψ	Temperature function in the K value correlation.

Subscripts and Superscripts

a	Available for specification.
b	Normal boiling point.
bh	Normal boiling point of the heaviest component of a mixture.
$b\ell$	Normal boiling point of the lightest component of a mixture.

c	Critical property.
c	Conditions of a system normally fixed.
e	An element.
e	Enriching section of a fractionator.
E	A complex element or system.
F	Final variable or function.
f	Feed or feed plate.
G	Gas or vapor phase.
he	Effective heavy component.
I	Initial variable or function.
I	Interface condition.
i	The general component of a mixture.
i	Independent variable.
j	A component.
k	An iteration or time interval.
L	Liquid phase.
ℓe	Effective light component.
m	The general plate in a column.
n	The top plate or total number of plates.
o	Ideal gas state.
p	Constant pressure.
pc	Pressure correction.
r	Reduced property.
s	Stripping section of a fractionator.
sc	Subcooled liquid.

t	Constant temperature.
V	Vapor phase.
v	Vaporization
v	Total number of variables.
x	Normally fixed variables.
' (prime)	A revised quantity.
*	Equilibrium value.
¯ (superscript bar)	An average value; a value to be used as the argument of a function.
_ (subscript bar)	A molal quantity.
→	A vector.
$\lvert\;\rvert$	Absolute magnitude or value.