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*I hereby recommend that the thesis prepared under my
supervision by* Charles E. Huckaba
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*be accepted as fulfilling this part of the requirements for the
degree of* Doctor of Philosophy

Approved by:

William Licht

DESIGN METHOD FOR BINARY BATCH RECTIFICATION

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Graduate School of Arts and Sciences
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by

Charles E. Huckaba

B.E. Vanderbilt University 1944

M.S. Massachusetts Institute of Technology 1947

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Table of Symbols

$$a = \frac{N^2 - 1}{N^2 + 2}; \quad a_1 = \frac{N_1^2 - 1}{N_1^2 + 2}; \quad a_2 = \frac{N_2^2 - 1}{N_2^2 + 2}; \quad a_s = \frac{N_s^2 - 1}{N_s^2 + 2}$$

$$b = \frac{N_2^2 - 1}{N_2^2 + 2}$$

c^* = mean specific heat with respect to temperature

c_M = specific heat of methanol

c_I = specific heat of isopropanol

$c_{Mix.}$ = specific heat of a mixture of methanol and isopropanol

d_1 = density of component No. 1

d_2 = density of component No. 2

d_s = density of a solution of components No. 1 and No. 2

D = rate of flow of product in pounds per hour

f = reflux fraction = $\frac{L_R}{V_t}$

$h_{HT} = \frac{\sum H_n h_n}{H}$ = mean specific enthalpy of total holdup in tower in Btu/lb.

h_L = specific enthalpy of a liquid mixture

h_{In} = specific enthalpy of the liquid mixture on plate n in Btu/lb.

h_S = specific enthalpy of the liquid mixture in the still pot at a given time in Btu/lb.

h_{So} = specific enthalpy of the liquid mixture in the still pot at the end of the warmup period in Btu/lb.

h_V = specific enthalpy of a vapor mixture in Btu/lb.

h_{Vn} = specific enthalpy of the vapor mixture on plate n in Btu/lb.

H = weight of total holdup in pounds in the tower or in the section of the tower under consideration

H_n = weight of holdup on plate n in pounds

H_T = weight of total holdup in tower in pounds

H_{TM} = weight of more volatile component in total tower holdup in pounds

H_P = mean weight of holdup per plate in pounds

$$k = \frac{d_1 - d_2}{d_1}$$

$$K = \frac{d_2}{d_1} \frac{N_1^2 - 1}{N_1^2 + 2} - \frac{N_2^2 - 1}{N_2^2 + 2}$$

l_M = latent heat of methanol vapor in Btu/lb.

l_I = latent heat of isopropanol vapor in Btu/lb.

$l_{Mix.}$ = latent heat of vapor mixture in Btu/lb.

L = rate of liquid flow in lbs./hr.; L_R refers to reflux.

$$m = \frac{M_2}{M_1}$$

M_1 = molecular weight of component No. 1

M_2 = molecular weight of component No. 2

N_P = number of plates

N_1 = refractive index of component No. 1

N_2 = refractive index of component No. 2

N_s = refractive index of solution

$r = \frac{a}{d}$ = specific refraction

r_1 = specific refraction of component No. 1

r_2 = specific refraction of component No. 2

r_s = specific refraction of solution

S = total weight of material in still pot in pounds at a given time

S_F = total weight of initial feed to still pot in pounds

S_0 = total weight of material in still pot at end of warmup period

t = time in minutes or hours, beginning at the end of the warmup period

V = rate of vapor flow in lbs./hr.

x = weight fraction of the more volatile component in liquid

x_D = weight fraction of the more volatile component in the product

x_{n+1} = weight fraction of the more volatile component in plate
n+1 liquid

x_H = weight fraction of the more volatile component in the holdup, H

x_{Hn} = weight fraction of the more volatile component in holdup liquid
on plate n

$x_{HT} = \frac{\sum H_n x_n}{H}$ mean weight fraction of more volatile component in
the total tower holdup at any time

x_{HT0} = same as x_{HT} but at the end of the warmup period

x_S = weight fraction of the more volatile component in still pot
liquid at a given time

x_{S0} = weight fraction of the more volatile component in the still
pot liquid at the end of the warmup period

y = weight fraction of the more volatile component in vapor

y_n = weight fraction of the more volatile component in plate n
vapor

$$z = \frac{Kx'}{m + x'} + b$$

α = relative volatility

$$\gamma = (1 - m - \frac{d_1 - d_2}{d_1})$$

$$\phi = \text{fraction distilled} = \frac{Dt}{S_0}$$

$$\psi = (x_D - x_S) \frac{dh_{HT}}{dx_{HT}} + (h_S - h_D)$$

Subscripts (other than those shown above)

$n, n+1, n+2$ refer to the plates under consideration

t refers to the top plate

Numerical subscripts except as otherwise indicated above refer
to plates in the experimental tower.

Superscripts

Primes ($'$) indicate quantities expressed in molal units instead
of ordinary weight units.

x', y' = mole fractions

Part I

ABSTRACT

Although considerable attention has been given to batch rectification during the past decade, a survey of the literature revealed no satisfactory means for treating the quantitative aspects of this operation. The previously proposed design procedures involve questionable assumptions which lead generally to unsatisfactory results. Most of the previous work has been of a theoretical nature without experimental verification. In fact no experimental data that included plate compositions were found in the literature.

The purpose of this investigation was to make an improved theoretical and experimental investigation of binary batch rectification. Accordingly, theoretical relationships for calculating plate compositions and their variation with fraction distilled, involving only justified assumptions, have been developed. These relationships are featured by the use of a weight basis rather than a molal basis and by use of a differential enthalpy balance in addition to differential material balances. Experimental data including all plate compositions were taken and used to check the assumptions on which the theoretical relationships are based. Moreover, these data have been used to show the fallacy of some of the assumptions previously employed in batch rectification calculations.

Using these relationships, a complete procedure has been developed that will permit, for the first time, design calculations for batch rectification that are of comparable validity to those that can be made for continuous rectification. The possibility of simplifying these calculations through use of additional simplifying assumptions has also been investigated and the error caused by the use of the simplified equations has been shown for a variety of operating conditions.

PART II

INTRODUCTION

Batch rectification is a distillation operation that has characteristics in common with both continuous rectification and simple batch distillation. A batch rectification unit consists of a rectification tower mounted over a still pot into which is charged all of the feed at the beginning of the operation. The distillation may be conducted at constant reflux ratio which gives a varying product composition or at variable reflux ratio adjusted continuously in order to maintain a constant product composition.

Batch rectification is employed by industry in those cases where the amount of a given feed to be processed is either small or only available at indefinite times where continuous units would be uneconomical and inflexible. This situation exists especially in plants that manufacture relatively small amounts of a large variety of products. One notable application is in the processing of the "light oil" resulting from the destructive distillation of coal. Wilson and Wells (31) describe the role played by batch rectification in this industry.

The theoretical aspects of both continuous rectification and simple batch distillation are well developed and methods that are both convenient and sufficiently accurate are available for the design of equipment for these operations. However, the same has

not been true for batch rectification even in the case of binary mixtures and this unfortunate circumstance has probably been due to two reasons. Firstly, until recently, there was no general recognition of the fact that many of the steady state assumptions usually made for continuous rectification, and the methods based thereon, cannot be applied to batch rectification calculations. For instance, the McCabe-Thiele method for continuous (steady state) distillation has often been applied to calculate plate compositions (erroneously) for the batch process. Secondly, since conditions vary progressively with time in all parts of a batch rectification unit throughout the entire course of the distillation, the mathematical treatment of the operation tends to be somewhat complex. For this latter reason no work of any importance has been done concerning the batch rectification of multi-component mixtures.

In order to design a batch rectification tower or to determine the optimum conditions of operation for an existing tower, one must be able to calculate the composition of the product as a function of the fraction distilled. This curve, as explained by Rose (16), is the key to the effectiveness of the separation. This computation in turn requires the calculation of still pot composition and of all plate compositions as a function of the product composition. If there were no holdup in the tower, the Rayleigh equation could be used to make the former computation, and the McCabe-Thiele method the

latter. However, the presence of appreciable holdup in the tower greatly limits the use of both of these methods.

A survey of the literature revealed the need for an improved theoretical and experimental investigation of the factors involved in batch rectification. Most of the work in this field consists of attempts to evaluate the effect of various variables on the operation, or of the development of various methods of calculation, most of which are based on wrong or highly questionable assumptions*. For example, many relationships were derived assuming no holdup or constancy of moles of holdup.

The only experimental data reported for plate columns are those of Colburn and Stearns (5) and of Rose et al. (20). However, the value of these data is greatly restricted by the fact that no plate compositions were reported.

Considerable interest has been shown in the nature of the operating "lines" for batch rectification. Although in two publications (5, 18) evidence is presented concerning the non-validity of the McCabe-Thiele lines, there still remained considerable doubt as to both the actual shape of these so-called "lines" and the manner in which they varied during the course of the distillation.

*A more detailed account of the previous work is given in appendix A.

Several authors (5, 11, 14, 15) have written differential material balances for batch rectification but only Rose et al. (18, 19) and Pigford et al. (13) have tried to effect even an approximate solution. Rose and coworkers converted their differential equations into forms involving finite increments by replacing the differentials by Δ 's (e.g. dx became Δx , etc.). They also made the very dubious assumptions of constancy of moles of holdup and of equal molal overflow. Then they calculated in a stepwise incremental fashion the effect down the tower of withdrawing, successively, small finite increments of product. The calculations are very complex and laborious and are best done with the aid of an electronic punched card calculator as described by Rose et al. (19). One of the serious limitations of this method pointed out by the authors is that for a large number of plates, the capacity of the machine is exceeded. Pigford and coworkers, assuming constant moles of holdup, equal molal overflow and an approximate analytical expression for the equilibrium data, combined the latter with the material balance equations in differential form, and effected a solution using a differential analyzer.

The use of an enthalpy balance to aid in the solution of the problem has not been reported in the literature.

In summary, it is fair to say that prior to this investigation neither satisfactory calculational techniques nor adequate experimental data were available even for the case of binary mixtures. Therefore, limiting consideration to binary mixtures, the

purpose of this thesis was two-fold; (1) to obtain accurate experimental data, including all plate compositions, so that complete composition curves and operating "lines" could be plotted, and (2) to use these data to check the results of a thorough investigation of possible theoretical relationships that would permit adequate and straightforward design calculations.

Part III

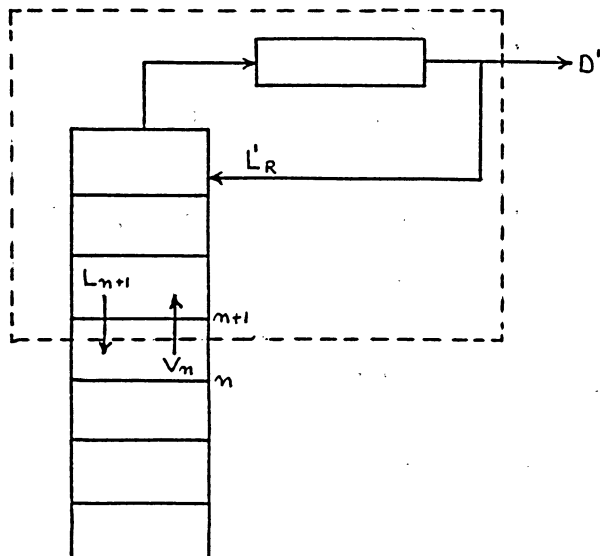
THEORETICAL INVESTIGATION

A. Methods of Approach

In previous investigations it has been customary to derive the theoretical equations for batch rectification in terms of molal quantities, i.e. material quantities were expressed in terms of moles and compositions in terms of mole fractions. The reason for this choice of units probably lies in the fact that they are used in the theoretical derivations for continuous rectification. In this latter case the use of molal quantities is advantageous because with many systems, the components have molal latent heats of vaporization that are very closely equal, whereas the latent heats per pound may differ widely. In continuous rectification a system with equal molal heats of vaporization gives equal molal overflow of liquid from plate to plate down the tower. Under this condition, the operating relationship becomes a straight line which facilitates the plate calculations through use of the convenient McCabe-Thiele method.

Before adopting the same units for batch rectification, one should determine if the same advantages accrue, and at the same time be sure that other means of expression do not offer greater advantages. These questions are best analyzed through consideration of the following differential material balance for batch rectification written in terms of molal quantities around the section of the tower above plate n .

$$V'_n - L'_{n+1} - D' = \frac{dH'_n}{dt}^*$$



With equal molal heats of vaporization (and strictly speaking, equal molal heat capacities), one mole of vapor from plate n condensing on plate $n+1$ would produce one mole of vapor on that plate, so that

$V'_n = V'_{n+1}$: Also at any instant D' is the same for each plate, and therefore if $\frac{dH}{dt}$ for each plate were the same, then L' would be the same; i.e. equal molal overflow would exist. However, $\frac{dH}{dt}$ refers to rate of change of the total holdup above a given plate and this will be different for each plate because compositions (and therefore moles) are changing at different rates on every plate. Therefore, equal molal heats of vaporization do not produce equal molal overflow in batch rectification. Experimental verification of this argument is presented on p. 40. In addition, it can be seen from the following component balance (written around the same section)

*Primes are used to distinguish molal quantities from the ordinary weight quantities used in most of the equations that follow.

that even if equal molal overflow did occur (i.e. $L_n^i = L_{n+1}^i = L_{n+2}^i$ etc.), the operating relationship $y_n = f(x_{n+1})$ would probably not be linear because of the holdup term.

Component balance, basis: dt ,

$$y_n^i V_n^i - x_{n+1}^i L_{n+1}^i - x_D^i D^i = \frac{d}{dt} (x_H^i H^i)$$

$$y_n^i = x_{n+1}^i \frac{L_{n+1}^i}{V_n^i} + x_D^i \frac{D^i}{V_n^i} + \frac{1}{V_n^i} \frac{d}{dt} (x_H^i H^i)$$

At this point it is also easy to understand the inherent weakness in the assumption of constancy of moles of holdup in a batch rectification tower during the course of the distillation. As the compositions change, the number of moles must likewise change. Consequently, previous investigations based on this assumption are of questionable validity.

Thus with no apparent advantage to be gained from using molal quantities, it was decided to investigate the possibility of using ordinary weight units, i.e. pounds and weight fractions. As in the previous case, it can be concluded that the operating relationship will not be a straight line. On the other hand, in many systems, depending on the relative densities of the components, the pounds of holdup, both on a given plate and in the whole tower, will remain very closely constant. In any event, the assumption of constancy of amount of holdup is inherently better when holdup is expressed in terms of pounds than when expressed in terms of moles. Consideration of equations (1), (2), (3), (4), (5)

and (9) in the derivations that follow will show that the assumption of constancy of amount of holdup is desirable in order to reduce the complexity of the relationships.

In the following theoretical development material and enthalpy balances have been combined to give relationships that permit computation both of plate compositions and of product composition as a function of the fraction distilled. Thus, for the first time, it will be shown that one can perform design calculations for batch rectification that are of comparable validity to those one can make for both continuous rectification and simple batch distillation.

Assumptions Made in Derivation of Theoretical Relationships

The following assumptions will be made in the derivation of the basic theoretical relationships;

- (1) Amount of holdup per plate constant, i.e. $\frac{dH_n}{dt} = 0$.

From this it follows that the total holdup in the tower is assumed to be constant. For reasons mentioned previously, ordinary weight units will be used in order to obtain the best conditions for constancy of amount of holdup. It should be noted, however, that if cases should arise such that this condition would be better satisfied in terms of moles, the relationships can be adapted to these units with no change.

- (2) The weight of vapor holdup and its total enthalpy are negligible in comparison with the same for the liquid. A numerical check of this assumption is given in Part V.
- (3) Heat losses from the column are negligible.
- (4) Weight rate of product withdrawal from the tower is constant.

It should be noted that constancy of liquid and vapor flow rates in the tower is not assumed.

After the basic relationships have been developed, the effect of several simplifying assumptions will be investigated. Therefore, at the appropriate place, these other assumptions will be listed and discussed.

B. Derivation of Basic Relationships

It will be shown in Part VII that in order to make complete design calculations for batch rectification, relationships are needed for the calculation of plate compositions and of the product composition as a function of the fraction distilled. Making only the assumptions discussed above, equations and procedures will now be developed for each of these computations.

1. Calculation of Plate Compositions

In order to make plate-to-plate computations, two relationships are required, namely, $y_n = f(x_n)$ and $y_n = f(x_{n+1})$. The first of these relationships is available in the form of the equilibrium data which is generally used in continuous rectification

as such to make calculations for theoretical plates. However, in batch rectification, because of the effect of the changing holdup composition on the calculations, the equilibrium data should be corrected for plate efficiency and then used to make calculations for actual plates. The second relationship, which is usually referred to as the operating relationship or as the operating "line" equation, can be derived by taking balances around an appropriate section of the tower. Since the methods for the procurement of the equilibrium data are the same for batch rectification as for other types of distillation operations, only the development of the operating relationship will be discussed.

Basis: All balances will be taken around plate $n+1$ for a differential increment of time, dt .

Application of Material Balances: (See Fig. 1a)

Total mass balance:

$$L_{n+2} + V_n - L_{n+1} - V_{n+1} = \frac{dH_{n+1}}{dt} = 0 \quad (1)$$

or

$$V_n - L_{n+1} = V_{n+1} - L_{n+2} = D \quad (1a)$$

Component balance:

$$\begin{aligned} L_{n+2} x_{n+2} + V_n y_n - L_{n+1} x_{n+1} - V_{n+1} y_{n+1} = \\ \frac{d}{dt}(H_{n+1} x_{n+1}) = H_{n+1} \frac{dx_{n+1}}{dt} + x_{n+1} \frac{dH_{n+1}}{dt} = \\ H_{n+1} \frac{dx_{n+1}}{dt} \end{aligned} \quad (2)$$

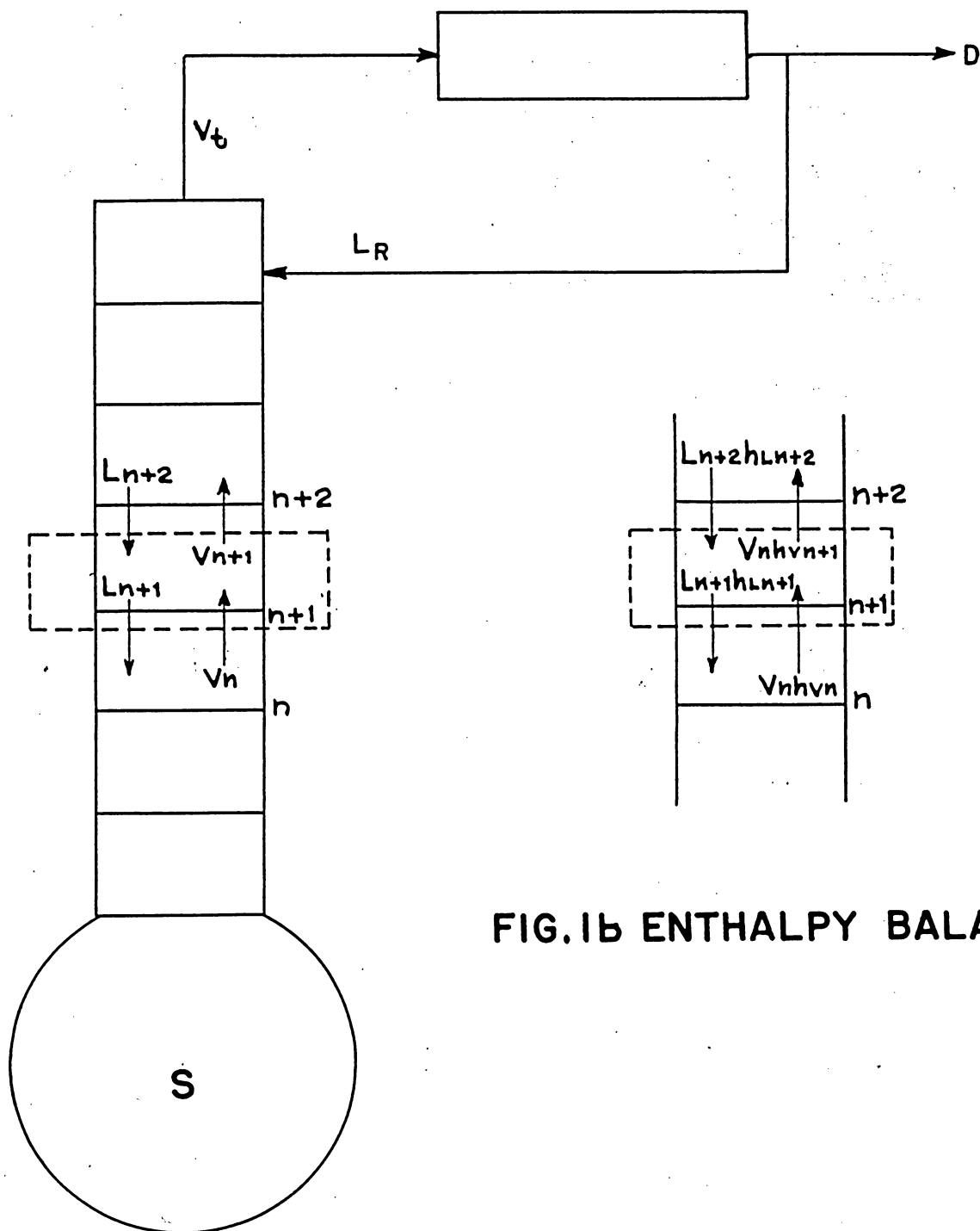


FIG.1B ENTHALPY BALANCE

FIG.1a MATERIAL BALANCE

Application of an Enthalpy Balance: (See Fig. 1b)

$$\begin{aligned}
 L_{n+2} h_{Ln+2} + V_n h_{Vn} - L_{n+1} h_{Ln+1} - V_{n+1} h_{Vn+1} &= \\
 \frac{d}{dt} (H_{n+1} h_{Ln+1}) &= H_{n+1} \cdot \frac{dh_{Ln+1}}{dt} + h_{Ln+1} \cdot \frac{dH_{n+1}}{dt} = \\
 H_{n+1} \cdot \frac{dh_{Ln+1}}{dt} & \quad (3)
 \end{aligned}$$

Equations (1), (2) and (3) are the only independent equations involving y_n and x_{n+1} that can be written around plate $n+1$. However, analysis will reveal that in stepwise computations of values for plates n using previously determined values there are only three independent unknowns, which, assuming that the calculations have been started at the top of the tower, are y_n , V_n , and L_{n+1} . The other/unknown, h_{Vn} , is a unique function of y_n . Therefore these equations can be combined to permit solution of y_n . To eliminate dependence on the rate of boilup, the equations can be written in terms of the fraction distilled, ϕ , as follows,

$$\phi = \frac{Dt}{S_o} \quad (4)$$

Expressed in terms of pounds, D is constant and

$$d\phi = \frac{D}{S_o} \cdot dt \quad \text{or} \quad dt = \frac{S_o}{D} \cdot d\phi \quad (5)$$

Substituting (5) into (2) and (3) and using (1a) to eliminate V_n and V_{n+1} ,

$$\begin{aligned}
 L_{n+2} (x_{n+2} - y_{n+1}) + L_{n+1} (y_n - x_{n+1}) + D (y_n - y_{n+1}) &= \\
 \frac{H_{n+1}}{S_o} \cdot \frac{dx_{n+1}}{d\phi} & \quad (2a)
 \end{aligned}$$

$$L_{n+2} (h_{Ln+2} - h_{Vn+1}) + L_{n+1} (h_{Vn} - h_{Ln+1}) + D (h_{Vn} - h_{Vn+1}) = \frac{H_{n+1}}{S_o} \cdot \frac{dh_{Ln+1}}{d\phi} \quad (3a)$$

The procedure for calculating plate compositions corresponding to a chosen value of ϕ using (2a) and (3a) is as follows:

Given a desired x_D vs. ϕ curve, S_o , and x_{S_o} .

- a. Select values for reflux fraction $\frac{L_R}{V_t} = f$ and rate of flow of product, D .
- b. Choose a series of product compositions from the x_D vs. ϕ curve, say at $\Delta \phi = 0.10$.
- c. With a total condenser $y_t = x_D = x_R$, and thus from corrected liquid-vapor composition curve, obtain values of x_t corresponding to each y_t .
- d. Plot x_t vs. ϕ and evaluate $\frac{dx_t}{d\phi}$ for each point; from an enthalpy-concentration chart obtain values for h_{Lt} corresponding to each x_t , plot h_{Lt} vs. ϕ and evaluate $\frac{dh_{Lt}}{d\phi}$ for each point.
- e. Obtain values of y_{t-1} as follows; ($n = t-1$, $n+1 = t$, and $n+2 = R$).

(1) Assume values for y_{t-1} and use equation (3a)

to obtain values of L_t . (H_{n+1} can be calculated from plate dimensions).

(2) Using these values of L_t , obtain values for y_{t-1} from equation (2a).

(3) Repeat until each calculated value of y_{t-1} checks its assumed value.

f. Obtain values of x_{t-1} by repeating step (c).

g. Obtain values of y_{t-2} by repeating steps (d) and (e).

Thus, the calculation of plate compositions can be continued to any desired point.

The trial and error involved in step (e) is caused by the fact that the relationship between enthalpy and concentration is in graphical form. Consideration was given to the possibility of effecting an analytical solution at this point. Among other things, this would require an analytical expression for temperature as a function of x and y . It was found that even the inadequate assumption of linear functions for these relationships leads to a very complex cubic equation. Consequently, no further attempt was made to obtain an analytical solution.

2. Computation of Product Composition as a Function of the Fraction Distilled

The required relationship can be derived by writing overall material and enthalpy balances.

Basis: Balances taken around the entire tower (see Fig. 1a) for a differential increment of time, dt .

Application of material balances;Total mass balance;

$$\frac{dS}{dt} + \frac{dH}{dt} = D \quad (4)$$

Assuming $\frac{dH}{dt} = 0$,

$$\frac{dS}{dt} = D \quad (4a)$$

Component balance;

$$\frac{d}{dt} (Sx_S) + \frac{d}{dt} (Hx_{HT}) = x_D D \quad (5)$$

$$\text{where } x_{HT} = \frac{\sum H_n x_n}{H}$$

Substituting for D from (4a) and assuming $\frac{dH}{dt} = 0$,

$$S \frac{dx_S}{dt} + x_S \frac{dS}{dt} + H \frac{dx_{HT}}{dt} = x_D \frac{dS}{dt} \quad (6)$$

or

$$S dx_S + (x_S - x_D) dS + H dx_{HT} = 0 \quad (6a)$$

Dividing by S and $(x_S - x_D)$ and separating the variables,

$$\begin{aligned} \frac{dS}{S} &= - \frac{dx_S}{(x_S - x_D)} - \frac{H}{S} \frac{dx_{HT}}{(x_S - x_D)} \\ &= \frac{dx_S}{(x_D - x_S)} + \frac{H}{S} \frac{dx_{HT}}{(x_D - x_S)} \end{aligned} \quad (7)$$

Integrating,

$$\ln \frac{S}{S_0} = \int_{x_{S_0}}^{x_S} \frac{dx_S}{(x_D - x_S)} + \int_{x_{HT_0}}^{x_{HT}} \frac{H}{S} \frac{dx_{HT}}{(x_D - x_S)} \quad (8)$$

To integrate the second integral, S must be known as a function of the other variables.

Application of an enthalpy balance:

$$\frac{d}{dt} (Sh_S) + \frac{d}{dt} (Hh_{HT}) = h_D D \quad (9)$$

$$\text{where } h_{HT} = \frac{\sum H_n h_n}{H}$$

Substituting for D from (4a) and assuming $\frac{dH}{dt} = 0$,

$$S \frac{dh_S}{dt} + h_S \frac{dS}{dt} + H \frac{dh_{HT}}{dt} = h_D \frac{dS}{dt} \quad (10)$$

$$\frac{dS}{S} = - \frac{dh_S}{(h_S - h_D)} - \frac{H}{S} \frac{dh_{HT}}{(h_S - h_D)} \quad (11)$$

Solving for $\frac{H}{S}$,

$$\frac{H}{S} = - \left(\frac{dS}{S} + \frac{dh_S}{h_S - h_D} \right) \frac{(h_S - h_D)}{dh_{HT}} \quad (12)$$

Substituting (12) into (7) to eliminate $\frac{H}{S}$,

$$\frac{dS}{S} = \frac{dx_S}{(x_D - x_S)} + \left[- \left(\frac{dS}{S} + \frac{dh_S}{h_S - h_D} \right) \left(\frac{h_S - h_D}{dh_{HT}} \right) \right] \frac{dx_{HT}}{(x_D - x_S)} \quad (13)$$

$$\frac{dS}{S} \left[1 + \left(\frac{h_S - h_D}{dh_{HT}} \right) \frac{dx_{HT}}{(x_D - x_S)} \right] = \frac{dx_S}{x_D - x_S} - \frac{dh_S}{(x_D - x_S) dh_{HT}} dx_{HT}$$

$$\frac{dS}{S} = \frac{\frac{dx_S}{(x_D - x_S)} - \frac{dh_S dx_{HT}}{(x_D - x_S)dh_{HT}}}{\frac{(x_D - x_S)dh_{HT} + (h_S - h_D)dx_{HT}}{(x_D - x_S)dh_{HT}}} =$$

$$\frac{dx_S}{(x_D - x_S)} \frac{(x_D - x_S)dh_{HT}}{(x_D - x_S)dh_{HT} + (h_S - h_D)dx_{HT}} - \frac{dh_S dx_{HT}}{(x_D - x_S)dh_{HT}} \frac{(x_D - x_S)dh_{HT}}{(x_D - x_S)dh_{HT} + (h_S - h_D)dx_{HT}}$$

$$\frac{dS}{S} = \frac{dx_S dh_{HT}}{(x_D - x_S)dh_{HT} + (h_S - h_D)dx_{HT}} - \frac{dh_S dx_{HT}}{(x_D - x_S)dh_{HT} (h_S - h_D)dx_{HT}}$$

$$\frac{dS}{S} = \frac{dx_S}{(x_D - x_S) + (h_S - h_D) \frac{dx_{HT}}{dh_{HT}}} - \frac{dh_S}{(x_D - x_S) \frac{dh_{HT}}{dx_{HT}} + (h_S - h_D)} \quad (14)$$

$$\int_{S_0}^S \frac{dS}{S} = \int_{x_{S_0}}^{x_S} \frac{\frac{dx_S}{(x_D - x_S) \frac{dh_{HT}}{dx_{HT}} + (h_S - h_D)}}{\frac{dh_{HT}}{dx_{HT}}} - \int_{h_{S_0}}^{h_S} \frac{\frac{dh_S}{(x_D - x_S) \frac{dh_{HT}}{dx_{HT}} + (h_S - h_D)}}{\frac{dh_{HT}}{dx_{HT}}} \quad (15)$$

$$\ln \frac{S}{S_0} = - \left[\int_{x_S}^{x_{S_0}} \frac{\frac{dx_S}{(x_D - x_S) \frac{dh_{HT}}{dx_{HT}} + (h_S - h_D)}}{\frac{dh_{HT}}{dx_{HT}}} + \int_{h_{S_0}}^{h_S} \frac{\frac{dh_S}{(x_D - x_S) \frac{dh_{HT}}{dx_{HT}} + (h_S - h_D)}}{\frac{dh_{HT}}{dx_{HT}}} \right] \quad (16)$$

Let ψ represent $\left[(x_D - x_S) \frac{dh_{HT}}{dx_{HT}} + (h_S - h_D) \right]$

But the fraction distilled, $\phi = \frac{S_0 - S}{S_0} = 1 - \frac{S}{S_0}$ or $\frac{S}{S_0} = (1 - \phi)$,

$$\ln (1 - \phi) = - \left[\int_{x_s}^{x_{s_0}} \frac{\frac{dh_{HT}}{dx_{HT}}}{\psi} dx_s + \int_{h_{s_0}}^{h_s} \frac{1}{\psi} dh_s \right] \quad (17)$$

It should be noted that h_{HT} and x_{HT} refer to the overall values for the total holdup in the column. In the usual case where there is equal weight of holdup on each plate, these values are the arithmetic mean of the compositions and liquid enthalpies on the plates. Thus, provided that curves relating compositions of the still pot and of each plate to product composition are available, the fraction distilled may be calculated from (17) using two graphical integrations.

C. Simplified Equations and Procedure

Since the previous procedure is somewhat time consuming, it is proposed to investigate means for simplifying the computations. Therefore, the possibility of making simplifying assumptions in addition to those discussed on pp. 11-12. will now be investigated. The validity of these assumptions will be tested with experimental data in Part V.

1. Assumption that the holdup terms are negligible.

a. Calculation of Plate Compositions.

Considering the relative magnitudes of the terms in equations (2) and (3), it can be concluded that the holdup terms $H \frac{dx}{dt}$ and $H \frac{dh}{dt}$, will probably be small in comparison to the other terms

in these equations. If these holdup terms are assumed to be negligible, equations (2a) and (3a) become,

$$L_{n+2} (x_{n+2} - y_{n+1}) + L_{n+1} (y_n - x_{n+1}) + D(y_n - y_{n+1}) = 0 \quad (2b)$$

$$L_{n+2} (h_{Vn+2} - h_{Vn+1}) + L_{n+1} (h_{Vn} - h_{Vn+1}) + D(h_{Vn} - h_{Vn+1}) = 0 \quad (3b)$$

The procedure for calculating plate compositions would now be greatly simplified and would involve only the following:

All values except L_{n+1} , y_n and h_{Vn} would be known.

- (1) Assume a value for y_n .
- (2) Obtain the corresponding value of h_{Vn} from an enthalpy-concentration chart.
- (3) Solve equations (3b) for L_{n+1} .
- (4) Use equation (2b) to calculate y_n .
- (5) Continue until the calculated value in step (4) checks the value assumed in step (1).

The degree of validity of the assumption on which this procedure is based is shown on pp. 42-43.

b. Calculation of x_D vs. ϕ .

Consideration of equation (6) will show that if $\frac{H}{S}$ is small, the term $H \frac{dx}{dt}$ would be small in comparison with the other terms in the equation. Now if $\frac{H}{S}$ is small enough to make $H \frac{dx}{dt}$ negligible, equation (6a) reduces to the Rayleigh equation;

$$\int_{S_0}^S \frac{dS}{S} = \int_{x_{s_0}}^{x_s} \frac{dx_s}{x_s - x_D} \quad (18)$$

$$\ln \frac{S}{S_0} = \int_{x_s}^{x_{s_0}} \frac{dx_s}{x_D - x_s} \quad (19)$$

$$\ln (1-\phi) = \int_{x_s}^{x_{s_0}} \frac{dx_s}{(x_D - x_s)} \quad (19a)$$

Having x_D as a function of x_s from the previous calculations, x_D as a function of ϕ can be readily evaluated by graphical integration of equation (19a). A comparison of the results obtained by using this simplified equation with experimental data is presented in Part V, p. 44.

2. Assumption of Constancy of Liquid and Vapor Flow Rates in the Tower.

The doubtful validity of this assumption has already been discussed. Since this doubt has been confirmed with experimental data in Part V, p. 40, the relationships involving this assumption will not be written. Inspection of equations (2a) and (3a) will indicate the simplification that would result if this assumption were possible.

Part IV

EXPERIMENTAL INVESTIGATION

The purpose of the experimental investigation was to obtain data that would lead to a better quantitative understanding of batch rectification. Only in two previous investigations (5, 20) were experimental data reported for plate columns and in both cases only still pot and overhead product compositions were given. Therefore, it was proposed in this investigation to measure all plate compositions as well as those of the still liquid and overhead product. It was especially desired to obtain data from which actual operating curves could be plotted in order that both the shape of these curves and the manner in which they vary during the course of the distillation might be clarified. Finally, it was proposed to use the experimental data as a means of making numerical checks of the relationships resulting from the theoretical investigation.

A. Description of the Apparatus

In Figures 2 and 3 is shown the batch rectification apparatus used in this investigation. Figure 4 shows the details of the plate layout.

The equipment consisted of an 8-inch tower, containing 12 bubble cap plates (see Figure 4 for plate layout), mounted over a 20 gallon steam-jacketed still pot. The average plate holdup was approximately 1000 cc per plate (about 2.6 pounds per plate under operating conditions). The average plate efficiency as determined

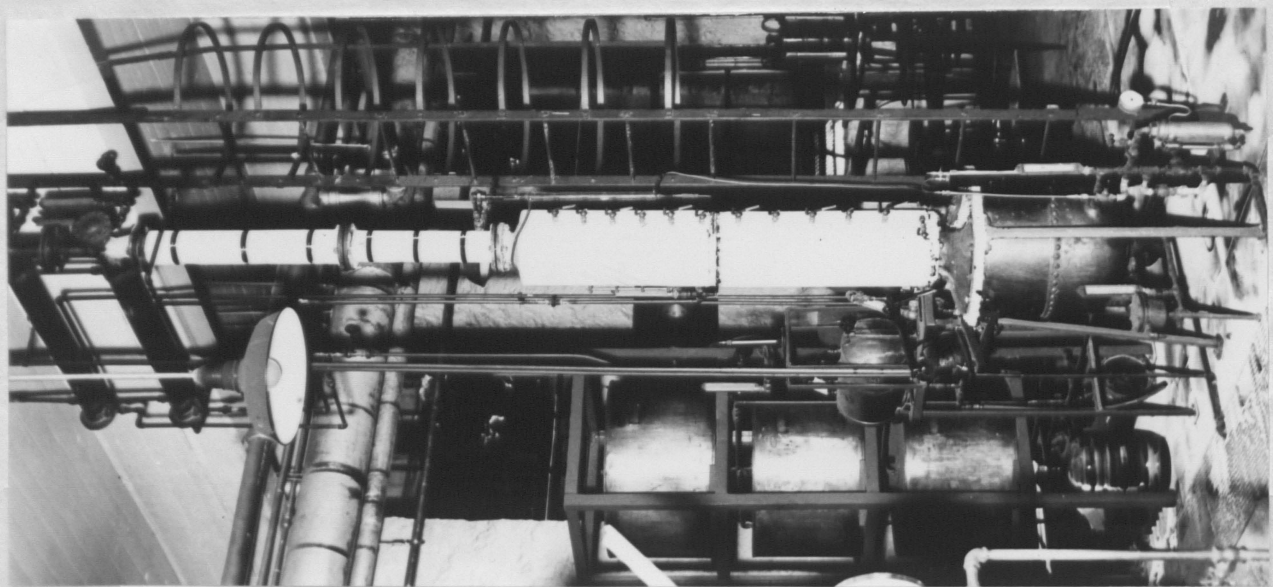
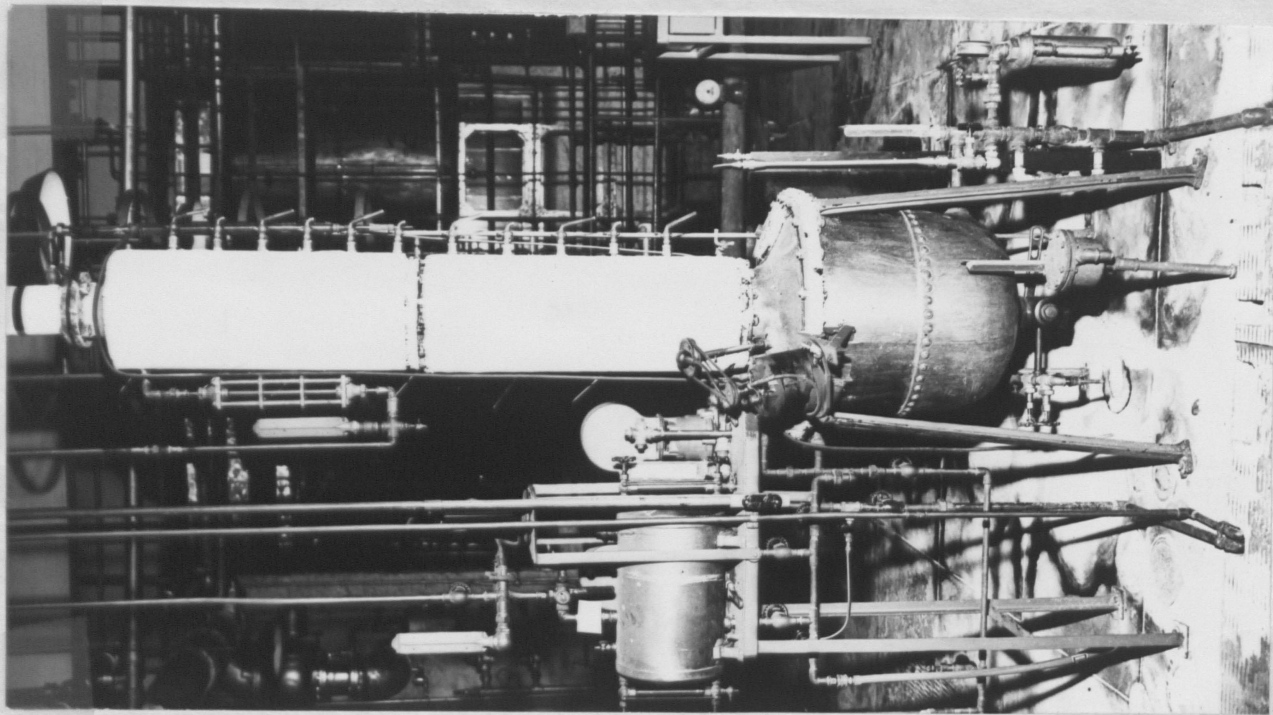


Fig. 2 Experimental Apparatus

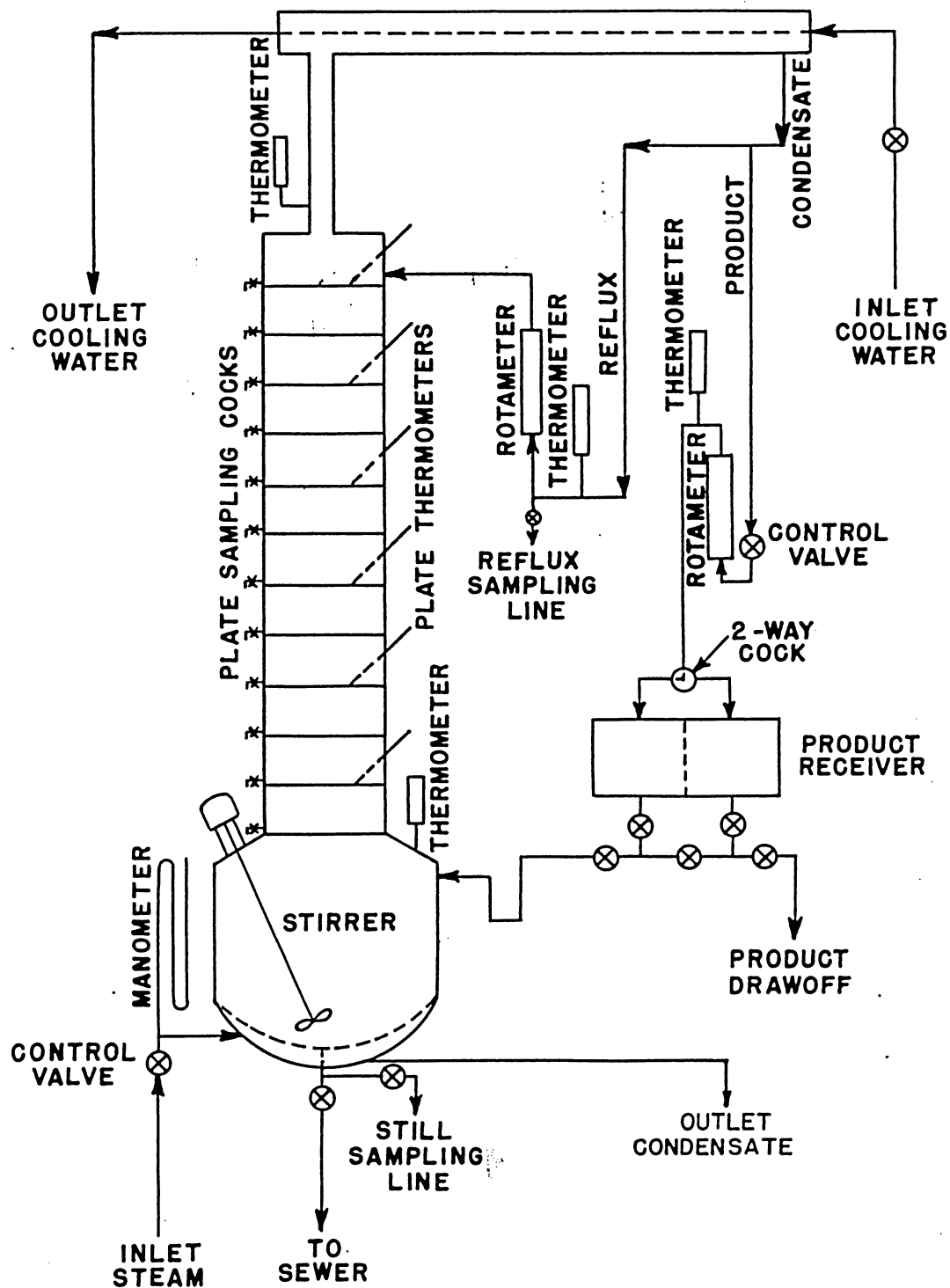


FIG. 3 EXPERIMENTAL APPARATUS

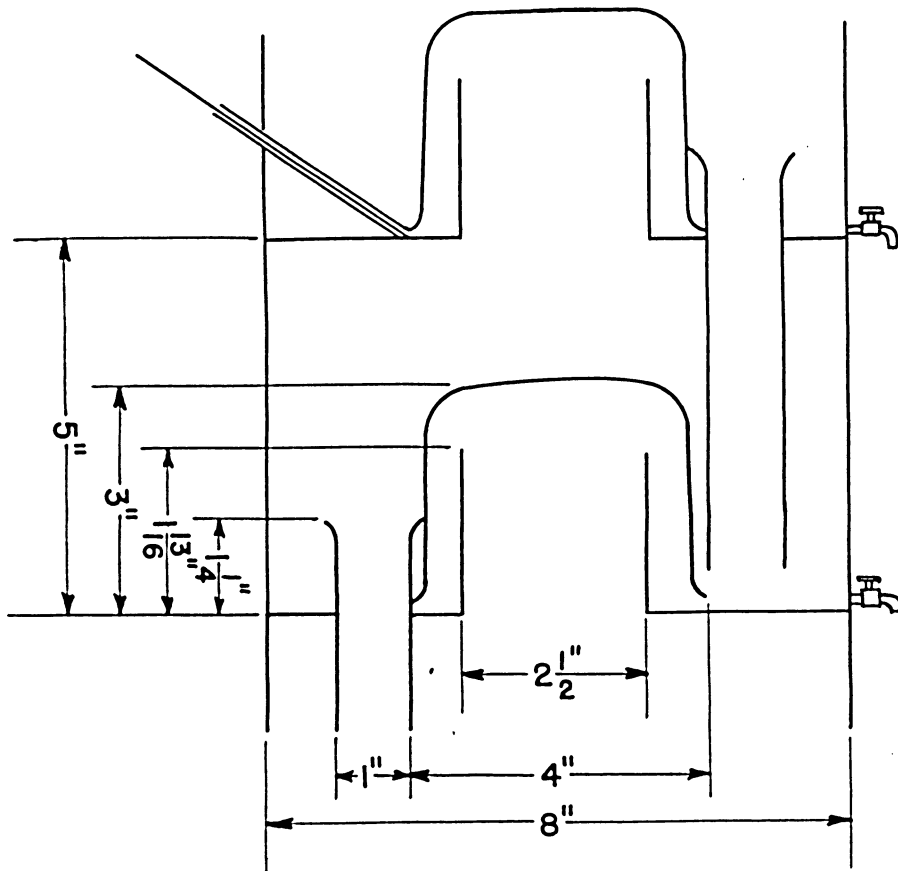
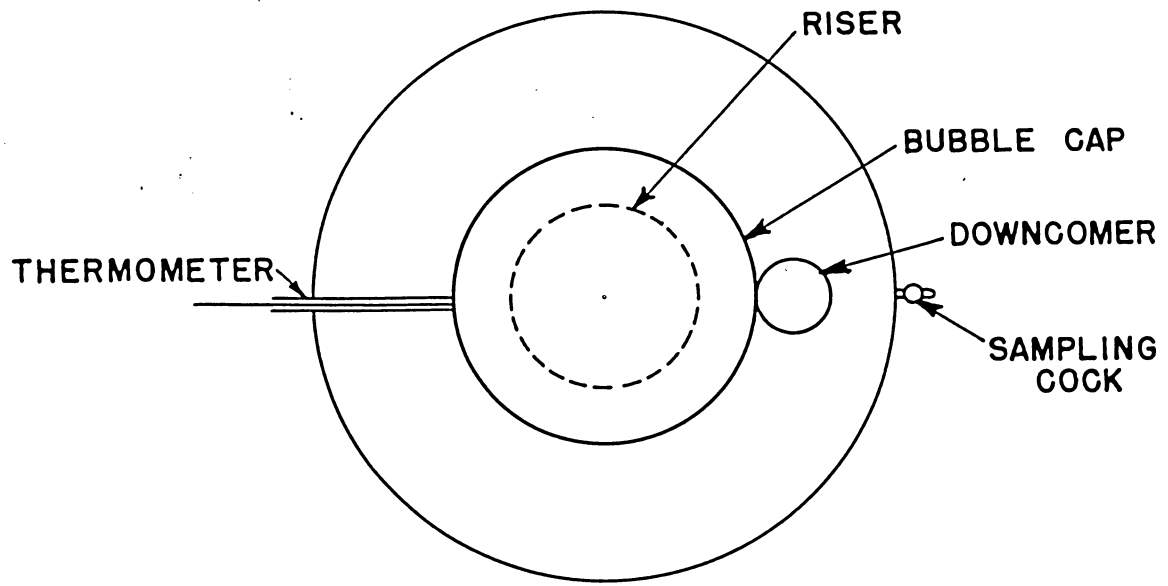


FIG.4 PLATE LAYOUT

experimentally was approximately 60 percent. The tower was insulated with a 2-inch layer of standard magnesia pipe insulation. Condensation of the overhead vapors was effected by means of a conventional shell and tube condenser mounted horizontally. The overhead condensate was divided into reflux and product by means of a control valve placed for convenience as shown in Figure 3. A motor driven stirrer operating at 600 RPM provided adequate mixing in the still pot. The size and pitch of the blade on the stirrer were adjusted to prevent any appreciable liquid entrainment in the vapors going to the first plate.

Mercury-in-glass thermometers were used to obtain temperatures on alternate plates and at other appropriate points in the system as shown in Figure 3. Rotameters were used to measure rates of flow of reflux and product. Also provision was made for obtaining samples of liquid from the plates, still pot, and reflux line. Reference to Figure 4 will show that representative samples could be obtained only from alternate plates, because it is seen that on the lower plate in the diagram the sampling cock is adjacent to the downcomer from the plate above. Therefore, samples could be taken only from the even numbered plates (counting from the bottom). Control of the steam to the calandria was afforded by means of a flow control valve used in conjunction with a mercury manometer.

B. Outline of the Experimental Procedure

Since a detailed step-by-step account of the procedure is given in Appendix B, only a brief outline will be presented here.

The system selected for this investigation was methanol-isopropanol and this choice was based on several considerations. The system closely approaches ideality and therefore has an approximately constant relative volatility, which being approximately 2, is also of suitable magnitude. Likewise, the properties of mixtures of these two components can be conveniently evaluated by means of the additive property rule. Because of the large number of samples to be taken, of major consideration is the fact that mixtures of these components can be rapidly analyzed by measuring their refractive indices. Finally, both methanol and isopropanol of a relatively high degree of purity (99⁺ percent) are readily available at relatively low cost.

The major items of data obtained at specified time intervals were:

- (1) Composition of the liquid on alternate plates, of the reflux, and of the liquid in the still pot.
The other plate compositions were later obtained by graphical interpolation. Composition of vapor on the plates was obtained from a liquid-vapor composition curve for the tower described below.
- (2) Rates of flow of reflux and product.
- (3) Weights of initial charge and of product collected during specified intervals of time.
- (4) Temperatures on the plates, in the still pot, and at each flow meter.

To start a run, the still pot was charged with feed of specified amount and composition and the stirrer, steam, and cooling water turned on. The column was operated at total reflux long enough to fill the plates with holdup. Then the reflux fraction was shifted to the value to be employed in the run and the warmup period continued for 2-1/2 hours in order to insure that steady state had been attained. During this period, the portion of the overhead condensate, which during actual operation would be withdrawn as product, was returned continuously to the still pot.

The batch rectification period was started by changing the product flow from the still pot to the product receiver. Generally, all meter readings, temperatures, and samples were taken at 30 minute intervals. Also product accumulations during these intervals were weighed. In an effort to minimize errors, sample lines were purged of stagnant liquid, and samples were withdrawn into chilled bottles. A constant boilup rate was maintained by occasional adjustment of the flow control valve on the steam line to the calandria.

The compositions of the liquid samples were determined by measuring their refractive indices at 20°C. A curve relating refractive index to composition was calculated applying the additive property rule to specific refractions of the components as developed

by Tour (30)*. This calculated curve was checked using test mixtures made up by combining weighed samples of the pure components. The test points showed an average absolute deviation of approximately 0.2 weight percent from the calculated curve.

Vapor compositions were not measured directly because it was recognized that it would not be possible to obtain vapor samples of sufficient size for accurate analysis from the plates without seriously disturbing the operation of the tower.** Therefore, it was necessary to determine these compositions from a liquid-vapor composition curve for the tower, previously determined by a series of runs at total reflux.* This liquid-vapor curve is actually the equilibrium curve corrected for plate efficiency. At total reflux, $y_n = x_{n+1}$, and this relationship provides a means for obtaining vapor compositions without directly measuring them. It would be expected that this corrected equilibrium curve obtained at total reflux would apply at other reflux ratios as well, provided that the factors affecting plate efficiency are kept the same. This fact has been confirmed by several investigators (9, 10, 12, 27) all of whom report no effect of reflux ratio per se on the plate efficiency provided that the tests are made at the same vapor velocity, same plate layout, etc. Care was taken to use the same

*See Appendix D for this curve and for the details of its construction.

**This difficulty did not occur with the liquid sampling because in this case only a 10 cc sample was taken from the 1000 cc of liquid on the plate.

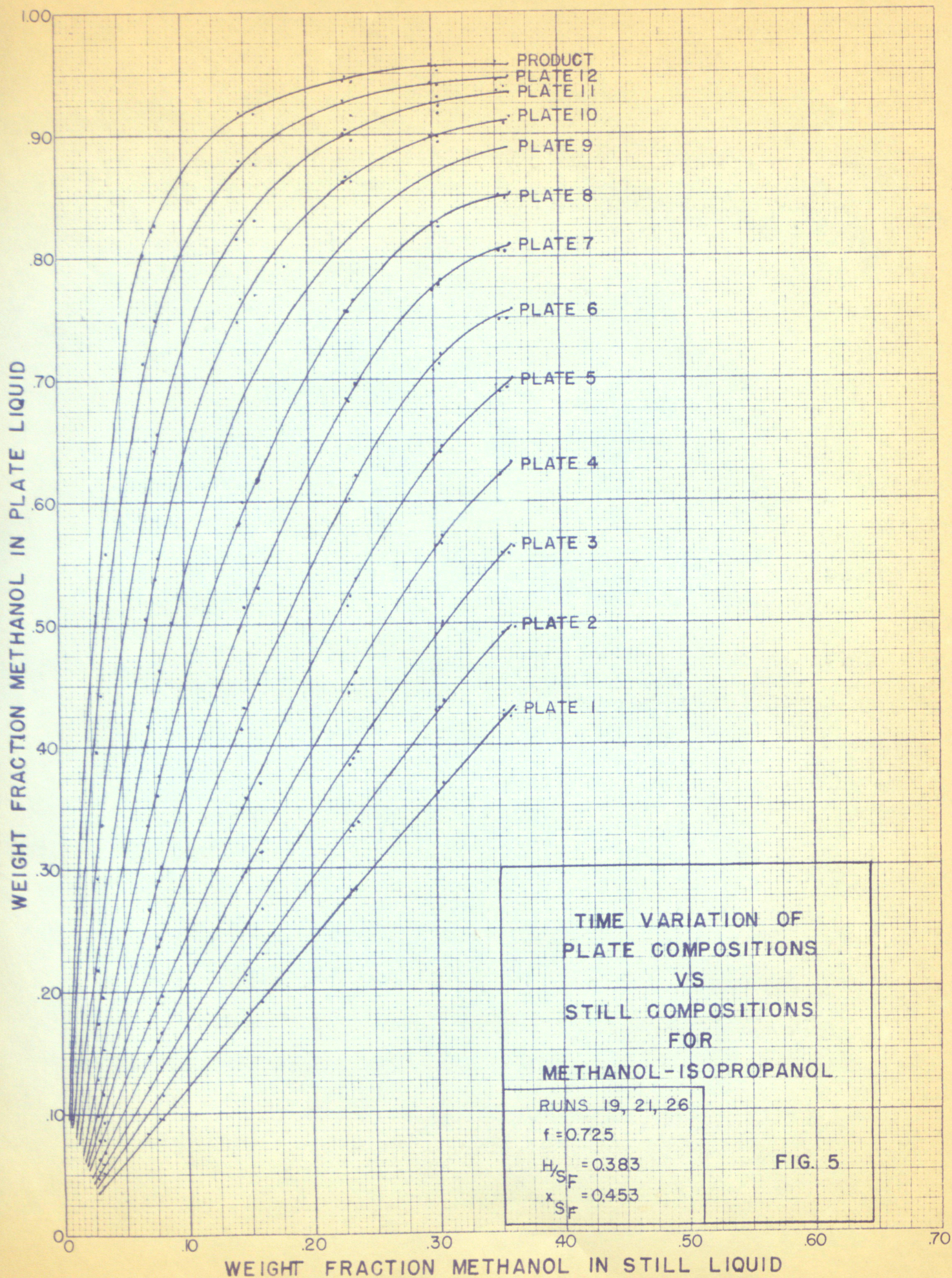
vapor velocity (approximately 3.7 ft./sec.) in the batch rectification runs as had been used in the determination of the liquid-vapor curve. Then the vapor composition, y , on a given plate corresponding to the measured liquid composition, x , was obtained from this curve.

C. Experimental Results

In distilling mixtures of two given components in a given column at a fixed pressure the most important variables that would appear to affect the course of the operation are reflux fraction, holdup to charge ratio, and initial charge composition. Runs were made under various conditions of these variables, but all at atmospheric pressure.*

Results typical of all the data are shown in Figures 5, 6, and 7. Figure 5 shows the time variation of plate compositions versus still pot compositions for runs 19, 21, 26, all of which were made at the same conditions. Each point in a cluster represents a different run. A plot of composition versus plate number was used to interpolate the values for the odd numbered plates and to smooth out any obvious irregularities in the experimental data. The average absolute deviation of the compositions shown in Figure 5 is approximately 0.3 weight percent. Figure 6 shows the variation of product composition with the fraction distilled for the same three runs. The average absolute deviation of compositions here varies

*A resume of all runs and tabulation of data are given in Appendix C.



COMPOSITION OF PRODUCT
VS.
FRACTION DISTILLED
FOR
METHANOL-ISOPROPANOL

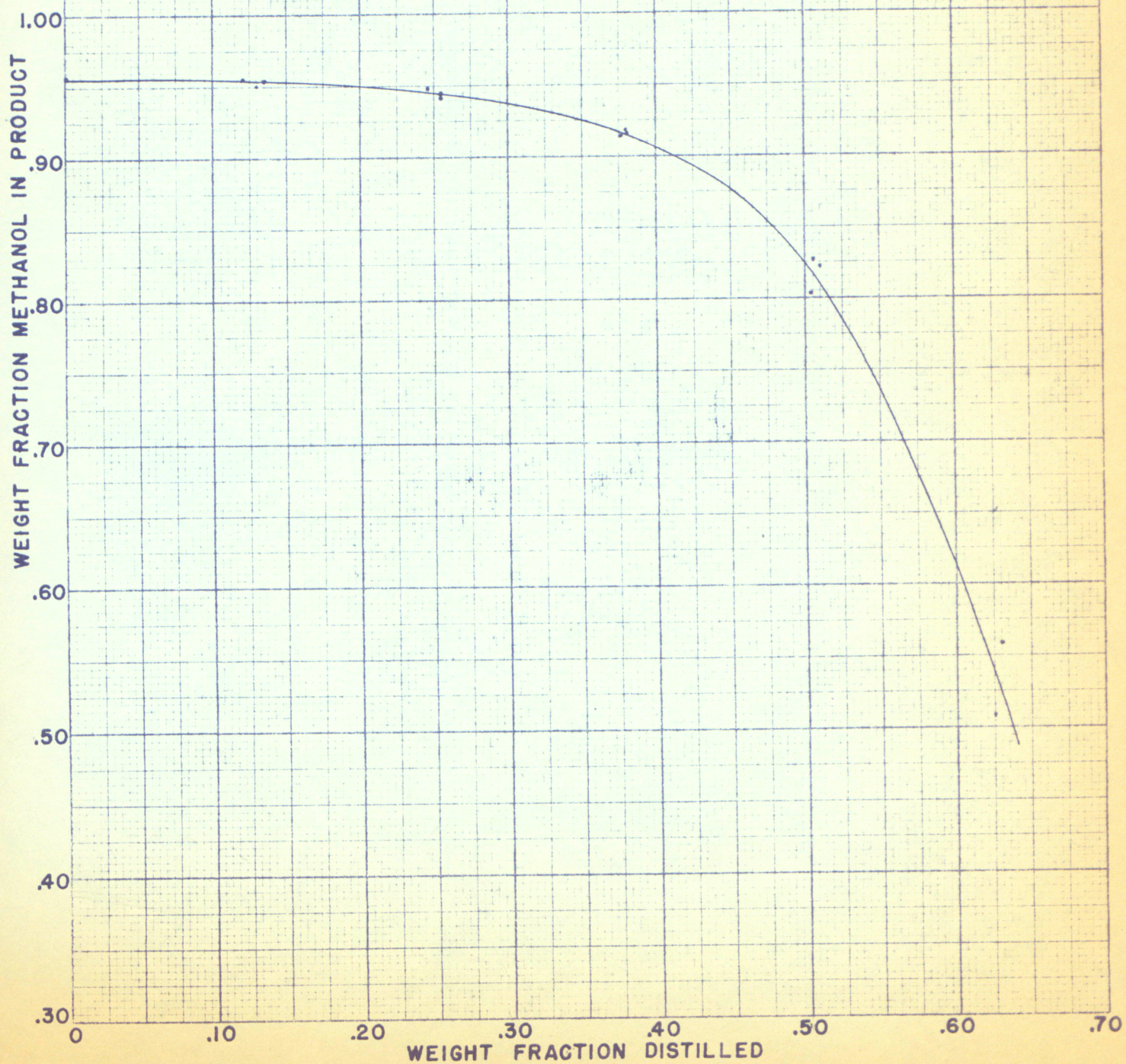
RUNS 19, 21, 26

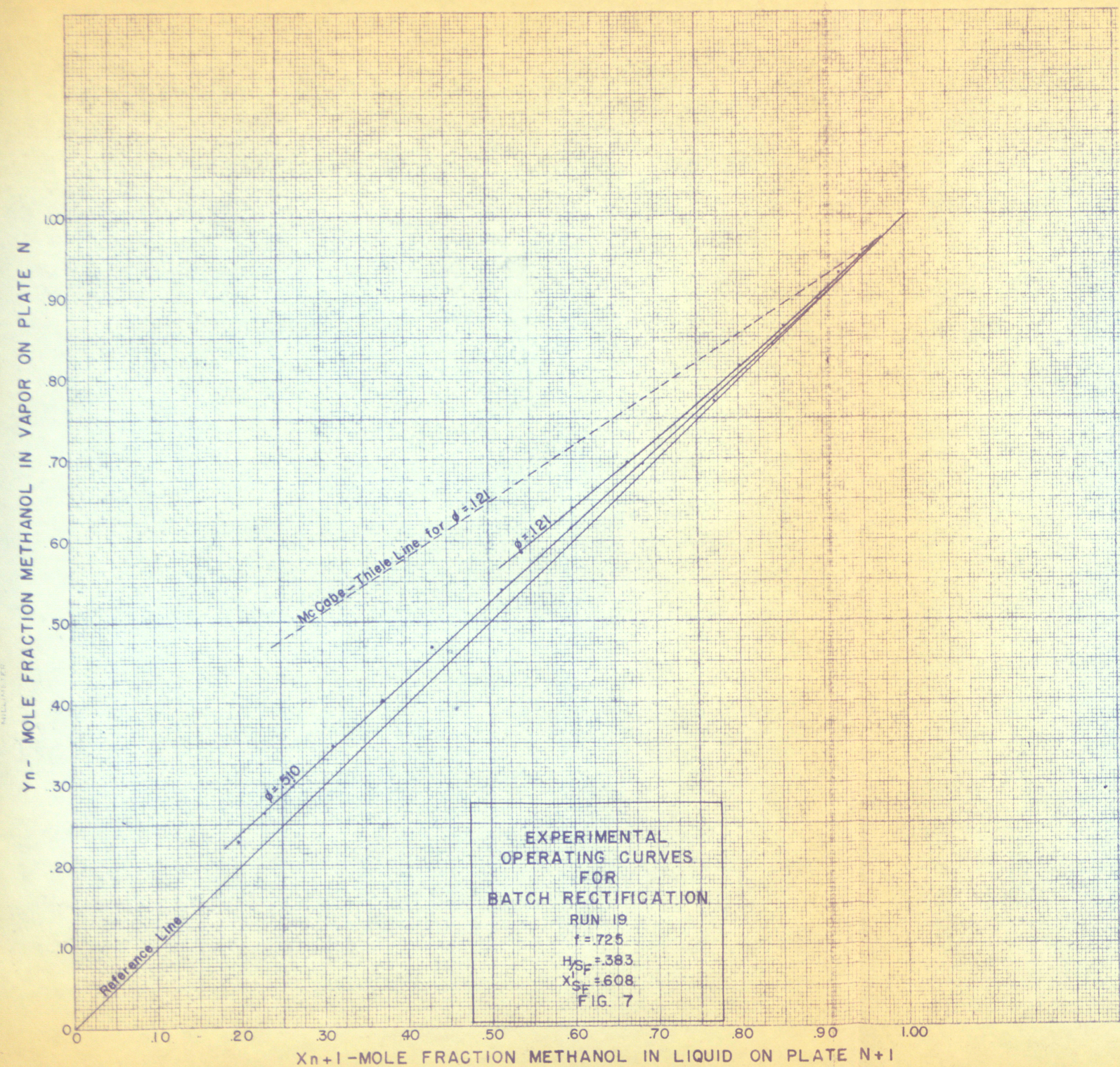
$f = .725$

$H_{SF} = 383$

$X_{SF} = 453$

FIG. 6





with ϕ . The progressive determination in precision is believed to be caused by cumulative error due to vapor loss from the condenser and to losses incurred in sampling.

Figure 7 shows typical operating curves (y_n vs. x_{n+1}) for batch rectification as determined experimentally in Run 19. The variation of these curves during the course of the operation from $\phi = .121$ to $\phi = .510$ is shown. This plot is of particular interest in that it shows the magnitude of the error that can be incurred by using the McCabe-Thiele operating line.

These and other data of the same type but at different values of reflux ratio, holdup to charge ratio, and initial charge composition will be used in Part V in evaluating the reliability of the theoretical relationships developed in Part III.

In addition to the test of consistency given by Figures 5 and 6, the data were also tested by both individual plate and over-all material balances. Equations 1a, 2 and 3 were used to make the plate-to-plate balances. Since flow rates inside the tower were not measured, equation (3) was used to solve for L_{n+1} , equation (1a) to obtain V_n and then these plus observed values of the other quantities were substituted in equation (2), rearranged to equate input to output:

$$L_{n+2} x_{n+2} + V_n y_n + H \left(- \frac{dx}{dt} \right)_{n+1} = L_{n+1} x_{n+1} + V_{n+1} y_{n+1}$$

where $\frac{dx}{dt}$ was evaluated graphically from a plot of x vs. t for each plate. The results of these plate balances are shown in Table I.

Table I

Results of Material Balances for Run 19
 Methanol Balances Around Each Plate at $\phi = 0.254$

Plate No. (n)	Input	Output	Percent Dev.
1	0.639	0.643	0.6
2	0.718	0.731	1.8
3	0.806	0.806	0.0
4	0.889	0.886	0.3
5	0.981	0.975	0.6
6	1.066	1.068	0.2
7	1.147	1.147	0.0
8	1.208	1.210	0.2
9	1.252	1.257	0.4
10	1.286	1.311	0.2
11	1.314	1.310	0.3

Furthermore, the overall mass balance for the entire Run 19 showed a deviation of about 2 percent. Therefore, it can be concluded that these data are suitable for use in checking the theoretical relationships.

Part V

CORRELATION OF THEORETICAL AND EXPERIMENTAL RESULTS

The purpose of this section is to determine the degree of correlation between the various theoretical relationships developed in Part III and the experimental data reported in Part IV. The various assumptions made in Part III will be checked using experimental data.

Since the theoretical relationships involve enthalpies, it was necessary to construct an enthalpy-concentration chart* for the system methanol-isopropanol. This chart was constructed for the conditions existing in the tower used in this investigation, i.e., the chart is based on the actual pressure, temperatures and corrected equilibrium conditions observed for this tower. Because of the effect of holdup on the calculations, the necessity for working with the actual liquid-vapor data and the actual enthalpy-concentration data must be clearly recognized.

Test of Basic Assumptions with Experimental Data

The basic assumptions discussed on pp. 11-12 will now be tested with experimental data.

(1) Constancy of weight of holdup.

Typical of general results are the data from Run 16. For a single plate (No. 6) the weight of holdup varied from 2.22 pounds to 2.21 pounds; the moles varied from 0.0465 to 0.0395 pound

* See Appendix D for this chart and for the details of its construction.

moles. The total holdup in the tower varied from 31-1/4 to 31 pounds, whereas the moles varied from 0.664 to 0.556 pound moles.* Thus the assumption of constancy of pounds of holdup holds very well for the system used in this investigation, but there is considerable variation on a molal basis.

(2) Weight and enthalpy of vapor holdup negligible.

The following typical results are offered in support of this assumption. The weight of vapor above a plate was found by calculation to average approximately 0.015 pounds. Certainly this value is negligible in comparison with the average value of 2.6 pounds of liquid holdup per plate. The corresponding enthalpy values are 6 Btu. and 260 Btu., respectively for vapor and liquid and again no serious error is incurred in neglecting the vapor enthalpy.

(3) Heat losses from column negligible.

Sufficient insulation was used on the column to insure that this condition was met, and the same can and should be done in practice.

(4) Constant rate of withdrawal of product from the system.

This condition was met in this investigation by control of the heat input to the calandria and the same can be done in practice.

*For description of holdup measurements and calculations see Appendices B and D.

The variation of liquid and vapor flow rates* from plate-to-plate in the tower at any given time is shown in Table I for a typical run No. 19. Therefore, it is well that the assumption of constancy of these rates was not made.

Table I

Rates of Flow of Liquid and Vapor in Tower for Run 19

at $\phi = .254$

Plate	<u>L</u> <u>lbs./min.</u>	<u>V</u> <u>lbs./min.</u>	
1	.895	1.077	Liquid overflow values expressed in terms of lb. moles per min.:
2	.860	1.041	
3	.824	1.007	
4	.790	.976	
5	.759	.941	Plate 5: 0.0168
6	.724	.907	Plate 10: 0.0157
7	.690	.878	
8	.661	.855	
9	.638	.839	
10	.622	.826	
11	.609	.819	
12	.602	.796	

Test of Simplifying Assumptions

In addition to the basic assumptions on which all the theoretical equations are based, additional simplifying assumptions were made that led to equations (2b), (3b), and (19a). These assumptions were that the time variation in weight of more volatile component in the holdup per plate $H_n \frac{dx_n}{dt}$, and of enthalpy of the holdup per plate, $H_n \frac{dh_n}{dt}$, were negligible. These assumptions will now be checked with experimental data from Runs 16, 19, 22, 23 and 28, covering a con-

*Calculated using equations 1a, 2, and 3 as explained in appendix D.

siderable range of operating conditions. Runs 16 and 19 were made at the same values of holdup to charge ratio and reflux fraction but at different values of charge composition. Runs 19, 22, and 23 were made at the same holdup to charge ratio and at the same initial charge composition but at different reflux fractions. Runs 19 and 28 were made at the same reflux fraction and at the same charge composition but at different holdup to charge ratios.

The tests of these assumptions were first made on the relationships for calculating plate compositions by using equations (2) and (3) to evaluate the percentage error caused by neglecting the holdup terms. In all cases the error caused by neglecting the holdup term in the enthalpy balance was never more than approximately 0.1 to 0.2 percent. The fact that the specific heats of methanol and isopropanol are of the same order of magnitude accounts largely for this small variation in the enthalpy of the holdup. The magnitude of the error will depend on the thermal properties of the components but in most cases it should be small.

On the other hand, the effect of neglecting the holdup term in the material balance is more pronounced. Table II shows the errors obtained for each of the runs mentioned above.

Table II

Error on each Plate Due to Neglecting
Change of Composition in the Holdup

Error = Percent of methanol flow leaving plate.

Except where noted, all values were computed at $\phi = 0.25$

Run 16		Run 19			
$f = 0.725$		$f = 0.725$			
$x_{S_0} = 0.231$		$x_{S_0} = 0.453$			
$\frac{H}{S_0} = 0.383$		$\frac{H}{S_0} = 0.383$			
Plate	Percent Error	Plate	Percent Error	For Plate 6; ϕ	
1	0.66	1	1.10		
2	.54	2	0.98		
3	.62	3	1.24	.121	0.42
4	.43	4	.90	.254	0.94
5	.57	5	1.12	.380	1.33
6	.53	6	.94	.510	1.38
7	.70	7	1.14		
8	.66	8	.74		
9	.83	9	.48		
10	.90	10	.39		
11	1.20	11	.23		
12	.92	12	.15		
Overall error based on plate 1 flow = 10 percent		Overall error based on plate 1 flow = 14.2 percent			

Table II (Continued)

Run 22		Run 23		Run 28	
$f = .850$		$f = .575$		$f = .725$	
$x_{S_o} = .453$		$x_{S_o} = .453$		$x_{S_o} = .453$	
$\frac{H}{S_o} = .383$		$\frac{H}{S_o} = .383$		$\frac{H}{S_o} = .272$	
Plate	Percent Error	Plate	Percent Error	Plate	Percent Error
1	1.04	1	1.38	1	0.85
2	0.90	2	1.24	2	0.75
3	1.05	3	1.40	3	0.88
4	0.69	4	1.04	4	0.58
5	0.83	5	1.37	5	0.78
6	0.64	6	1.18	6	0.61
7	0.59	7	1.43	7	0.62
8	0.37	8	1.14	8	0.43
9	0.30	9	1.11	9	0.40
10	0.20	10	0.95	10	0.28
11	0.23	11	0.98	11	0.28
12	0.15	12	0.51	12	0.09
Overall error based on Plate 1 flow = 11 percent		Overall error based on Plate 1 flow = 18.7 percent		Overall error based on Plate 1 flow = 9.9 percent	

It is seen that the errors range from a few tenths of a percent up to approximately 1.5 percent per plate. Whereas the errors per plate are small, it must be recognized that they would be cumulative when making plate-to-plate calculations. As indicated in the table these cumulative errors may be as large as 19 percent for a 12-plate calculation. No quantitative correlation was found to relate the percent error to any of the variables of operation. Several qualitative deductions will be mentioned in Part VII. The conclusion that must be drawn from this analysis is that for exact calculations, the holdup term in the component balance should not be neglected.

In accord with this conclusion regarding the individual plate balances, it is obvious that the holdup terms should not be neglected in the overall balances used to calculate the fraction distilled. The magnitude of the error caused by neglecting the holdup terms has been computed for Run 19. The value of the fraction distilled calculated using equation (19a) is 0.255 compared to the experimental value of 0.380. Therefore, the holdup terms must not be neglected in making this computation.

Part VI

COMPLETE DESIGN PROCEDURE FOR BINARY BATCH RECTIFICATION

The following procedure is recommended for the exact design of a batch rectification tower.

1. Given;
 - a. Weight of feed
 - b. Composition of feed
 - c. The desired curve relating composition of product to fraction distilled.
2. Select the following;
 - a. The plate design so that the holdup per plate can be calculated.
 - b. The reflux fraction to be used during the warmup period; probably would use total reflux.
3. Assume a plate efficiency and calculate the corrected liquid-vapor composition data and enthalpy data.
4. Calculate plate compositions for the steady state condition at the end of the warmup period;
 - a. Assume a number of plates, N .
 - b. Calculate x_{S0} at the end of the warmup period as follows;

(1) Calculate the total holdup in the column,

$$H_T = (N_p)(H_p)$$

- (2) $S_o = S_F - H_T$
 - (3) Assume x_{So} and step off compositions using steady state methods with equilibrium data corrected for plate efficiency.
 - (4) Knowing the weight and composition of the holdup, calculate the weight of the more volatile component in the total column holdup, $H_{TM} = (H_T)(x_{HT})$ where x_{HT} may be taken as the arithmetic average because of the approximately equal weight of holdup on each plate.
 - (5) By material balance calculate x_{So} ,

$$S_F x_{SF} = H_o x_{Ho \text{ ave.}} + S_o x_{So}$$
 Solve for x_{So} .
 - (6) Continue until the value calculated in (5) agrees with the value assumed in (3).
- c. After the value for x_{So} has been established, check to see if the corresponding value of x_{Do} agrees with the value of x_D at $\phi = 0$ on the graph mentioned in 1c. If not satisfactory, choose another value for the number of plates and repeat step 4b. When a satisfactory value for x_{Do} has been obtained, then the corresponding number of plates for the tower will be fixed.

5. Calculate plate compositions:

- a. Choose a reflux fraction for use during the batch rectification.
- b. Choose a rate of flow of product, D to give a suitable vapor velocity in the tower.
- c. Calculate all plate compositions and the still pot composition as a function of the fraction distilled using the procedure previously developed on p. 16
- d. Calculate the fraction distilled as a function of the product composition using the procedure previously developed on p. ~~18~~ 21.
- e. If these points do not check satisfactorily with the curve specified in 4c, assume a new reflux ratio and repeat steps 5b through 5d.

If it is desired to analyze the performance of an existing tower under various conditions of operation, only a few modifications would be necessary in the procedure. In step 4a the number of plates would be fixed and step 4c would be eliminated. In step 4c a curve relating x_D to ϕ would have to be assumed and then checked by step 5d. In this case it would be wise to defer this assumption until after step 4b(6), so that x_{D0} would be known.

Although several possibilities for simplifying this procedure are discussed in Part VII, it is believed that this is the only procedure that will lead to exact results.

Part VII

DISCUSSION OF RESULTS

The most important contributions resulting from this investigation are the relationships developed for the computation of plate compositions and for the computation of the fraction distilled as a function of the product composition. For the first time, equations involving only assumptions justified by experimental data are available for making these computations. The significant features that differentiate this work from that of other workers are the use of weight units rather than molal units and the application of a differential enthalpy balance in addition to the differential material balances. Another important contribution consists of the first experimental data complete with all plate compositions to be reported. The reliability of these data was established by material balances as reported in Part IV.

The basic assumptions of constancy of weight of holdup and of negligible amount of vapor holdup were justified in Part V. It is believed that the ratio of vapor holdup to liquid holdup, which is largely a function of plate design and spacing, would be negligible in all practical cases. However, the constancy of weight of holdup will depend on the relative densities of the components comprising the system and the extent and manner in which mixtures depart from ideal behavior. The excellent check of this assumption in this work was due largely to the closeness of the densities of

the two components, methanol and isopropanol. Although this situation occurs frequently in practice, it must be recognized that there will arise cases where this assumption will not hold as well as reported here. Nevertheless, the assumption should hold better in most cases in terms of pounds than in terms of moles. If the molecular weights of the components are closer in magnitude than are their densities, then the reverse will be true. In either case the relationships are used in the same manner. It is believed that the assumption of constancy of holdup will hold well enough in all cases to give results of desired validity. Although it would be possible to make the derivations without this assumption, the complexity of the equations would be increased to such a point as to make them of little value for practical use.

Of considerable importance is the proof given in Part V concerning the non-validity of one of the assumptions that has frequently been made in batch rectification calculations, namely, equal rate of overflow from plate-to-plate in the tower. This condition was found not to exist on either a weight or a molal basis. Therefore, the McCabe-Thiele method should not be used to calculate plate compositions in a batch rectification tower. Figure 7 shows the magnitude of the error that can be incurred by use of the McCabe-Thiele method.

Since the design procedure as outlined in Part VI is somewhat time consuming, several means for its simplification have been investigated. It was shown that the relationships for calculating

both plate compositions and fraction distilled would be simplified considerably if the holdup terms were neglected. Therefore, the magnitude of the error caused by neglecting the holdup terms in these equations has been evaluated.

The holdup term in equation (3) was found to be negligible and it is believed that this will generally be true. The errors caused by neglecting the holdup term in equation (2) were shown in Table II for a variety of operating conditions. Although the magnitude of these errors per plate is relatively small, it must be recognized that in making plate-to-plate calculations these errors will be cumulative. An indication of the magnitude of this cumulative effect is shown in Table II for the 12 plates in terms of the overall error based on plate 1 flow rates. Of course this effect will become greater as the number of plates increases.

Although no quantitative correlation was found between the magnitude of the errors shown in Table II and any of the pertinent variables of operation, several qualitative deductions can be made. Comparing Runs 19, 22, and 23, it is seen that for fixed values of charge composition and holdup to charge ratio, the higher the reflux fraction the smaller the errors. Comparing Runs 19 and 28, it is seen that for the same charge composition and reflux fraction, the smaller the holdup to charge ratio the smaller the errors. At fixed values of reflux fraction and holdup to charge ratio, the effect of charge composition will depend on the portion of the equilibrium

curve that is involved. At the two extremities of the curve the error would be zero. However, assuming a normal equilibrium curve, as the middle portion of the curve is approached from either direction the difference between liquid and vapor compositions increases. This causes an increased rate of variation of plate compositions, which in turn increases the magnitude of the holdup term relative to the other terms in the equation, and thereby the percentage of error increases. This contention is substantiated by the errors shown for Run 16.

The variation of error with the fraction distilled is shown in Table II for Plate 6 of Run 19. Although in the range of the fraction distilled covered there is a progressive increase in the magnitude of the error with increase in fraction distilled, it is believed that the data end near a point of inflection, and therefore, the value at the fraction distilled equal to 0.51 should represent very closely the maximum percent of error for that plate.

In addition to the above factors, the relative volatility plays an important role in determining the magnitude of the holdup terms. The greater the relative volatility, the greater the rate of change of compositions. Therefore, the absolute magnitudes of the errors reported herein hold only for systems having a relative volatility of approximately 2.

It is recognized that the data reported do not cover sufficient ranges of the possible operating conditions to permit completely general quantitative conclusions to be made. Nevertheless, it is

believed that enough data have been included to guide the designer in estimating the approximate validity of the results obtained from use of the simplified equations (2b) and (3b) in calculating plate compositions. However, because of the cumulative effect of these errors on the plate calculations, it is believed that in general the added confidence in the results will justify the slightly greater expenditure of time required for the use of the basic equations (2a) and (3a), which allow for the variation in the composition of the holdup.

If the holdup terms are neglected in the overall material balances used in the derivation of the relationship for calculating the fraction distilled, it was shown on p. 73 that the Rayleigh equation will result. An overall balance is subject to the total cumulative error, and therefore, results obtained by use of the Rayleigh equation would be expected to contain considerable error. Since this fact has previously been reported (3), (5), only one evaluation of this error was made. The 30 percent error obtained for Run 19 on p. 128 indicates the hazard involved in using the Rayleigh equation for calculation of the fraction distilled in batch rectification. It should be noted however, that the magnitude of the error will depend (in addition to the factors mentioned above) on the holdup to charge ratio. The smaller this ratio the smaller the error incurred, but since the effect is probably not

great, under most practical conditions the Rayleigh equation would probably give highly questionable results. Fortunately, after plate compositions have been calculated, equation (17) can be used without too much inconvenience to calculate the fraction distilled.

Other approximations might be made under some conditions to simplify the design procedure. For instance, if the holdup to charge ratio is small, the still pot composition at the end of the warmup period might be approximated, and thereby, this trial and error computation would be eliminated.

Although the design procedure given in Part VI is somewhat time consuming, it is much less so than in previously attempted calculations. In the procedure used by Rose et.al. (18), the concentration range to be considered is divided into a series of very small finite increments. Complete calculations must then be made successively for each of the small intervals of concentration. Pigford et al. (13) tried to make the calculations by using a differential analyzer. Both methods, in addition to requiring a prohibitive amount of time, are based on several highly questionable assumptions and approximations, such as constancy of moles of holdup and equal molal overflow.

In summary, a rigorous but somewhat time consuming design procedure has been developed. Several means of simplification and the magnitudes of the accompanying errors have been considered.

However, only experience in using the relationships will indicate which, if any, of the simplifications can be generally applied with confidence.

Part VIII

CONCLUSIONS

1. A complete and rigorous design procedure for batch rectification of binary mixtures involving only equations based on justified assumptions has been developed. Therefore, for the first time, design calculations can be made for batch rectification that are of comparable validity to those that can be made for continuous rectification.

2. The procedure can also be used to analyze the performance of an existing tower.

3. The procedure is time consuming but much less so than previously proposed methods, which, although accounting for the holdup in the tower, involved several very dubious assumptions.

4. The errors involved in using several simplifications have been considered. However, it is believed that the added confidence in the results justifies the additional expenditure of time required to use the basic equations that do not involve any of the simplifying approximations. Further experience may indicate which, if any, of these approximations can be generally applied with confidence.

5. The questionable validity of previous procedures involving the McCabe-Thiele method and the Rayleigh equations has been demonstrated.

Part IX

APPENDICES

- A. Review of Previous Work
- B. Details of Apparatus and Experimental Procedure
- C. Experimental Data
- D. Sample Calculations
- E. Tabulation of Calculated Data
- F. Literature Cited

APPENDIX A
REVIEW OF PREVIOUS WORK

Since Rose and Rose (22) have given a detailed review of all work prior to 1951, only the more important contributions before that time will be mentioned. In addition a review of the work since that time will be presented.

Arthur Rose has been the foremost pioneer in the study of batch rectification, and to him and his coworkers must go the credit for much of the preliminary spade work that has resulted in a clearer understanding of the basic principles. For instance, in 1940-41, Rose and Welshans (23), Rose, Welshans, and Long (24), Rose (15), and Rose and Long (21), discussed the general status of the problem and some of the difficulties to be encountered in both theoretical and experimental investigations. In addition, they attempted to evaluate theoretically the effect of such variables as number of plates, reflux ratio, holdup, and composition of the feed on the sharpness of separation produced by batch rectification. The utility of all of these results is tempered by questionable assumptions or by impractical conditions of operation such as total reflux. Of greater significance, however, is the contributions by Rose and Welshans (23) and Rose (16) in which they explain the correct criteria to use in judging the effectiveness of a separation through analysis of curves showing product composition as a function of fraction distilled. They conclude that a curve with a small inter-

mediate fraction is the most desirable.

About the same time several design methods were presented by various authors (1, 16, 28) but they all neglected the effect of holdup and usually made other assumptions of questionable validity.

Colburn and Stearns (5) also made an early contribution of considerable significance. They presented a good analysis of the situation based on differential material balances and gave, although incomplete, the first experimental data for batch rectification in a plate column. Also they were the first to recognize clearly the non-applicability of the McCabe-Thiele method to batch rectification calculations.

In 1943-44 Edgeworth-Johnstone (7, 8) presented an analysis of operation under conditions of varying reflux ratio to maintain constant product composition. He presented methods for calculating the "yield fraction" of a component under various conditions, but assumed constant moles of holdup, constant average composition of holdup, and the validity of the McCabe-Thiele operating line in computing composition. Chu (3) later presented an analytical solution of Edgeworth-Johnstone's graphical method. The limitations of this work are discussed by Rose and Chu (17).

Bowman and Cichelli (2) and Cichelli et al (4) introduced the concept of a so-called "pole-height" in an effort to relate empirically the effect of various operating variables to the size of the intermediate fraction. Again the assumptions of no holdup and of equal molal overflow limit the usefulness of this work.

The recent work of Rose and associates (18, 19, 20, 25) involving the use of finite incremental calculations has already been discussed in the introduction to this thesis. In addition, using data from a small packed column, Rose et al (26) have recently discussed the effect of reflux ratio on the relationship between hold-up to charge ratio and sharpness of separation.

Marshall and Pigford (11) and Pigford et al (13) have presented the basic differential material balances with the assumption of constancy of moles of holdup and of equal molal overflow. They also discuss various possible techniques for effecting the solution of these equations. If the differential material balances are combined with an analytical expression for the equilibrium data, a differential-difference equation will result. Then, if the expression for the equilibrium data were linear, the differential-difference equation could be solved by use of the Laplace transform. Since the non-linearity of the equilibrium data eliminates this possibility, they used a differential analyzer to solve the equations in differential form using an approximate expression for the equilibrium relationship.

From this review, it can be seen that prior to this investigation neither satisfactory calculational techniques nor adequate experimental data were available for batch rectification.

APPENDIX B

DETAILS OF APPARATUS AND EXPERIMENTAL PROCEDURE

1. Description of Apparatus

Figures 2 and 3 (pp. 25-26) show the general arrangement of the apparatus used in this investigation. Figure 4 (p. 27) shows the plate layout and includes the pertinent dimensions.

The apparatus was set up by revamping a tower of somewhat ancient vintage. The best information indicates that the tower was installed in the unit operations laboratory around 1925. Nevertheless, the tower was in perfect operating condition and it was necessary only to rearrange some of the lines, add insulation, and to install a stirrer in the still pot and a rotameter in the product line. The reflux rotameter had to be calibrated, but a calibration curve was obtained from the manufacturer for the newly installed product rotameter. The exact calibration of the latter was of little importance because the product was weighed at 30 minute intervals. However, this meter was of value in setting the control valve to maintain a constant rate of product withdrawal. The reflux rotameter was calibrated by connecting rubber tubing from the bottom of a constant level tank to the inlet of the rotameter. The rate of flow, adjusted to a desired value by a screw clamp on the tubing, was obtained by noting the time required to fill a 1000 cc volumetric flask. The results of this calibration are shown in Figure 12, p. 130.

Although the plate layout (one four-inch, non-slotted cap per plate) does not represent modern construction, the plate efficiency of the tower (60 percent) was nevertheless of the same order of magnitude as is usually found in distillation towers of the most modern design. Dimensions were measured on the top plate of the bottom section. The volume of holdup on the individual plates was obtained while the tower was disassembled by measuring the amount of water that could be drained from each plate after it had been filled to overflowing. It was recognized that the volumes of holdup would be greater during actual operation than these values obtained under static conditions. Therefore, the total holdup was later measured under dynamic conditions and then the values for each plate were adjusted by the ratio of total dynamic holdup to total static holdup. This ratio amounted to 1.43. In Table XXVII, p. 124 are given the dynamic holdup values for each plate.

The variation in these holdup values is probably due to the poor construction of the downcomers which among other things varied in height from plate-to-plate. In towers of more modern construction these values would be more nearly constant.

Conventional laboratory thermometers marked with 1°C intervals were used on the plates. These thermometers were calibrated against one having a Bureau of Standards certificate of calibration. The average deviation was about $1/3^{\circ}\text{C}$. All other thermometers in the system were of the industrial type and were reliable to $\pm 1^{\circ}\text{F}$ or 2°F .

2. Detailed Experimental Procedure

a. Total Reflux Runs

The still pot was filled about half full of liquid of desired composition and the distillation was carried out at total reflux for approximately 3 hours to insure the attainment of steady state. Then the samples were taken, the temperatures recorded, and reflux meter read. The initial still pot compositions were varied from 0.03 to 0.15 weight fraction methanol in order that the points on the curve would cover a wide range of compositions.

b. Batch Rectification Runs

(1) Charging the still pot

All holdup in the column from the previous run was drained from the column. Then the still pot was filled with the desired amount of liquid of specified composition.

(2) Startup and warmup period

The cooling water for the condenser was turned on, the steam valve was opened to give about 0.5 inch Hg. pressure (flo-control valve set at a position of about 0.65), and the stirrer was started. In approximately 15 minutes the first reflux appeared, and all of it was returned to the column (total reflux) for approximately half an hour in order to fill the plates with liquid. Then partial reflux, equal to the value to be employed in the run, was used for an additional 2-1/4 hours. During this latter period of

time the "product" was returned continuously to the still pot. Thus the total warmup time was 3 hours, and in all cases, all temperatures were observed to be constant during the last 60-90 minutes of this period. Meanwhile, the cooling water to the condenser was adjusted to give a reflux temperature of approximately 125°F. (a higher value gave rise to serious vapor losses from the vent of the condenser).

(3) Batch rectification period

The batch rectification was started by closing the valves between the still pot and the product receiver so that product was removed from the system. At this moment (time = 0 min.) the stop-watch was started. In runs 14 to 18 constant reflux was maintained by adjusting the reflux control valve. In runs 18 to 28 constant reflux and at the same time constant vapor flow were maintained by adjusting the flo-control valve in the steam line to the calandria.

The column had thermometer wells only on alternate plates and therefore temperatures could be obtained only for the even numbered plates (counting from the bottom). As explained previously (p. 28) representative samples of liquid could be obtained only from the same plates. To enhance the accuracy of the results, several precautions were observed in regard to the sampling. All sampling lines were purged adequately before the actual samples were taken. The volume purged depended on the dimensions of the sampling line and a considerable factor of safety was used. For all plates, 15 cc of purge liquid was withdrawn before the sample was taken;

for the reflux the purge was 25 cc; for the still pot 400 cc. The volume of the samples was between 10 and 15 cc. To prevent loss of vapor, chilled bottles with necks that fit closely to the sampling lines were used. These sampling bottles consisted of dropping bottles each of which had its own medicine dropper to prevent contamination.

The order in which the data were taken was as follows;
-6 min. to -4 min.*; Temperatures of still vapor, of liquid on plates 2, 4, 6, 8, 10, 12, and of reflux taken in that order.

-4 min. to -1 min.*; Sampling of liquid from still, plates 2, 4, 6, 8, 10, 12, and reflux in that order.

0 min.: Beginning of product withdrawal from the system; stopwatch started.

25-27 min.: Temperatures recorded as described above.

28-29 min.: Meters read.

30 min.: Product flow changed to other side of product receiver.

30-33 min.: Liquid samples taken as described above.

34 min.: If necessary, steam valve was adjusted to maintain a constant vapor rate as indicated by constancy of product and reflux meters.

*A negative time indicates time prior to the start of the batch rectification period.

35 min.; Product collected during the time interval from 0 to 30 min. was withdrawn from the receiver and weighed. The set of readings listed for 25-35 min. was repeated at 30 min. intervals until the end of the run. The batch rectification was continued for 2 to 2-1/2 hours, giving 5 or 6 complete sets of data.

3. Analysis

The compositions of the samples were determined by measuring their refractive indices at 20°C ($\pm 0.1^\circ\text{C}$). These measurements were made with an Abbe refractometer which was adjusted (using conductivity water) to give readings that required no subsequent correction. A curve relating composition to refractive index (Fig. 8, p. 94) was calculated theoretically using the procedure described in Appendix D. This theoretical curve was later confirmed experimentally with mixtures made up by combining weighed amounts of each of the two pure components. The average deviation between the theoretical and experimental values is approximately 0.2 weight fraction.

APPENDIX C
EXPERIMENTAL DATA

In Table III is given a resume of all the runs made in the experimental investigation.

The data for the total reflux runs 2-9 are given in Table IV.

Runs 16, 19, 22, 23, and 28 were chosen in Part V to test the theoretical relationships because these runs represent the widest range of variables. Therefore, the experimental data for these runs plus that for Runs 21 and 26, the runs made to check Run 19, are given in Tables V-XI.

Table XII presents the holdup measurements; miscellaneous data are presented in Table XIII.

Table III
Resume of Experimental Runs

This table gives a resume of all experimental runs including the pertinent conditions of operation.

Run	Reflux Fraction	Wt. Fraction Methanol in Initial Charge	Weight Ratio Holdup to Charge	Remarks
1	---	---	---	Preliminary Test Run
2-9	Total Reflux	---	---	Runs made to determine the liquid-vapor composition curve for the column.
10-13	---	---	---	Practice runs at partial reflux
14	.865	.229	.383	Because of low charge composition plate compositions covered narrow range. Reflux fraction varied slightly during these runs.
15	.815	.231	.383	
16	.725	.231	.383	
17	.575	.233	.383	
18	.575	.233	.383	First run in which boilup rate and reflux fraction held constant. Data covered narrow range of plate compositions.

Table III (continued)

Run	Reflux Fraction	Wt. Fraction Methanol in Initial Charge	Weight Ratio Holdup to Charge	Remarks
19	.725	.453	.383	Increased charge concentration gave satisfactory range of plate compositions
20	.725	.451	.352	The molal ratio of holdup to charge was the same in Runs 19 and 20
21	.725	.453	.383	Made to check Run 19
22	.850	.453	.383	---
23	.575	.453	.383	---
24	.575	.453	.383	Made to check Run 23
25	.725	.438	.383	Error in initial charge composition
26	.725	.453	.383	Made as an additional check on Runs 19 and 21
27	---	---	---	Run discarded because entire warmup at total reflux
28	.725	.453	.273	---

Table IV

Experimental Data for Runs 2-9 (Total Reflux)

(Place 1.3 before all values of refractive index listed)

Plate 2		Plate 4		Plate 6		Plate 8		Plate 10		Plate 12		Plate 12	
Liquid	(°C)	Liquid	(°C)	Liquid	(°C)	Liquid	(°C)	Liquid	(°C)	Liquid	(°C)	Vapor	Reflux
												(°F)	(°F)
Run 2: Barometer 29.82" mercury; Reflux Meter 64 $\pm$ 1 mm.													
Temperatures	80 $\frac{1}{3}$	77 $\frac{1}{2}$	75	71	68	65 $\frac{1}{2}$	150 $\frac{1}{2}$						130
Refractive Indices of Samples	743	710	653	567	474	410	-						*
Run 3: Barometer 29.55" mercury; Reflux Meter 31 $\pm$ 2 mm.													
Temperatures	81 $\frac{1}{3}$	80	78 $\frac{1}{2}$	75 $\frac{1}{3}$	72	68 $\frac{1}{2}$	155						113
Refractive Indices of Samples	760	746	721	675	598	497	-						*
Run 4: Barometer 29.50" mercury; Reflux Meter 118 $\pm$ 2 mm.													
Temperatures	81 $\frac{2}{3}$	80 $\frac{1}{3}$	79	76	72 $\frac{2}{3}$	69	156 $\frac{1}{2}$						122
Refractive Indices of Samples	765	752	730	688	614	513	-						*

*Faulty samples due to insufficient purging of reflux sampling line.

Table IV (continued)

Plate 2		Plate 4	Plate 6	Plate 8	Plate 10	Plate 12	Plate 12	Reflux
Liquid		Liquid	Liquid	Liquid	Liquid	Liquid	Vapor	($^{\circ}\text{F}$)
($^{\circ}\text{C}$)		($^{\circ}\text{C}$)	($^{\circ}\text{C}$)	($^{\circ}\text{C}$)	($^{\circ}\text{C}$)	($^{\circ}\text{C}$)	($^{\circ}\text{F}$)	($^{\circ}\text{F}$)
<u>Run 5:</u> Barometer 29.60" mercury; Reflux Meter 72 $\pm$ 2mm.								
Temperatures	78 $\frac{1}{2}$	75	72	68	66	64 $\frac{2}{3}$	148 $\frac{1}{2}$	120
Refractive Indices of Samples*	717	665	579	478	400	361	-	352
<u>Run 6:</u> Barometer 29.59" mercury; Reflux Meter 71 $\pm$ 2 mm.								
Temperatures	73	69	67	65	64 $\frac{1}{4}$	64	147 $\frac{1}{2}$	120
Refractive Indices of Samples*	606	503	409	350	328	325	-	328
<u>Run 7:</u> Barometer 29.59" mercury; Reflux Meter 71 $\pm$ 2 mm.								
Temperatures	73 $\frac{1}{2}$	69	67	65	64 $\frac{1}{3}$	64	147 $\frac{1}{2}$	120
Refractive Indices of Samples*	616	512	410	351	329	325	-	329

*Place 1.3 before each value of refractive index listed.

Table IV (continued)

Plate 2		Plate 4		Plate 6		Plate 8		Plate 10		Plate 12		Plate 12	
Liquid		Liquid		Liquid		Liquid		Liquid		Liquid		Vapor	
(°C)		(°C)		(°C)		(°C)		(°C)		(°C)		(°F)	
<u>Run 8:</u> Barometer 29.46" mercury; Reflux Meter 72± 2 mm.													
Temperatures	74½	70	67½	65¼	64½	64	147½	120					
Refractive Indices of Samples*	642	543	437	367	333	324	-	326					
<u>Run 9:</u> Barometer 29.57" mercury; Reflux Meter 74± 2 mm.													
Temperatures	77	73	69¾	66⅔	65	64½	148	120					
Refractive Indices of Samples*	685	618	514	415	356	330	-	327					

*Place 1.3 before each value of refractive index listed.

Table V

Experimental Data for Run 16

Barometer: 29.75 in. Hg.; Still Charge: Weight 81 lbs., Refractive Index 1.3662

Time "0 minutes" refers to the beginning of the batch rectification period at the end of the 3 hour warmup period; readings made in order listed during time interval indicated.

<u>Temperatures</u>	<u>Time (Min.)</u>			
	0*	25-27	55-57	85-87
Still Vapor °F	162 $\frac{1}{2}$	164	167 $\frac{1}{2}$	172
Plate 2 Liquid °C	76	77	79	80 $\frac{1}{3}$
Plate 4 Liquid °C	75	75 $\frac{2}{3}$	77 $\frac{1}{2}$	79 $\frac{1}{2}$
Plate 6 Liquid °C	74	74 $\frac{3}{4}$	76 $\frac{2}{3}$	79
Plate 8 Liquid °C	72	72 $\frac{3}{4}$	75	77 $\frac{1}{2}$
Plate 10 Liquid °C	69 $\frac{1}{2}$	70	72 $\frac{1}{4}$	75 $\frac{1}{3}$
Plate 12 Liquid °C	67 $\frac{1}{4}$	67 $\frac{2}{3}$	69 $\frac{1}{3}$	72 $\frac{1}{3}$
Plate 12 Vapor °F	153	154	157	162 $\frac{1}{2}$
Reflux °F	127	127	127	130
Product °F (at meter)	112	112	112	115

(continued next page)

*These readings made during the warmup period just prior to time 0.

Table V -- Run 16 (continued)

<u>Material Quantities</u>									
	Time (Min.)	0*		29	59	89			
Reflux Meter-float level in mm. (±2 mm.)	52	52½		53	57				
Product Meter-float level in mm. (±½ mm.)	58½	48½		48	50				
Accumulated Product									
Accumulation time (min.)	-	0-30		30-60	60-90				
Weight (lbs.-ozs.)		6-9		6-5	6-5				
<u>Refractive Indices of Samples (Place 1.3 before each value of R.I. listed)</u>									
	Time (Min.)	0*		30-33	60-63	90-93			
Still Liquid		684		709	731	753			
Plate 2 Liquid		670		697	724	748			
Plate 4 Liquid		658		682	713	742			
Plate 6 Liquid		633		659	698	732			
Plate 8 Liquid		594		619	669	717			
Plate 10 Liquid		530		553	614	682			
Plate 12 Liquid		450		466	525	617			
Reflux		409		421	471	560			

*See footnote on previous page.

Table VI

Experimental Data for Run 19

Barometer: 29.44 in. Hg.; Still Charge: Weight 81 lbs., Refractive Index 1.3552

Time "0 minutes" refers to the beginning of the batch rectification period at the end of the 3 hour warmup period; readings made in order listed during time interval indicated.

Temperatures

	Time (Min.)	0*	25-27	55-57	85-87	115-117
Still Vapor °F		156 $\frac{1}{2}$	159 $\frac{1}{2}$	162	166 $\frac{1}{2}$	172
Plate 2 Liquid °C		70 $\frac{1}{3}$	71	73	75 $\frac{1}{3}$	78
Plate 4 Liquid °C		67 $\frac{2}{4}$	68 $\frac{1}{2}$	70	72 $\frac{2}{3}$	76
Plate 6 Liquid °C		66 $\frac{2}{3}$	67	68	70 $\frac{1}{2}$	74 $\frac{1}{3}$
Plate 8 Liquid °C		65 $\frac{1}{2}$	65 $\frac{1}{2}$	66	67 $\frac{2}{3}$	71 $\frac{1}{4}$
Plate 10 Liquid °C		64 $\frac{1}{2}$	64 $\frac{2}{3}$	65	66	68
Plate 12 Liquid °C		64 $\frac{1}{3}$	64 $\frac{1}{3}$	64 $\frac{1}{2}$	65	66
Plate 12 Vapor °F		148	148	148 $\frac{1}{4}$	149	151 $\frac{1}{2}$
Reflux °F		125	126	125	125	126
Product °F (at meter)		112	113	113	113	113

(continued next page)

*These readings made during the warmup period just prior to time 0.

Table VI - Run 19 (continued)

Material Quantities

	Time (Min.)	0*	29	59	89	119
Reflux Meter-float level in mm. (± 2 mm.)		52	52	52	52	52
Product Meter-float level in mm. ($\pm \frac{1}{2}$ mm.)		48 $\frac{1}{2}$	48 $\frac{1}{2}$	48 $\frac{1}{2}$	48 $\frac{1}{2}$	48 $\frac{1}{2}$

Accumulated Product

Accumulation time (Min.)	-	0-30	30-60	60-90	90-120
Weight (lbs.-ozs.)		6-6	6-5	6-5	6-6

Refractive Indices of Samples (Place 1.3 before each value of refractive index listed)

	Time (Min.)	0*	30-33	60-63	90-93	120-123
Still Liquid		605	635	662	697	735
Plate 2 Liquid		532	565	614	670	718
Plate 4 Liquid		472	498	557	630	696
Plate 6 Liquid		410	430	481	562	659
Plate 8 Liquid		361	372	407	481	599
Plate 10 Liquid		331	337	355	402	511
Plate 12 Liquid		315	316	323	347	417
Reflux		310	310	314	329	371

*See footnote on previous page.

Table VII

Experimental Data for Run 21

Barometer: 29.35 in. Hg.; Still Charge: Weight 81 lbs., Refractive Index 1.3551

Time "0 minutes" refers to the beginning of the batch rectification period at the end of the 3 hour warmup period; readings made in order listed during time interval indicated.

<u>Temperatures</u>	<u>Time (Min.)</u>	<u>0*</u>	<u>25-27</u>	<u>55-57</u>	<u>85-87</u>	<u>115-117</u>	<u>145-147</u>
Still Vapor °F		158	159½	163	167	172	176½
Plate 2 Liquid °C		70	71	72¾	75½	78½	80½
Plate 4 Liquid °C		67½	68¾	70	72¾	76¾	79¾
Plate 6 Liquid °C		66½	67	68	70¾	75	78½
Plate 8 Liquid °C		65¾	65½	66	67¾	71¾	76¾
Plate 10 Liquid °C		64½	64½	65	66	68¾	74½
Plate 12 Liquid °C		64¾	64¾	64½	65	66½	70½
Plate 12 Vapor °F		147½	148	148¾	149	152	159
Reflux °F		125	125	123	124	125	127
Product °F (at meter)		112	114	112	113	112	113

(continued next page)

*These readings made during the warmup period just prior to time 0.

Table VII - Run 21 (continued)

<u>Material Quantities</u>		Time (Min.)				
		0*	29	59	89	119
Reflux Meter-float level in mm. (± 2 mm.)		52	52	52	52	52
Product Meter-float level in mm. ($\pm \frac{1}{2}$ mm.)		48 $\frac{1}{2}$	48 $\frac{1}{2}$	48 $\frac{1}{2}$	48 $\frac{1}{2}$	48 $\frac{1}{2}$
Accumulated Product						
Accumulation time (min.)		-	0-30	30-60	60-90	90-120
Weight (lbs.--ozs.)			6-12	6-9	6-8	6-4
Refractive Indices of Samples						
	Time (Min.)	0*	30-33	60-63	90-93	120-123
Still Liquid		1.3599	1.3626	1.3661	1.3703	1.3740
Plate 2 Liquid		1.3527	1.3562	1.3612	1.3673	1.3724
Plate 4 Liquid		1.3467	1.3497	1.3553	1.3632	1.3703
Plate 6 Liquid		1.3405	1.3428	1.3480	1.3571	1.3670
Plate 8 Liquid		1.3360	1.3370	1.3407	1.3489	1.3611
Plate 10 Liquid		1.3330	1.3337	1.3353	1.3410	1.3526
Plate 12 Liquid		1.3314	1.3318	1.3324	1.3351	1.3427
Reflux		1.3312	1.3312	1.3315	1.3330	1.3381

*See footnote on previous page.

Table VIII

Experimental Data for Run 22

Barometer: 29.33 in. Hg.; Still Charge: Weight 81 lbs.; Refractive Index 1.3552

Time "0 minutes" refers to the beginning of the batch rectification period at the end of the 3 hour warmup period; readings made in order listed during time interval indicated.

<u>Temperatures</u>	<u>Time (min.)</u>						
	0*		25-27	55-57	85-87	115-117	175-177
Still Vapor °F	157	159	160½	162½	165½	173	
Plate 2 Liquid °C	69½	69¾	71	72½	74½	79	
Plate 4 Liquid °C	66½	67	67¾	69	71	76¾	
Plate 6 Liquid °C	65¾	66	66¾	67¾	68½	74¾	
Plate 8 Liquid °C	64½	64¾	65	65½	66¼	71½	
Plate 10 Liquid °C	64½	64¾	64¾	65½	65	68	
Plate 12 Liquid °C	64	64	64¾	65½	66¾	66	
Plate 12 Vapor °F	147	147	147½	147½	148	151	
Reflux °F	126	125	125	125	125	125	
Product °F (at meter)	107	105	103	103	102	103	

(continued next page)

* These readings made during the warmup period just prior to time 0.

Table VIII -- Run 22 (continued)

<u>Material Quantities</u>								
	Time (Min.)	0*						
		29	59	89	119	179		
Reflux Meter-float level in mm.(±2 mm.)	59	59	59	59	59	59	59	
Product Meter-float level in mm.(±½ mm.)	34½	34½	34½	34½	34½	34½	34½	
Accumulated Product								
Accumulation time (min.)	-	0-30	30-60	60-90	90-120	120-180		
Weight (lbs.-ozs.)		4-6	4-5	4-4	4-3	8-9		
<u>Refractive Indices of Samples</u> (Place 1.3 before each value of refractive index listed)								
	Time (Min.)	0*						
		30-33	60-63	90-93	120-123	180-183		
Still Liquid	606	625	649	671	702	752		
Plate 2 Liquid	507	530	562	607	652	733		
Plate 4 Liquid	431	448	480	528	585	710		
Plate 6 Liquid	372	381	402	441	499	668		
Plate 8 Liquid	338	340	351	374	413	595		
Plate 10 Liquid	320	321	325	335	354	499		
Plate 12 Liquid	313	314	313	318	322	402		
Reflux	316	318	313	312	313	366		

*See footnote on previous page.

Table IX

Experimental Data for Run 23

Barometer: 29.64 in. Hg.; Still Charge: Weight 81 lbs.; Refractive Index 1.3552

Time "0 minutes" refers to the beginning of the batch rectification period at the end of the 3 hour warmup period; readings made in order listed during time interval indicated.

Temperatures

	Time (min.)	0*	25-27	55-57	85-87	105-107
Still Vapor °F		155	156	159½	164½	168
Plate 2 Liquid °C		71½	72½	74¾	78	80¾
Plate 4 Liquid °C		70	71	73¼	77	79¾
Plate 6 Liquid °C		69½	70	72¼	76¼	79
Plate 8 Liquid °C		67⅔	68	70¼	74½	77½
Plate 10 Liquid °C		66⅓	66⅔	68¼	72¼	76
Plate 12 Liquid °C		65½	65⅔	66½	69½	73⅓
Plate 12 Vapor °F		149½	150	151½	167	164
Reflux °F		125	125	125	125	127
Product °F (at meter)		120	120	120	120	121

(continued next page)

*These readings made during the warmup period just prior to time 0.

Table IX - Run 23 (continued)

<u>Material Quantities</u>		Time (Min.)				
		0*	29	59	89	109
Reflux Meter-float level in mm. (± 2 mm.)		40	40	40	40	41
Product Meter-float level in mm. ($\pm \frac{1}{2}$ mm.)		70	70	70	70	70
Accumulated Product						
Accumulation time (min.)	-		0-30	30-60	60-90	90-110
Weight (lbs.-ozs.)			10-6	10-4	10-4	6-15
<u>Refractive Indices of Samples (Place 1.3 before each value of refractive index listed)</u>						
	Time (Min.)	0*	30-33	60-63	90-93	110-113
Still Liquid		582	623	674	727	754
Plate 2 Liquid		556	598	653	714	748
Plate 4 Liquid		531	569	636	704	740
Plate 6 Liquid		496	532	603	691	732
Plate 8 Liquid		450	481	559	668	720
Plate 10 Liquid		401	423	492	621	697
Plate 12 Liquid		358	369	414	537	640
Reflux		340	343	371	472	583

*See footnote on previous page.

Table X

Experimental Data for Run 26

Barometer: 29.34 in. Hg.; Still Charge: Weight 81 lbs., Refractive Index 1.3552

Time "0 minutes" refers to the beginning of the batch rectification period at the end of the 3 hour warmup period; readings made in order listed during time interval indicated.

Temperatures

	Time (min.)	0*	25-27	55-57	85-87	115-117	145-147
Still Vapor °F		157	157	159½	162	165½	170
Plate 2 Liquid °C		70¼	71	72⅔	75	78	80¼
Plate 4 Liquid °C		67⅔	68¼	69⅔	72½	76	79
Plate 6 Liquid °C		66⅔	67	68	70¼	74	78
Plate 8 Liquid °C		65⅓	65½	66	67⅔	71	76
Plate 10 Liquid °C		64½	64⅔	65	66	68	73
Plate 12 Liquid °C		64¼	64⅓	64½	65	66	70
Plate 12 Vapor °F		147½	147½	148	148½	151	157½
Reflux °F		122	122	123	123	125	126
Product °F (at meter)		112	112	113	113	115	116

(continued next page)

*These readings made during the warmup period just prior to time 0.

Table X - Run 26 (continued)

<u>Material Quantities</u>		Time (Min.)	0*	29	59	89	119	149
Reflux Meter-float level in mm. (± 2 mm.)			52	52	52	52	52	52
Product Meter-float level in mm. ($\pm \frac{1}{2}$ mm.)			$48\frac{1}{2}$	$48\frac{1}{2}$	$48\frac{1}{2}$	$48\frac{1}{2}$	$48\frac{1}{2}$	$48\frac{1}{2}$
Accumulated Product								
Accumulation time (min.)			-	0-30	30-60	60-90	90-120	120-150
Weight (lbs.-ozs.)				6-6	6-5	6-5	6-4	6-3
<u>Refractive Indices of Samples (Place 1.3 before each value of refractive index listed)</u>								
	Time (Min.)	0*	30-33	60-63	90-93	120-123	150-153	
Still Liquid		601	630	663	700	734	761	
Plate 2 Liquid		530	560	608	663	717	750	
Plate 4 Liquid		469	493	550	622	693	741	
Plate 6 Liquid		410	424	471	557	656	728	
Plate 8 Liquid		361	372	402	473	591	700	
Plate 10 Liquid		333	340	354	400	502	649	
Plate 12 Liquid		322	322	329	348	410	557	
Reflux		321	321	321	330	371	494	

*See footnote on previous page.

Table XI

Experimental Data for Run 28

Barometer: 29.47 in. Hg.; Still Charge: Weight 115 lbs., Refractive Index 1.3552

Time "0 minutes" refers to the beginning of the batch rectification period at the end of the 3 hour warmup period; readings made in order listed during time interval indicated.

<u>Temperatures</u>						
Time (min.)	0*	25-27	85-87	115-117	145-147	190-192
Still Vapor °F	156½	158	162	164½	167½	173
Plate 2 Liquid °C	69⅔	70	72½	74¼	76	79
Plate 4 Liquid °C	67⅓	67⅔	69⅔	71⅔	74	77⅔
Plate 6 Liquid °C	66⅓	66⅔	68	69⅔	72	76⅔
Plate 8 Liquid °C	65¼	65⅓	66	67⅓	69⅓	74
Plate 10 Liquid °C	64⅔	64⅔	65	65⅔	67	71
Plate 12 Liquid °C	64⅓	64⅓	64⅔	65	65⅔	68¾
Plate 12 Vapor °F	147½	147½	148	148½	149½	154½
Reflux °F	127	127	125	124	124	125
Product °F (at meter)	117	117	116	115	115	115

(continued next page)

(continued next page)

*These readings made during the warmup period just prior to time 0.

Table XI - Run 28 (continued)

<u>Material Quantities</u>							
Time (Min.)	0*	29	89	119	149	194	
Reflux Meter-float level in mm.(±2 mm.)	52	52	52	52	52	52	
Product Meter-float level in mm.(±½ mm.)	48½	48½	48½	48½	48½	48½	
Accumulated Product							
Accumulation time (min.)	-	0-30	30-90	90-120	120-150	150-195	
Weight (lbs.-ozs.)		6-11	13-5	6-11	6-6	9-7	
<u>Refractive Indices of Samples</u> (Place 1.3 before each vlue of refractive index listed)							
Time (Min.)	0*	30-33	90-93	120-123	150-153	195-198	
Still Liquid	587	602	649	677	701	740	
Plate 2 Liquid	511	531	599	639	680	730	
Plate 4 Liquid	452	470	539	592	647	718.	
Plate 6 Liquid	399	409	468	528	596	696	
Plate 8 Liquid	358	362	401	451	523	657.	
Plate 10 Liquid	331	336	357	387	440	591	
Plate 12 Liquid	322	322	330	341	371	491	
Reflux	322	322	322	330	346	434	

*See footnote on previous page.

Table XII
Experimental Holdup Measurements

A. Static Holdup

Plate Number (Counting from bottom)	Vol. Static Holdup (cc. of water, - 10cc.)
1	1125
2	955
3	1130
4	785
5	1085
6	955
Total (bottom section)	<u>6025</u>
7	1220
8	1000
9	1140
10	290*
11	1400
12	985
Total (top section)	<u>6035</u>

Independent cumulative measurements for top and bottom sections:

Bottom section	6000 ($\pm$ 50 cc.)
Top section	5980 ($\pm$ 50 cc.)

B. Dynamic Holdup

Feed to still pot:	Volume	1.71 cu. ft.
	Mole fraction	0.362
	Temperature	75°F

Liquid remaining in still pot after equilibrium had been attained at total reflux:

	Volume	1.10 cu. ft.
	Mole fraction	0.300
	Temperature	162 °F

*Low value due to small hole which passed liquid under static conditions but not under dynamic conditions.

Table XIII
Miscellaneous Experimental Data

A. Check Points for Calculated Refractive Index Curve (Fig. 8).

Refractive Index	Weight Methanol (grams)	Weight Isopropanol (grams)	Wt. Fraction Methanol (x)
1.3665	2.9380	10.2415	.225
1.3667	4.0610	14.4690	.218
1.3758	0.5945	15.5690	.033
1.3714	2.0735	14.8200	.123
1.3594	7.1210	12.3280	.370
1.3503	9.0005	7.2865	.557
1.3409	15.3420	5.1030	.750
1.3341	17.6140	2.1755	.893
1.3540	10.0840	10.8880	.480
1.3694	3.1670	16.2820	.164
1.3753	0.7550	17.4610	.043
1.3552	8.6920	10.6435	.453
1.3288	100% Methanol		
1.3776	100% Isopropanol		

The values for the two pure components agree exactly with those given in Lange's Handbook.

B. Sizes of Purges and Samples for Batch Rectification Runs

Material	Vol. Purged (cc.)*	Vol. of Sample (cc.)
Liquid on plates	15	10 - 15
Reflux	25	10 - 15
Still pot liquid	400	10 - 15

Total weight of all samples plus purges for Runs 19, 20, and 21 ranged from 5 to $5\frac{1}{4}$ pounds.

C. Physical Properties of Methanol and Isopropanol

Vapor pressures, densities, specific heats, and heats of vaporization taken from Timmermans (30).

*Governed by the size of the sampling line.

APPENDIX DCALCULATION PROCEDURES AND SAMPLE CALCULATIONS

The various calculations performed in the course of this investigation will be grouped and discussed as follows;

1. Calculation of refractive indices of mixtures of methanol and isopropanol.
2. Preparation of the liquid-vapor composition curve using data obtained at total reflux; calculation of plate efficiency.
3. Preparation of the enthalpy-concentration chart for mixtures of methanol and isopropanol.
4. Calculations made in the evaluation and presentation of the batch rectification data.
5. Calculations made in Part V to check assumptions made in Part III.

1. Calculation of refractive indices of mixtures of methanol and isopropanol.

The following relationships are based on some unpublished work of Professor R. S. Tour (30). The underlying principle consists of applying the additive property rule to the specific refractions of components that exhibit additive volumes on mixing. This relationship can be expressed mathematically as follows;

$$r_S = x_1 r_1 + (1-x_1)r_2 \quad (20)$$

Let $\frac{n^2-1}{N+2}$ be represented by a .

$$\text{then } r = \frac{a}{d} \quad (21)$$

$$\frac{a_S}{d_S} = x_1 \frac{a_1}{d_1} + (1-x_1) \frac{a_2}{d_2} \quad (22)$$

Basis: 1 gram of solution (assume additive volumes)

$$\begin{aligned} d_S &= \frac{1}{\frac{x_1}{d_1} + \frac{(1-x_1)}{d_2}} = \frac{1}{\frac{d_2 x_1 + d_1(1-x_1)}{d_1 d_2}} = \frac{d_1 d_2}{d_1 - (d_1 - d_2)x_1} \\ d_S &= \frac{d_2}{1 - \frac{d_1 - d_2}{d_1} x_1} \end{aligned} \quad (23)$$

Substituting (23) into (22),

$$a_S \left[\frac{1 - \frac{d_1 - d_2}{d_1} x_1}{\frac{d_2}{d_1}} \right] = x_1 \frac{a_1}{d_1} + (1-x_1) \frac{a_2}{d_2} =$$

$$\begin{aligned}
&= x_1 \left(\frac{a_1}{d_1} \right) + \frac{a_2}{d_2} - x_1 \left(\frac{a_2}{d_2} \right) \\
&= \frac{x_1 a_1}{d_1} - \frac{x_1 a_2}{d_1} + \frac{d_2 x_1 a_2}{d_2 d_1} + \frac{a_2}{d_2} - \frac{x_1 a_2}{d_2} \\
&= \frac{x_1}{d_1} (a_1 - a_2) + \frac{1}{d_2} \left[1 - \left(1 - \frac{d_2}{d_1} \right) x_1 \right] a_2 \\
&= \frac{x_1}{d_1} (a_1 - a_2) + \left[\frac{1 - \left(\frac{d_1 - d_2}{d_1} \right) x_1}{d_2} \right] a_2 \\
(a_S - a_2) &= \frac{x_1}{d_1} \left[\frac{d_2}{1 - \frac{d_1 - d_2}{d_1} x_1} \right] (a_1 - a_2) = \frac{x_1 d_S}{d_1} (a_1 - a_2) \quad (24)
\end{aligned}$$

Now substitute for $a = \frac{N^2 - 1}{N^2 + 2}$

$$\frac{N_S^2 - 1}{N_S^2 + 2} - \frac{N_2^2 - 1}{N_2^2 + 2} = \frac{x_1}{d_1} \left[\frac{d_2}{1 - \frac{d_1 - d_2}{d_1} x_1} \right] \left[\frac{N_1^2 - 1}{N_1^2 + 2} - \frac{N_2^2 - 1}{N_2^2 + 2} \right]$$

$$\frac{N_S^2 - 1}{N_S^2} - b = \frac{K x_1}{1 - K x_1}$$

where,

$$K = \frac{d_2}{d_1} \frac{N_1^2 - 1}{N_1^2 + 2} - \frac{N_2^2 - 1}{N_2^2 + 2}$$

$$k = \frac{d_1 - d_2}{d_1} ; b = \frac{N_2^2 - 1}{N_2^2 + 2}$$

$$\frac{N_S^2 - 1}{N_S^2 + 2} = \frac{Kx_1}{1 - Kx_1} + b \quad (25)$$

Converting to mole fraction;

$$x_1 = \frac{x_1^i M_1}{x_1^i M_1 + (1 - x_1^i) M_2} = \frac{1}{1 + \frac{1 - x_1^i}{x_1^i} \frac{M_2}{M_1}} = \frac{1}{1 + \frac{(1 - x_1^i)}{x_1^i} m}$$

$$\text{let } m = \frac{M_2}{M_1}$$

$$\frac{N_S^2 - 1}{N_S^2 + 2} = \frac{K \left[\frac{1}{1 + \frac{(1 - x_1^i)}{x_1^i} m} \right]}{1 - K \left[\frac{1}{1 + \frac{(1 - x_1^i)}{x_1^i} m} \right]} + b$$

By algebraic manipulation this equation can be rearranged to give,

$$\frac{N_S^2 - 1}{N_S^2 + 2} = \frac{Kx_1^i}{m + \gamma x_1^i} + b \quad (26)$$

where,

$$\gamma = 1 - m = \frac{d_1 - d_2}{d_1}$$

let z represent $\frac{Kx_1^I}{m + \gamma x_1^I} + b$

$$\text{Then } \frac{N_S^2 - 1}{N_S^2 + 2} = z$$

$$N_S^2 - 1 = z N_S^2 + 2z$$

$$(1 - z)N_S^2 = 2z + 1$$

$$N_S = \sqrt{\frac{2z + 1}{1 - z}} \quad (27)$$

Since Fig. 8 in its final form involves weight fractions, equation (25) could have been used directly to compute the refractive indices. However, when this plot was initially prepared, it was thought that mole fractions would be desired. Therefore, equation (27) was used to compute refractive indices for various mole fractions, and then later these mole fractions were converted to weight fractions and used to prepare Fig. 8. The calculation procedure will be illustrated for a mixture having a weight fraction, $x = 0.347$ (mole fraction, $x^I = 0.500$).

Component 1 = methanol; component 2 = isopropanol; temp. 20°C

$M_1 = 32.04$; $N_1 = 1.3288$; $d_1 = 0.7914$; $M_2 = 60.09$; $N_2 = 1.3776$;

$d_2 = 0.7853$

$$m = \frac{M_2}{M_1} = \frac{60.09}{32.04} = 1.8755$$

$$\frac{N_2^2-1}{N_2^2+2} = \frac{(1.3776)^2-1}{(1.3776)^2+2} = \frac{1.8978 - 1.0000}{1.8978 + 2.0000} = \frac{0.8978}{3.8978} = .2303$$

$$\gamma = (1 - m \frac{d_1-d_2}{d_1}) = (1 - 1.8755 - \frac{.7914 - .7853}{.7914}) = -.8755 - .0077079$$

$$= - .0.8832$$

$$K = \frac{d_2}{d_1} \left[\frac{N_1^2-1}{N_1^2+2} - \frac{N_2^2-1}{N_2^2+2} \right] = \frac{.7853}{.7914} \left[\frac{(1.3288)^2-1}{(1.3288)^2+2} - \frac{(1.3776)^2-1}{(1.3776)^2+2} \right] =$$

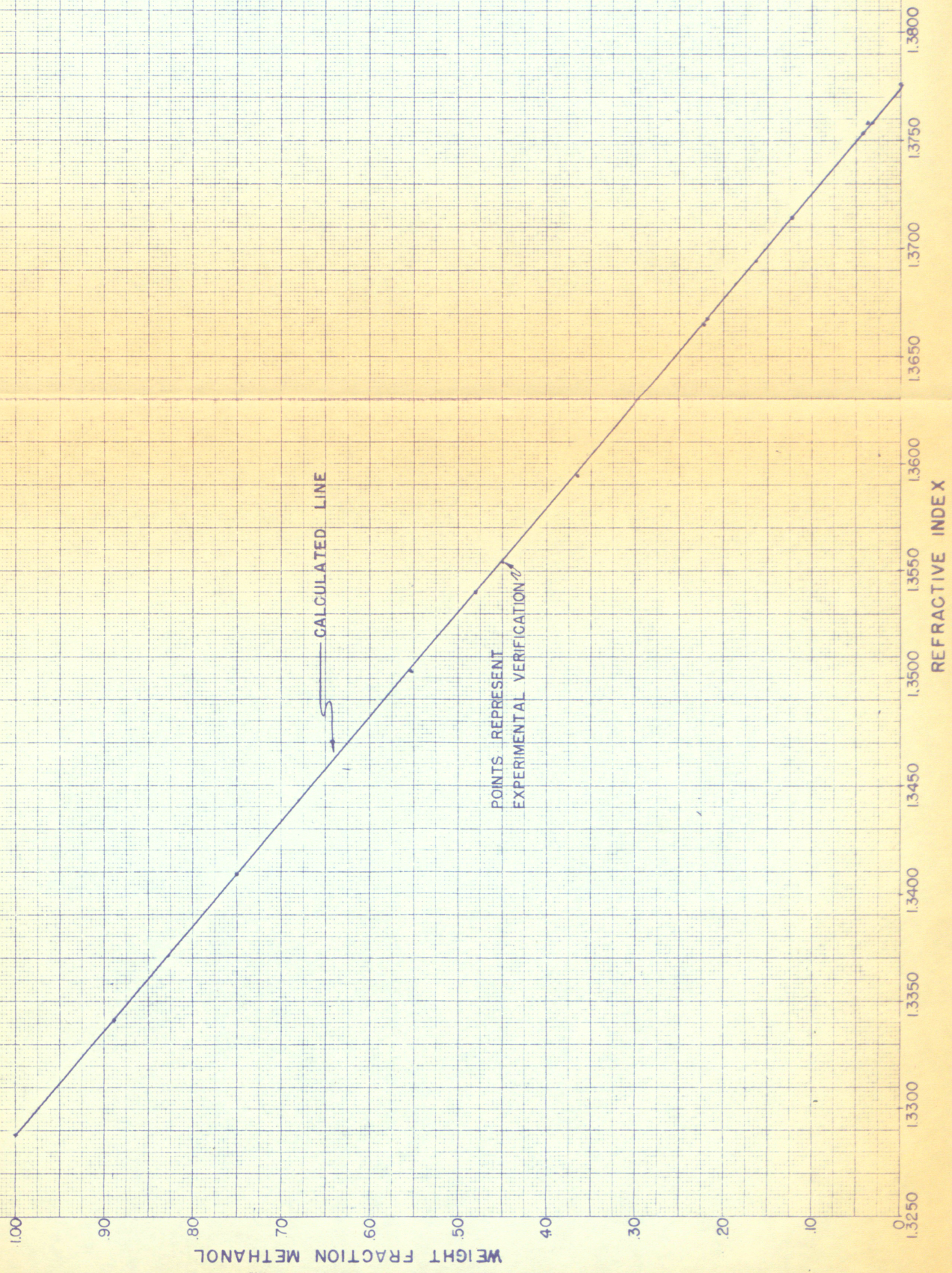
$$= .9923 \left[\frac{1.7657-1}{1.7657+2} - .2303 \right] = - .0268$$

$$x_1 = .347 \quad x_1^i = .500 \quad \gamma x_1^i = -.4416 \quad m + \gamma x_1^i = 1.4339 \quad Kx_1 = -.01340$$

$$\frac{Kx_1^i}{m + \gamma x_1^i} = -.0093 \quad \frac{Kx_1^i}{m + \gamma x_1^i} + b = z = 0.2210 \quad 2z+1 = 1.4420 \quad 1-z = .7790$$

$$\frac{2z+1}{1-z} = 1.8511 ; \sqrt{\frac{2z+1}{1-z}} = N_S = 1.3606$$

REFRACTIVE INDEX
OF
METHANOL-ISOPROPANOL MIXTURES
AT 20°C.
FIG. 8



REFRACTIVE INDEX

WEIGHT FRACTION METHANOL

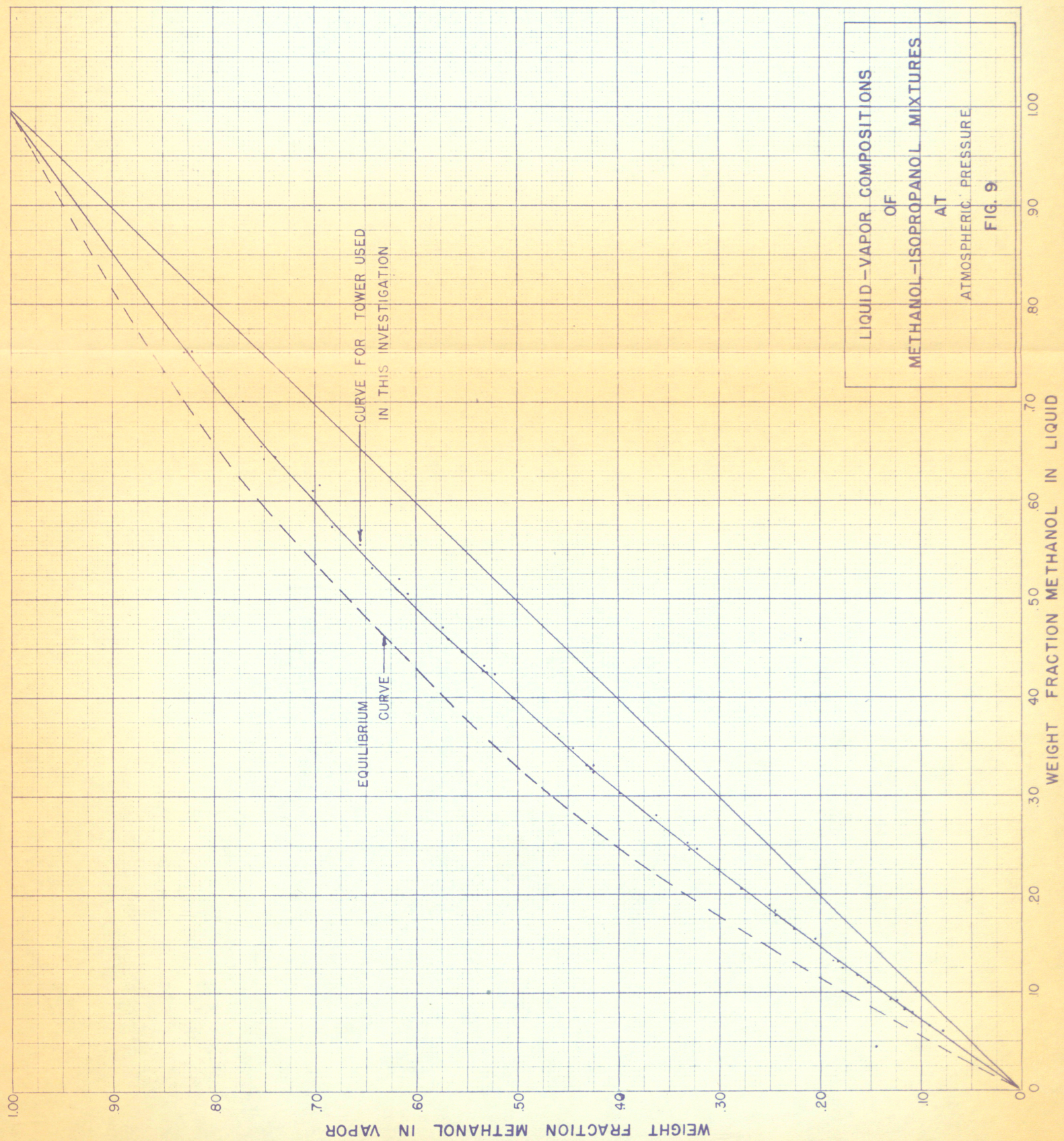
2. Preparation of the liquid-vapor composition curve using data obtained at total reflux.

The liquid-vapor composition curve Fig. 9, p. 96 , (actually the equilibrium curve corrected for plate efficiency) was prepared from the data taken at total reflux where $y_n = x_{n+1}$. In this manner vapor compositions at total reflux were obtained by determining the composition of the liquid on the plate above. The data from total reflux Runs 2-9 were smoothed by least squares with inconsistent points being statistically eliminated. After this had been done, the remaining 58 points showed an average absolute deviation of approximately 0.3 weight percent from the curve.

The smoothing was done by first converting the experimental liquid-vapor composition data to relative volatilities:

$$\alpha = \frac{\frac{y_1}{x_1}}{\frac{y_2}{x_2}}$$

A plot of these relative volatilities versus their respective liquid compositions in terms of mole fractions was best fitted by a linear equation. The constants for this equation were determined by least squares. Using this equation, values of relative volatility were calculated corresponding to each point of data and the inconsistent points were rejected in accord with Chauvenet's criterion as described by Crumpler and Yoe (6). Then the constants were recomputed using



least squares and the resulting equation, $\alpha = 1.4395 + 0.1475x'$, was used to compute relative volatilities, which in turn were used to compute values of y' corresponding to the various values of x' shown in Table XXIV. The weight fraction values shown in this table were used to plot the liquid-vapor composition curve shown in Fig. 9. The experimental points are included on this plot to show the consistency of the results. For comparison, the ideal liquid-vapor equilibrium curve, as computed from Raoult's and Dalton's laws*, is also shown on Fig. 9.

Once these curves have been constructed, the plate efficiency can be computed graphically. For example at $x = 0.600$,

$$\text{P.E.} = \frac{.700 - .600}{.754 - .600} \times 100 = 65 \text{ percent}$$

3. Preparation of Enthalpy-Concentration Chart.

Choosing a datum plane of 0°F. , the standard procedure was used in the preparation of this chart. The most reliable thermal data were obtained from Timmermans (29). The specific heats and latent heats of vaporization of both methanol and isopropanol are linear with temperature over the range of temperature between the boiling points of the two pure components. These thermal data were expressed algebraically with the aid of least squares as follows:

Specific heats:

$$\text{Methanol} = C_M = 0.564 + 0.000470T$$

$$\text{Isopropanol: } C_I = 0.489 + .00177T$$

*This standard calculation is indicated in Table XXV.

Heats of vaporization:

$$\text{MeOH: } l_M = 554 - 0.564T$$

$$\text{ISOOH: } l_I = 332 - 0.235T$$

Because of the negligible heat of mixing of the two components, thermal properties of their mixtures were computed by the additive property rule. The following sample calculation illustrates the procedure in detail;

- (1) Choose temperature = 149°F.
- (2) From a plot of temperature versus liquid composition, obtain value of $x = 0.900$
- (3) Calculate mean values of the specific heats of each component between datum plane 0°F. and 149°F.
Because of linear function the mean value is the arithmetic average, i.e.,

$$C_M^* = \frac{0.564 + 0.564 + .000470 (t-0)}{2} = 0.564 + 0.000235t$$

$$C_M^* = 0.564 + 0.000235 (149)$$

$$C_M^* = 0.599$$

Likewise,

$$C_I^* = 0.489 + 0.000885t$$

$$C_I^* = 0.489 + 0.000885 (149)$$

$$C_I^* = 0.621$$

(4) Calculate the specific heat of the mixture

$$C_{\text{Mix.}}^* = C_M^* x_M + C_I^* (1-x_M)$$

$$C_{\text{Mix.}}^* = 0.9 (599) + 0.1 (.621)$$

$$C_{\text{Mix.}}^* = 0.601$$

(5) Calculate enthalpy of liquid

$$h_L = C_{\text{Mix.}}^* (T-0)$$

$$h_L = 0.601 (149)$$

$$h_L = 89.5 \text{ Btu./lb.}$$

(6) Obtain value of vapor composition corresponding to value of $x = 0.900$. From Fig. 9, $y = 0.935$. Note that this is the actual, not the equilibrium composition.

(7) Calculate mean heat of vaporization of both pure components, at 149°F. ;

$$l_M = 554 - 0.546T$$

$$l_M = 554 - 0.546 (149)$$

$$l_M = 473 \text{ Btu./lb.}$$

$$l_I = 332 - 0.235T$$

$$l_I = 332 - 0.235 (149)$$

$$l_I = 297 \text{ Btu./lb.}$$

(8) Calculate the heat of vaporization of the mixture;

$$l_{\text{Mix.}} = l_M y_M + l_I (1 - y_M)$$

$$l_{\text{Mix.}} = 473 (.935) + 297 (.065)$$

$$l_{\text{Mix.}} = 461 \text{ Btu./lb.}$$

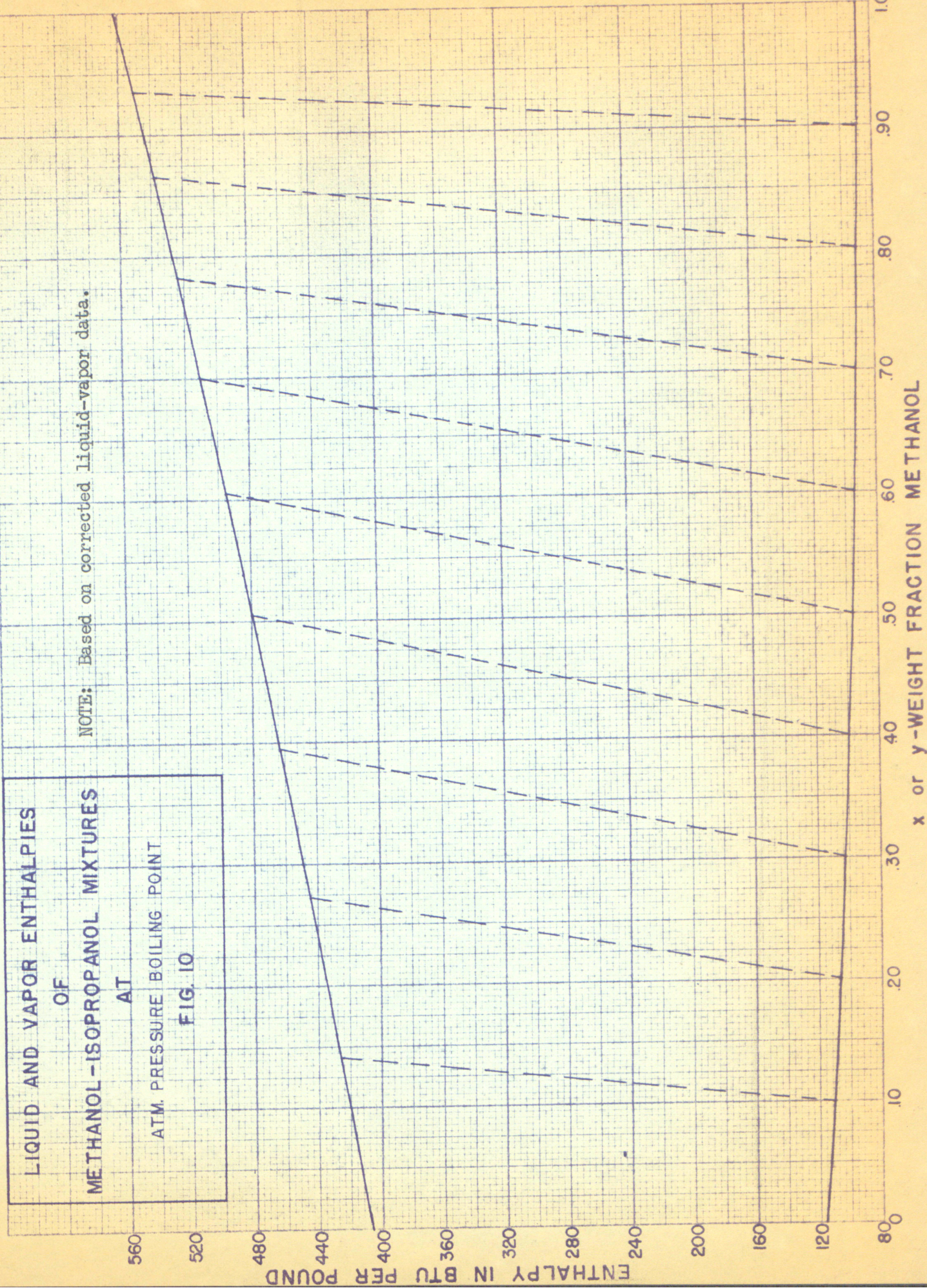
(9) Calculate the enthalpy of the vapor.

$$h_v = h_L + l_{\text{Mix.}}$$

$$h_v = 89.5 + 461$$

$$h_v = 551 \text{ Btu./lb.}$$

On Fig. 10 the h_L is plotted against x and h_v vs. y .



4. Calculation procedure for the batch rectification data.

a. Holdup

The values for the individual plates measured under static conditions were corrected to dynamic conditions as follows:

Total static holdup by measurement = 12,875 cc.

Estimation of total "dynamic" holdup (i.e. under operating conditions) on plates in column;

Initial still pot data;

Vol. = 1.71 cu.ft.

Conc. = 0.362

Temp. = 75°F. = 24°C.

Sp.gr. = .784

Still pot data at end of warmup period;

Vol. = 1.10 cu.ft.; corrected to initial

temp., Vol. = $1.10 \frac{.740}{.784} = 1.04$ cu.ft.

Conc. = 0.300

Temp. = 162°F. = 72°C.

Estimated holdup in product line = 175 cc.

Vapor holdup assumed negligible.

Total amount dynamic holdup = 1.71 - 1.04 = 0.67 cu.ft.

Estimated holdup in condenser and reflux line = 2(175) = 350 cc.

Dynamic holdup on plates alone = .67(28,320) - (175 + 350) = 18,415 cc.

Thus total plate holdup ratio, $\frac{H_{\text{dynamic}}}{H_{\text{static}}} = \frac{18415}{12875} = 1.43$

This value was used to convert the static holdup on each plate to the corresponding dynamic value. (See Table XXVII) Using the densities of the various liquids, the volumetric values were converted to pounds.

b. Compositions

(1) Liquid compositions for the even numbered plates corresponding to the observed refractive indices were obtained from Fig. 8.

(2) These liquid compositions were plotted versus plate number as shown in Fig. 11 for Run 19. Values for the liquid compositions of the odd numbered plates were read from these curves. Also any obvious irregularities in the experimental data were smoothed out with the aid of this type of plot.

(3) Vapor compositions corresponding to the various liquid compositions were read from Fig. 9.

c. Flow rates, vapor velocity, reflux fraction, fraction distilled.

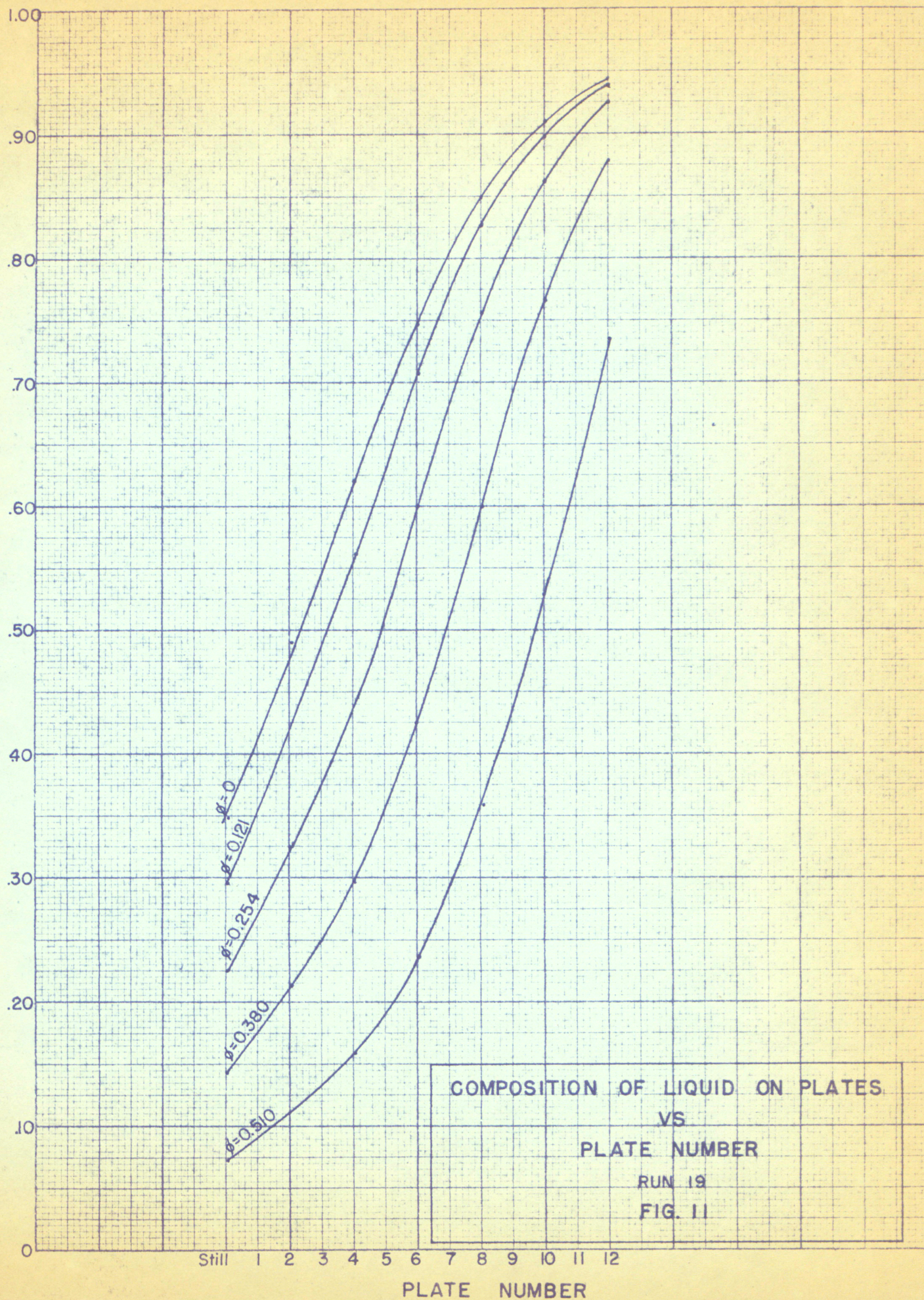
(1) Product rate, D.

$$D \text{ in lbs./min.} = \frac{\text{weight for a time interval}}{\text{time interval}}$$

(2) Reflux rate, L_R .

(a) Apparent volumetric flow rate corresponding to the observed float level was read from Fig. 12.

WEIGHT FRACTION METHANOL IN LIQUID



(b) This volumetric rate was corrected for the density of the material passing through the meter.

(c) Volumetric rate converted to weight rate in lbs./min.

$$(3) \text{ Reflux fraction} = \frac{L_R}{L_R + D}$$

(4) Calculation of internal liquid and vapor rates.

Using data from Run 19, (time = 60 min.):

Following procedures as outlined above, previous calculation gave, $D = 0.217$ lbs./min. and

$$L_R = 0.579 \text{ lbs./min.}$$

$$V_{12} = L_R + D = 0.579 + 0.217 = 0.796 \text{ lbs./min.}$$

Rearranging equations (1a) and (3),

$$L_{12} = \frac{L_R (h_{v12} - h_{LR}) + D (h_{v12} - h_{v11}) + H_{12} \frac{dh_{L12}}{dt}}{(h_{v11} - h_{v12})}$$

Enthalpy values corresponding to compositions in Table XV were obtained from Fig. 10 with the exception of that of the reflux, which had to be computed separately because its temperature was below its boiling point.

The holdup value for plate 12, obtained from Table XXVII, is 2.33 lbs.; $\frac{dh_{L12}}{dt}$ was obtained graphically from a plot of h_{L12} vs. time.

Substituting,

$$L_{12} = \frac{.579 (552 - 74) + .217 (552 - 551) + 2.33 (.0113)}{(551 - 89)}$$

$$L_{12} = .602 \text{ lbs./min.}$$

(Note that the holdup term is negligible in comparison to the other terms in the equation.)

$$V_{11} = L_{12} + D$$

$$V_{11} = .602 + .217 = .819 \text{ lbs./min.}$$

These calculations can be carried out successively from plate-to-plate down the tower to obtain the flow rates for any plate.

(5) Vapor velocity.

The vapor rate in lbs./min. was converted to cu. ft./sec. and this value divided by the cross-sectional area of the tower to give the superficial vapor velocity in ft./sec.

(6) Fraction distilled, ϕ .

$$\phi = \frac{\text{wt. distilled}}{\text{wt. initial feed} - \text{wt. of total column holdup}}$$

d. Material balances.

(1) Overall balances for entire run.

$$\begin{aligned} \text{wt. initial feed} &= \text{wt. product} + \text{wt. residue} + \\ &\text{wt. total holdup} + \text{wt. samples and purges} \end{aligned}$$

(2) Individual plate balances.

Using equation (2), p. 36 and data from Run 19,
(time = 90 min.)

$$L_R x_R + V_{11} y_{11} + H_{12} \left(-\frac{dx_{12}}{dt}\right) = L_{12} x_{12} + V_{12} y_{12}$$

The derivative was obtained graphically from a plot of x_{12} vs. time. L_R , V_{11} , H_{12} , L_{12} and V_{12} obtained as previously described.

$$\begin{aligned} &.579(.945) + .819(.934) + 2.33(0.000907) = \\ &.602(.927) + .796(.945) \\ &1.314 = 1.310 \end{aligned}$$

5. Calculations made in Part V to check assumptions of Part III.

a. Constancy of weight of holdup.

For each plate the weight of holdup as desired above was computed at beginning and at end of a run. Likewise the moles of holdup was computed at the two times for each plate. Total values obtained as the sums of the individual values.

b. Negligence of amount and total enthalpy of vapor.

From dimensions given on Fig. 4, the volume of the vapor space was calculated and then the mass of vapor was calculated using the ideal gas law. Total enthalpy = (wt.) (unit enthalpy).

c. Errors reported in Table II.

Referring to the individual plate balance shown above

the error for plate 12 that would be incurred
by neglecting the holdup term is,

$$\text{Percent error} = \frac{2.33(.000907)}{1.312}(100) = 0.15 \text{ percent}$$

$$\text{Overall error} = \frac{\sum \text{values of holdup terms}}{\text{plate 1 input}}(100)$$

d. Rayleigh equation calculations.

Standard numerical integration using
Simpson's rule.

APPENDIX E

Tabulation of Calculated Data

Table XIV

Calculated Data for Run 16

Composition of feed: $x = 0.231$		Reflux fraction = 0.725		$H/S_0 = 0.383$	
Time (min.)*		0		30-33	
		60-63		90-93	
Compositions:					
		x	y	x	y
Still		.186	.252	.133	.184
Plate 1		.196	.265	.145	.199
2		.208	.283	.158	.217
3		.223	.300	.173	.236
4		.241	.323	.190	.258
5		.262	.347	.208	.282
6		.292	.383	.237	.317
7		.327	.423	.275	.364
8		.371	.471	.320	.415
9		.430	.535	.377	.477
10		.497	.605	.450	.557
11		.577	.677	.530	.636
12		.667	.757	.633	.728
Product		.754	-	.728	-
Fraction distilled	0.000		.121		.257
					.384

*See experimental data for explanation.

Table XV

Calculated Data for Run 19

Composition of feed: $x = 0.453$		Reflux fraction = 0.725				$H/S_o = 0.383$					
Time (min.)*		0		30-33		60-63		90-93		120-123	
Compositions:		x	y	x	y	x	y	x	y	x	y
Still		.350	.447	.298	.397	.228	.310	.145	.217	.075	.105
Plate 1		.423	.534	.360	.458	.277	.367	.182	.250	.097	.134
2		.492	.600	.427	.531	.330	.428	.214	.290	.114	.157
3		.558	.663	.492	.600	.384	.487	.255	.338	.135	.185
4		.621	.718	.563	.617	.443	.549	.298	.392	.160	.218
5		.689	.776	.637	.730	.515	.621	.358	.459	.192	.260
6		.748	.824	.707	.790	.600	.699	.432	.535	.237	.317
7		.804	.864	.772	.843	.684	.769	.514	.619	.290	.383
8		.850	.897	.827	.884	.756	.830	.600	.699	.360	.461
9		.884	.921	.865	.911	.812	.874	.694	.778	.443	.549
10		.910	.940	.898	.935	.861	.908	.766	.838	.537	.642
11		.935	.957	.925	.952	.900	.934	.830	.885	.642	.735
12		.944	.964	.941	.963	.927	.952	.879	.921	.735	.813
Product		.957	-	.956	-	.943	-	.918	-	.822	-
Fraction distilled		0.000		.121		.254		.380		.510	

*See experimental data for explanation.

Table XVI

Data Used in Preparation of Fig. 7

A. Experimental Operating Data - Run 19

Fraction distilled	.121		.510	
Compositions (mole fractions)	y_n^i	x_{n+1}^i	y_n^i	x_{n+1}^i
	.522	.482	.228	.196
	.585	.540	.264	.227
	.641	.600	.303	.264
	.696	.666	.347	.311
	.755	.738	.402	.371
	.814	.802	.469	.436
	.863	.854	.539	.515
	.902	.891	.617	.599
	.928	.921	.695	.685
	.948	.943	.771	.771
	.963	.959	.840	.840
	.971	.971	.897	.897

B. McCabe-Thiele Operating Line

Constructed as a line having a slope of 0.725 (reflux fraction) passing through the point 0.971 (product composition) on the 45° reference line.

Table XVII

Calculated Data for Run 21

Feed composition: $x = 0.453$		Reflux fraction = 0.725			$H/S_o = 0.383$		
Time (min.)*	0	30-33	60-63	90-93	120-123	150-153	
Liquid compositions:	x^{**}	x	x	x	x	x	
Still	.360	.302	.230	.142	.067	.027	
Plate 1	.428	.368	.281	.174	.084	.034	
2	.497	.432	.335	.208	.102	.042	
3	.563	.497	.389	.250	.122	.047	
4	.632	.565	.450	.293	.147	.053	
5	.700	.640	.523	.350	.175	.064	
6	.757	.712	.602	.414	.215	.079	
7	.810	.777	.682	.495	.267	.099	
8	.851	.831	.755	.583	.336	.129	
9	.891	.870	.812	.670	.417	.169	
10	.913	.897	.866	.748	.505	.218	
11	.933	.922	.904	.815	.602	.293	
12	.947	.938	.926	.870	.714	.397	
Product	.956	.955	.948	.914	.802	.508	
Fraction distilled	0	.135	.246	.376	.503	.625	

*See experimental data for explanation.

**Since the only purpose of this run was to check the validity of the observed data of Run 19 (see Figs. 5 and 6), only liquid compositions (x) were computed; if desired, the corresponding vapor compositions (y) may be read from Fig. 9.

Table XVIII

Calculated Data for Run 22

Composition of feed: $x = 0.453$		Reflux fraction = 0.850		$H/S_0 = 0.383$	
Time (min.)*		0		90-93	
Compositions:		30-33		60-63	
		120-123		180-183	
		x		x	
		y		y	
Still		.347	.445	.307	.400
Plate 1		.450	.557	.404	.507
2		.544	.649	.496	.605
3		.628	.725	.586	.686
4		.706	.790	.667	.757
5		.774	.843	.749	.824
6		.827	.886	.801	.862
7		.870	.912	.857	.902
8		.892	.927	.894	.929
9		.915	.943	.914	.943
10		.931	.954	.930	.954
11		.940	.961	.940	.961
12		.948	.967	.947	.966
Product		.955	-	.955	-
Fraction distilled	0	.088		.174	
				.259	
				.345	
				.516	

*See experimental data for explanation.

Table XIX

Calculated Data for Run 23

Composition of feed: $x = 0.453$			Reflux fraction = 0.575			$H/S_0 = 0.383$											
Time (min.)*			0			30-33			60-63			90-93			110-113		
Compositions:			x	y	x	y	x	y	x	y	x	y	x	y	x	y	
Still		.393	.495	.311	.406	.206	.278	.095	.132	.044	.097						
Plate 1		.418	.523	.336	.426	.230	.310	.111	.154	.047	.066						
2		.444	.550	.362	.461	.251	.335	.123	.170	.055	.078						
3		.467	.575	.389	.491	.266	.353	.131	.180	.063	.088						
4		.495	.603	.418	.524	.285	.376	.144	.199	.070	.099						
5		.530	.626	.450	.556	.312	.406	.157	.213	.077	.107						
6		.567	.670	.492	.600	.350	.447	.171	.232	.086	.121						
7		.616	.715	.542	.646	.390	.494	.191	.259	.092	.128						
8		.667	.757	.600	.700	.438	.543	.217	.292	.110	.152						
9		.716	.798	.661	.752	.503	.608	.257	.243	.129	.177						
10		.767	.837	.723	.804	.576	.677	.315	.410	.158	.218						
11		.822	.877	.771	.840	.654	.738	.384	.485	.195	.265						
12		.855	.900	.834	.885	.741	.814	.481	.579	.257	.342						
Product		.900	-	.886	-	.824	-	.608	-	.366	-						
Fraction distilled	0			.208		.413		.618		.756							

*See experimental data for explanation.

Table XX

Calculated Data for Run 26

Feed composition: $x = 0.453$		Reflux fraction = 0.725		$H/S_0 = 0.383$		
Time (min.)*	0	30-33	60-63	90-93	120-123	150-153
Liquid compositions:		x^{**}	x	x	x	x
Still	.356	.303	.234	.157	.077	.031
Plate 1	.423	.368	.282	.190	.096	.042
2	.496	.437	.338	.230	.116	.051
3	.557	.500	.395	.267	.139	.059
4	.627	.572	.461	.314	.167	.068
5	.692	.645	.538	.370	.197	.079
6	.748	.720	.622	.450	.244	.094
7	.803	.779	.697	.530	.302	.117
8	.847	.827	.765	.617	.377	.153
9	.885	.868	.817	.702	.463	.197
10	.907	.893	.862	.769	.556	.258
11	.933	.915	.895	.830	.656	.337
12	.938	.929	.915	.876	.749	.443
Product	.956	.950	.942	.917	.827	.559
Fraction distilled	0	.128	.254	.380	.505	.630

*See experimental data for explanation.

**Since the only purpose of this run was to check the validity of the observed data of Run 19 (see Figs. 5 and 6), only liquid compositions (x) were computed; if desired, the corresponding vapor compositions (y) may be read from Fig. 9.

Table XXI
Calculated Data for Run 28

Feed composition: x = 0.453		Reflux fraction = 0.725				H/S ₀ = 0.273							
Time (min.)*		0		30-33		90-93		120-123		150-153		195-198	
Compositions:		x	y	x	y	x	y	x	y	x	y	x	y
Still		.386	.487	.355	.454	.258	.345	.199	.270	.144	.198	.070	.098
Plate 1		.409	.513	.419	.524	.302	.395	.238	.320	.162	.220	.079	.111
2		.531	.637	.494	.603	.360	.459	.280	.370	.190	.258	.090	.126
3		.597	.697	.559	.663	.416	.519	.323	.418	.222	.299	.100	.139
4		.661	.753	.624	.721	.477	.585	.373	.475	.263	.350	.114	.159
5		.725	.805	.695	.781	.554	.658	.432	.537	.306	.399	.132	.182
6		.772	.841	.751	.825	.628	.723	.502	.610	.367	.467	.160	.218
7		.821	.877	.801	.863	.706	.787	.580	.682	.429	.535	.193	.263
8		.861	.904	.845	.893	.767	.840	.665	.756	.511	.618	.242	.325
9		.887	.922	.877	.916	.819	.875	.735	.713	.597	.695	.298	.390
10		.910	.940	.902	.934	.857	.902	.797	.858	.687	.775	.376	.476
11		.922	.947	.918	.945	.886	.923	.845	.893	.764	.835	.467	.575
12		.930	.953	.930	.953	.913	.944	.891	.926	.827	.880	.567	.669
Product		.942	-	.942	-	.936	-	.921	-	.884	-	.690	-
Fraction distilled	0			.080		.240		.320		.400		.510	

*See experimental data for explanation.

Table XXII

Refractive Indices of Methanol-Isopropanol Mixtures at 20°C

A. Calculated Values

(See Appendix D for calculation procedure)

x_M	x'_M	N_S
0.000	0.000	1.3776
.056	0.100	1.3748
.117	.200	1.3717
.186	.300	1.3684
.262	.400	1.3648
.347	.500	1.3606
.444	.600	1.3556
.554	.700	1.3504
.680	.800	1.3443
.827	.900	1.3372
1.000	1.000	1.3288

Table XXII (Continued)

B. Comparison of Experimental and Calculated Values

R. I.	Expt'l. x	Calc'd.* x	Absolute Deviation
1.3758	0.038	0.033	0.005
1.3753	.043	.043	.000
1.3714	.122	.123	.001
1.3694	.163	.164	.001
1.3667	.218	.218	.000
1.3665	.222	.225	.003
1.3594	.365	.370	.005
1.3552	.449	.453	.004
1.3540	.480	.480	.000
1.3503	.553	.557	.004
1.3409	.750	.750	.000
1.3341	.893	.893	.000
Ave. Dev.			.002

Experimental refractive indices for pure components;

Methanol 1.3288

Isopropanol 1.3776

Both values agree exactly with the values given in Lange's Handbook.

*Values read from calculated line on Fig. 8.

Table XXIII

Experimental Compositions for Total Reflux Runs

All compositions are expressed in weight fractions.

	<u>x</u>	<u>y</u>		<u>x</u>	<u>y</u>
Run 2	.064	.091	Run 5	.301	.398
	.091	.130	(Cont.)	.398	.504
	.130	.186		.504	.608
	.186	.250		.608	.700
	.250	.330		.700	.768
	.330	.423		.347	.445
	.423	.520		.445	.554
	.520	.615		.554	.654
	.615	.695		.654	.751
Run 3	.059	.077		.751	.819
	.077	.107	Run 7	.326	.425
	.107	.152		.425	.533
	.152	.204		.533	.641
	.204	.278		.641	.749
	.278	.362		.749	.827
	.362	.457	Run 8	.273	.367
	.457	.567		.367	.470
Run 4	.065	.090		.470	.572
	.090	.123		.572	.682
	.123	.177		.682	.768
	.177	.243	Run 9	.129	.182
	.243	.330		.182	.244
	.330	.431		.244	.321
	.431	.532		.321	.424
Run 5	.080	.116		.424	.530
	.116	.163		.530	.643
	.163	.225		.643	.737
	.225	.301		.737	.811

Table XXIV
Smoothed Liquid-Vapor Compositions*

x	x'	$0.1475x'$	α	$\alpha x'$	$(\alpha - 1)x'$	y'	y
.056	0.10	0.0148	1.4543	0.1454	0.0454	.139	.079
.086	.15	.0221	1.4616	0.2192	0.0692	.205	.120
.117	.20	.0295	1.4690	0.2938	0.0938	.269	.163
.151	.25	.0369	1.4764	0.3691	0.1191	.330	.207
.186	.30	.0443	1.4838	0.4451	0.1451	.389	.252
.222	.35	.0516	1.4901	0.5215	0.1715	.445	.297
.262	.40	.0590	1.4985	0.5994	0.1994	.500	.347
.302	.45	.0664	1.5059	0.6777	0.2277	.552	.395
.347	.50	.0738	1.5133	0.7567	0.2567	.602	.445
.393	.55	.0811	1.5206	0.8363	0.2863	.650	.497
.444	.60	.0885	1.5280	0.9168	0.3168	.696	.549
.497	.65	.0959	1.5354	0.9980	0.3480	.740	.602
.554	.70	.1033	1.5428	1.0800	0.3800	.783	.658
.616	.75	.1106	1.5501	1.1626	0.4126	.823	.712
.680	.80	.1180	1.5575	1.2460	0.4460	.862	.767
.750	.85	.1254	1.5649	1.3302	0.4802	.899	.825

*Values computed using these equations:

$$\alpha = 1.4395 + 0.1475x'; \quad y' = \frac{x'}{1 + (\alpha - 1)x'}$$

Table XXV

Calculated Equilibrium Data for Methanol-Isopropanol

Assuming Raoult's and Dalton's Laws

Total pressure = 760 mm Hg

t°C	P _{Me}	P _{Iso}	P _{Me-P_{Iso}}	760-P _{Iso}	$x'_{Me} = \frac{760-P_{Iso}}{P_{Me}-P_{Iso}}$	x	$y'_{Me} = \frac{x'_{Me} P_{Me}}{760}$	y
65	772	363	409	397	0.971	.948	0.986	.975
68	865	417	448	343	0.766	.636	0.872	.783
70	935	455	480	305	0.635	.481	0.781	.642
73	1046	516	530	244	0.460	.311	0.633	.478
75	1124	561	563	199	0.353	.225	0.522	.367
78	1250	635	615	125	0.203	.118	0.334	.210
79	1297	663	634	97	0.153	.087	0.261	.158
80	1341	692	649	68	0.105	.059	0.185	.107

Table XXVI

Calculated Enthalpy - Concentration Data

Composition of Liquid x	Temperature $^{\circ}\text{F}$	Enthalpy of Liquid h_L	Composition of Vapor y	Enthalpy of Vapor h_V
0.000	179.6	116.4	0.000	406.4
.100	173.1	110.4	.141	424.9
.200	167.5	105.5	.272	444.4
.300	163.2	101.8	.394	463.0
.400	159.4	98.5	.505	480.1
.500	156.9	96.5	.605	496.4
.600	154.6	94.3	.699	511.5
.700	152.4	92.5	.783	525.4
.800	150.4	90.8	.865	539.0
.900	149.0	89.5	.935	550.6
1.000	147.9	88.6	1.000	561.7

Table XXVII

Calculated Dynamic Holdup

Plate	Volume of Holdup cc	Weight of Holdup* lbs.
1	1600	2.62
2	1365	2.24
3	1615	2.64
4	1120	1.84
5	1550	2.55
6	1365	2.25
7	1745	2.88
8	1430	2.36
9	1630	2.68
10	1645	2.68
11	2000	3.30
12	1410	2.33
Condenser and lines	350	<u>0.58</u>
Total	-	30.95

*Values at the beginning of the batch rectification period of Run 19; only very slight change in density with change in composition for the system used in this investigation.

Table XXVIII

Data Used in Preparation of Table II

Run 16 $\phi = .26$

Plate	Methanol Input (lbs/min)	H (lbs)	(- dx/dt)	H(- dx/dt) (lbs/min)	Percent Error
1	0.639	2.62	0.00160	0.0042	0.66
2	.718	2.24	.00173	.0039	.54
3	.806	2.64	.00187	.0050	.62
4	.889	1.84	.00208	.0038	.43
5	.981	2.55	.00219	.0056	.57
6	1.066	2.25	.00246	.0056	.53
7	1.147	2.88	.00279	.0080	.70
8	1.208	2.36	.00338	.0080	.66
9	1.251	2.68	.00388	.0104	.83
10	1.286	2.68	.00430	.0115	.90
11	1.311	3.30	.00476	.0157	1.20
12	1.314	2.33	.00518	.0121	.92
				<u>.0638</u>	

$$\text{overall error} = \frac{.0638}{.639} = 10 \text{ percent}$$

Run 19 $\phi = 0.25$

1	0.639	2.62	0.00283	0.007	1.10
2	.718	2.24	.00337	.007	0.98
3	.806	2.64	.00380	.010	1.24
4	.889	1.84	.00445	.008	0.90
5	.981	2.55	.00445	.011	1.12
6	1.066	2.25	.00458	.010	0.94
7	1.147	2.88	.00458	.013	1.14
8	1.208	2.36	.00388	.009	0.74
9	1.251	2.68	.00232	.006	0.48
10	1.286	2.68	.00212	.005	0.39
11	1.311	3.30	.00091	.003	0.23
12	1.314	2.33	.00070	.002	0.15
				<u>.091</u>	

Table XXVIII (continued)

Run 19 (continued)

Overall error based on Plate 1 input;

$$\frac{0.091}{0.639}(100) = 14.25 \text{ percent}$$

For Plate 6;

ϕ	Methanol Input (lbs/min)	H (lbs)	(- dx/dt)	H(- dx/dt) (lbs/min)	Percent Error
0.121	1.066	2.25	0.0020	0.0045	0.42
.254	1.066	2.25	.0046	.0104	0.94
.380	1.066	2.25	.0063	.0142	1.33
.510	1.066	2.25	.0065	.0146	1.38

Run 22

$$\phi = 0.26$$

Plate	Methanol Input (lbs/min)	H (lbs)	(- dx/dt)	H(- dx/dt) (lbs/min)	Percent Error
1	0.648	2.62	0.00258	0.007	1.04
2	0.740	2.24	.00301	.007	0.90
3	0.871	2.64	.00347	.009	1.05
4	0.989	1.84	.00370	.007	0.69
5	1.100	2.55	.00355	.009	0.83
6	1.191	2.25	.00340	.008	0.64
7	1.270	2.88	.00262	.007	0.59
8	1.319	2.36	.00204	.005	0.37
9	1.346	2.68	.00149	.004	0.30
10	1.373	2.68	.00101	.003	0.20
11	1.373	3.30	.00094	.003	0.23
12	1.379	2.33	.00090	.002	0.15
				<u>.071</u>	

Overall error based on plate 1 input;

$$\frac{0.071}{0.648}(100) = 11.0 \text{ percent}$$

Table XXVIII (continued)

Run 23

$\phi = 0.25$

Plate	Methanol Input (lbs/min)	H (lbs)	(- dx/dt)	H(- dx/dt) (lbs/min)	Percent Error
1	0.633	2.62	0.00344	0.009	1.38
2	.659	2.24	.00366	.008	1.24
3	.708	2.64	.00377	.010	1.40
4	.733	1.84	.00406	.008	1.04
5	.775	2.55	.00415	.011	1.37
6	.819	2.25	.00429	.010	1.18
7	.876	2.88	.00433	.013	1.43
8	.931	2.36	.00450	.011	1.14
9	.987	2.68	.00408	.011	1.11
10	1.033	2.68	.00366	.010	0.95
11	1.085	3.30	.00321	.011	0.98
12	1.109	2.33	.00240	.006	0.51
				<u>0.118</u>	

Overall error based on Plate 1 input;

$$\frac{0.118}{0.633}(100) = 18.7 \text{ percent}$$

Run 28

$\phi = 0.25$

1	0.639	2.62	0.00207	0.00542	0.85
2	.718	2.24	.00240	.00537	.75
3	.806	2.64	.00268	.00708	.88
4	.889	1.84	.00278	.00512	.58
5	.981	2.55	.00299	.00764	.78
6	1.066	2.25	.00281	.00633	.61
7	1.147	2.88	.00246	.00709	.62
8	1.208	2.36	.00218	.00515	.43
9	1.251	2.68	.00190	.00510	.40
10	1.286	2.68	.00133	.00356	.28
11	1.311	3.30	.00110	.00363	.28
12	1.314	2.33	.00052	.00121	.09
				<u>.06270</u>	

Overall error based on Plate 1 input;

$$\frac{0.0627}{0.639}(100) = 9.86 \text{ percent}$$

Table XXIX

Rayleigh Equation Calculations

$$\ln (1 - \phi) = \int_{x_s}^{x_{s_0}} \frac{dx_s}{x_D - x_s}$$

Using data from Run 19:

x_s	x_D	$x_D - x_s$	$\frac{1}{x_D - x_s}$
0.350	0.957	0.607	1.650
.303	.956	.653	1.531
.230	.943	.713	1.403
.145	.918	.773	1.293

Using Simpson's rule with increments
of $x_s = 0.010$,

$$\ln (1 - \phi) = - 0.2952$$

$$(1 - \phi) = 0.745 \text{ or } \phi = 0.255$$

By experiment, $\phi = 0.380$

$$\text{Percent error} = \frac{0.380 - 0.255}{0.380} = 32 \text{ percent}$$

Table XXX

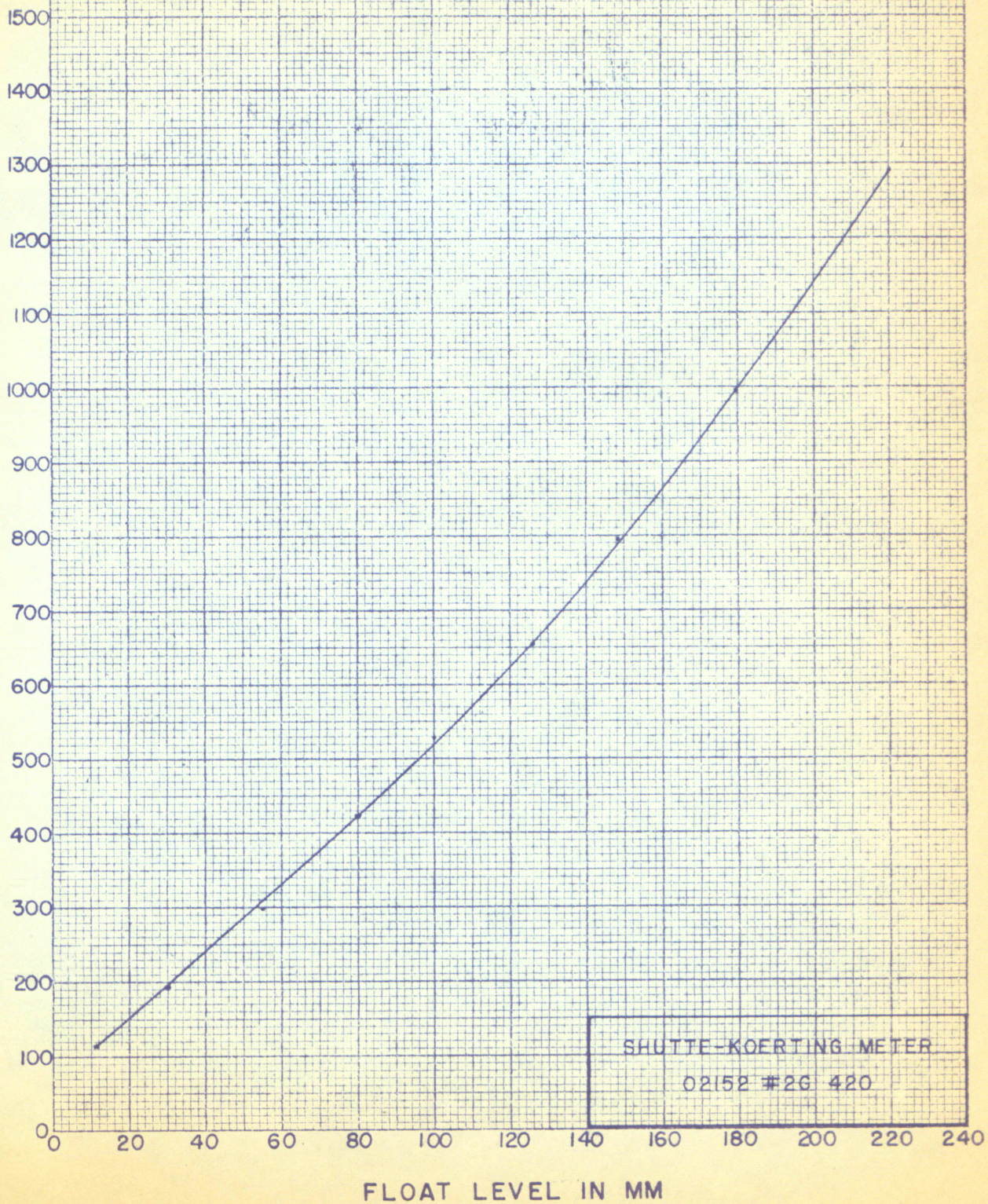
Calibration of Reflux Rotameter

Shutte - Koerting Meter: 02152 #2G 420

Float Level (mm.)	Flow Rate (cc./min. of H ₂ O)
11	114
30	192
55	298
80	422
100	528
126	653
148 $\frac{1}{2}$	795
179 $\frac{1}{2}$	994
220	1290

CALIBRATION CURVE
FOR
REFLUX ROTAMETER
FIG. 12

RATE OF FLOW IN CC OF WATER PER MINUTE



SHUTTE-KOERTING METER

02152 #2G 420

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