

DOCTORAL DISSERTATION SERIES

Publication No. : 11,388

AUTHOR: Thomas Samuel Heines, Jr., Ph. D., 1954
University of Michigan

TITLE: OPERATION OF CONTINUOUS THERMAL
DIFFUSION COLUMNS FOR LIQUIDS

University Microfilms, Ann Arbor, Michigan

OPERATION OF
CONTINUOUS THERMAL DIFFUSION
COLUMNS FOR LIQUIDS

by
Thomas Samuel Heines, Jr.

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in the
University of Michigan

Committee in charge:

Associate Professor J. J. Martin, Chairman
Assistant Professor J. T. Banchemo
Associate Professor L. O. Case
Associate Professor C. M. Sliepcevich
Associate Professor G. B. Williams

January 5, 1954

OPERATION OF CONTINUOUS THERMAL DIFFUSION COLUMNS FOR LIQUIDS

by Thomas Samuel Heines, Jr.

The purpose of this investigation was to study the operation of continuous thermal diffusion columns for the separation of liquids. Each of the four columns used was constructed of two concentric aluminum tubes, one heated and the other cooled, which enclosed the system separated. The columns were operated in continuous fashion, with a feed stream introduced in the center and products removed from the top and bottom of the column. Information on the total reflux case was provided by extrapolation of the experimental data to zero feed rate. The n-heptane - benzene system was used to perform the experimental work, analysis of the feed and products having been accomplished by means of refractive index measurements. The variables studied and the range over which they were varied were as follows:

1. Feed rate to the column (0.005 to 0.15 gm/sec)
2. Temperature difference between the heated and cooled tubes (10 to 55C)
3. Column height (150 to 300 cm)
4. Spacing between the heated and cooled tubes (0.1 to 0.25 cm)
5. Column diameter (constant at 4.5 cm)
6. Feed composition (0.10, 0.26, 0.45, 0.59, and 0.82 weight fractions n-heptane)
7. Ratio of top to bottom product rates (0.2 to 14)
8. Average temperature in the column (20 to 40C)
9. Separation, or difference in composition between top and bottom products (0.01 to 0.15 weight fractions n-heptane)

The results of this investigation show that the separation for both continuous operation and total reflux was correlated by simple empirical modifications of the Furry, Jones, and Onsager theory of the thermal diffusion column. For continuous operation, a dimensionless group from the theory was related to the separation with an empirical equation. For total reflux, the theoretical relation was modified by inclusion of an empirical function of spacing.

It was concluded from this investigation that the most important variables affecting the separation attainable in a given thermal diffusion column were the feed rate and temperature difference. The important column dimensions were found to be the height and spacing of the column. It was found that the average temperature and the ratio of top to bottom product rates did not affect the separation to any great extent. The total reflux separation was found to be independent of tempera-

ture difference and inversely proportional to the square of the spacing rather than the fourth power predicted by the theory. In addition, it was found that the n-heptane was more concentrated in the top products from the columns.

To My Wife

ACKNOWLEDGEMENTS

The author wishes to acknowledge the assistance and guidance offered by the members of his doctoral committee; Assistant Professor J. T. Banchemo, Associate Professor L. O. Case, Associate Professor C. M. Sliepcevich, Associate Professor G. B. Williams, and particularly Associate Professor J. J. Martin, who helped immeasurably in the execution of this study. In addition, the author wishes to thank Dr. A. L. Jones of the Standard Oil Company of Ohio for his valuable advice.

Gratitude is also extended for the financial assistance provided by the University of Michigan through teaching fellowships. The Shell Oil Company, too, is gratefully acknowledged for the financial support rendered through the Shell Fellowship in Chemical Engineering.

Finally, the author thankfully acknowledges the invaluable assistance of his wife, Barbara A. Heines, in the preparation of the final manuscript.

CONTENTS

LIST OF FIGURES	vi
LIST OF TABLES	vii
INTRODUCTION	1.
LITERATURE SURVEY	5.
THEORY OF THE THERMAL DIFFUSION COLUMN	12.
Total Reflux	12.
Continuous Operation	20.
EXPERIMENTAL WORK	25.
Description of the Equipment	25.
Column Construction	25.
Assembly of Columns with Auxiliary Equipment	29.
Experimental Procedure	32.
Operation of Equipment	32.
Criterion for the End of a Run	34.
Variation of Operating Conditions	34.
Data Taken	35.
Analysis	35.
Calibration	37.
Rotameters in the Water Streams	37.
Rotameters in the Feed and Product Streams	37.
Thermocouples	38.
Column Dimensions	38.
System Used	40.
Ethanol - Benzene System	40.
n-Heptane - Benzene System	41.
Physical Properties of the System Used	41.
Pure Components	42.
Refractive Index	42.
Density and Coefficient of Expansion	44.
Viscosity	45.
Diffusivity	46.

CONTENTS - cont.

RESOLUTION OF OBSERVED DATA	48.
Compositions	48.
Flow Rates	49.
Temperatures	50.
Correction of Spacing for Thermal Expansion	50.
Calculation of Transport Coefficients and Dimensionless Groups	51.
Summary of Data Resolution	52.
RESULTS	53.
Continuous Operation	53.
Effect of $FL/4K$	53.
Effect of D/B	60.
Empirical Correlation	60.
Total Reflux	63.
Effect of HL/K	63.
Effect of Temperature Difference	71.
Empirical Correlation	71.
CONCLUSIONS AND RECOMMENDATIONS	79.
APPENDIX	81.
Sample Calculation	82.
Experimental Data	86.
Summary of Calculations	95.
NOMENCLATURE	111.
REFERENCES	113.

LIST OF FIGURES

I	COLUMN DESCRIBED BY THEORY	13.
II	FLOW DIAGRAM FOR CONTINUOUS OPERATION	21.
III	DIAGRAM OF A THERMAL DIFFUSION COLUMN	26.
IV	FLOW SHEET OF EQUIPMENT	30.
V	EXPERIMENTAL EQUIPMENT	31.
VI	LOG SEPARATION VS. $FL/4K$	54.
VII	SEPARATION VS. D/B	61.
VIII	DETERMINATION OF EXPONENT OF $FL/4K$	62.
IX	LOG SEPARATION VS. $(FL/4K)^{0.75}$	64.
X	CORRECTION FACTOR - A - FOR CONTINUOUS OPERATION	67.
XI	CORRELATION OF SEPARATION FOR CONTINUOUS OPERATION	68.
XII	THEORETICAL THERMAL DIFFUSION COEFFICIENT - α	70.
XIII	SEPARATION VS. FEED RATE AND TEMPERATURE DIFFERENCE	72.
XIV	EMPIRICAL RELATIVE THERMAL DIFFUSION COEFFICIENT - α'	75.
XV	TOTAL REFLUX CORRECTION FACTOR - f	76.
XVI	EMPIRICAL TOTAL REFLUX CORRELATION	78.
XVII	ROTAMETER CALIBRATIONS	102.
XVIII	REFRACTIVE INDEX DEVIATION OF N-HEPTANE - BENZENE MIXTURES	104.
XIX	DENSITY OF N-HEPTANE - BENZENE MIXTURES	105.
XX	EXPANSION COEFFICIENT OF N-HEPTANE - BENZENE MIXTURES	106.
XXI	VISCOSITY OF N-HEPTANE - BENZENE MIXTURES	107.
XXII	ACTIVITY COEFFICIENTS FOR N-HEPTANE - BENZENE MIXTURES	108.
XXIII	D_m/T FOR N-HEPTANE - BENZENE MIXTURES	109.

LIST OF TABLES

I	Column Dimensions	28.
II	Variation in Operating Conditions	36.
III	Physical Properties of Pure Materials	43.
IV	Experimental Data	86.
V	Summary of Calculations	95.
VI	Total Reflux Calculations	101.

INTRODUCTION AND SCOPE OF THE WORK

Thermal diffusion is a type of mass transfer by which the components of an initially uniform mixture tend to separate when the mixture is subjected to a temperature gradient. This separation, which is of rather small magnitude in itself, is the basis for a relatively new process for producing much larger separations. The apparatus used to take advantage of the basic thermal diffusion effect and produce the larger separations is called a thermal diffusion column. The column consists of two vertical surfaces, one heated and the other cooled, with the system to be separated between the two surfaces. The horizontal temperature gradient thus produced causes some kinds of molecules to migrate toward the heated surface by thermal diffusion while other kinds migrate toward the cooled surface. The horizontal temperature gradient also causes a horizontal density gradient. This density gradient produces thermal convection which subjects the molecules migrating toward the heated surface to a rising action and the molecules migrating toward the cooled surface to a falling action. Thus, the rising molecules concentrate at the top of the column and the falling molecules at the bottom. The concentrated products can either be collected in reservoirs or be removed continuously.

This work is a study of continuous operation of thermal diffusion columns for liquids. The emphasis in this study is on the variation in separation produced in thermal diffusion columns by different operating conditions and column

designs using a single liquid system. The system used to perform the experimental work was the binary n-heptane - benzene system. The columns used for this study were of concentric tube construction. This type of column encloses the system to be separated between two concentric tubes, one heated and the other cooled. A feed stream is introduced between the two tubes at some point along the column and products are removed from the top and bottom. There are no reservoirs in this type of column when it is operated continuously, since there is no need to accumulate any material in the column.

A number of variables are important in describing the operation of thermal diffusion columns. The difference in weight fraction between top and bottom products is called the separation, which is considered the dependent variable in this study. The height of the column is one of the significant variables affecting the separation, higher columns producing larger separations. The distance between the heated and cooled surfaces is called the spacing, which is important because it is the length of the path over which thermal diffusion occurs. The circumference, or width, of the column is a significant dimension because it determines the area and consequently the capacity of a column.

Among the operating variables, the temperature difference between the hot and cold walls is important in determining the rates of thermal diffusion and thermal convection, the latter of which may also be called the reflux rate. The feed rate to

the column is significant because it limits the time during which material can be retained in the column. The maximum separation for a given column design is obtained when the feed rate is zero, this situation being termed the total reflux case. The ratio between the top and bottom product rates in conjunction with the feed location determines the percentages of the total separation which are performed in the sections above and below the point where the feed stream is introduced. The composition of the feed stream is important because it determines the difficulty of the separation as well as the physical properties which control column performance. The average temperature in the column helps to determine such physical properties as viscosity and diffusivity, which affect the rates of thermal convection and thermal diffusion.

In this study, the following quantities were given significant variation:

1. Separation
2. Column height
3. Spacing
4. Feed rate
5. Top to bottom product ratio
6. Temperature difference
7. Feed composition

Circumference was not varied in this study, but comparison of the results of this study with the results of another investigator provided information on the effect of circumference.

The feed location was kept constant at a point midway up each

column. There was some variation of the average temperature in the column, but not enough to provide significant information on the effect of this variable.

LITERATURE SURVEY

The existence of thermal diffusion was first demonstrated by Ludwig (28) in 1856. He showed that the components of an initially uniform salt solution would separate in the presence of a temperature gradient. This separating effect has come to be known as thermal diffusion. In addition, Soret (32,33,34) did further pioneering work on thermal diffusion in liquids so that thermal diffusion in liquids is also termed the Soret effect. The theoretical basis for thermal diffusion was developed by Chapman (3) and by Enskog (11), using kinetic theory considerations. The theoretical work was developed for gases, for which it was shown that the laws governing the exchange of momentum and energy of translation required that the lighter molecules should migrate to the hotter part of the system and the heavier molecules to the cooler part. Chapman and Dootson (4) then demonstrated thermal diffusion in gases experimentally.

It was not until Clusius and Dickel (6) conceived of the idea of a thermal diffusion column that the process became capable of practical application. The column made use of the fact that the temperature gradient necessary for thermal diffusion also caused a density variation in the system. Clusius and Dickel constructed a column consisting of a vertical cooled tube with an electrically heated wire located axially inside. The density variation set up a vertical convection pattern which combined with the horizontal thermal diffusion to produce much greater separations. They also discovered that the concentrated products could be removed continuously

from the top and bottom of the column if a feed were introduced in the middle.

Another important development in the study of thermal diffusion was the theoretical work of Furry, Jones, and Onsager (16,17,18,24). They integrated the heat, mass, and momentum transfer differential equations which described the performance of thermal diffusion columns. These equations correlated the separation attainable with the column dimensions, operating conditions, and physical properties of the system. The derivation of these equations is presented in a separate chapter of this volume.

An important development in describing the behavior of thermal diffusion columns for liquids was the understanding of the so-called "forgotten effect". This was the name given to the effect on column performance of density variations caused by composition variations in the system separated. These density variations with composition were neglected by Furry, Jones, and Onsager when they derived the equations which were used to describe column behavior. The forgotten effect received its name because these equations were used without modification for cases in which the density variations with composition were significant. The forgotten effect has been studied and analyzed by de Groot (11,12,13)

The forgotten effect can conveniently be studied by describing the variation with time of the separation at total reflux for a column initially charged with a uniform binary mixture. It should be recalled that the convection pattern in the column depends on the density gradient. For the case

in which the forgotten effect is absent or can be neglected, the density gradient is determined solely by the temperature gradient. The total reflux separation begins at zero and increases uniformly to the steady state value. The component diffusing toward the hot wall concentrates at the top of the column in a normal manner. When the forgotten effect is present, two cases are possible. First, if the component diffusing toward the hot wall is the less dense, the convection pattern is stable, since the less dense material concentrates at the top of the column. The variation of separation with time would be similar to that for the normal case. Second, if the component diffusing toward the hot wall is the more dense, an unstable situation arises. Initially, the separation would start to increase from zero, with the denser component beginning to concentrate at the top of the column. Eventually, the denser material becomes concentrated enough at the top that it begins to proceed toward the bottom of the column. At that point, the separation has reached a maximum and is beginning to decrease. The separation decreases to zero and reverses direction so that the hot wall product concentrates at the bottom of the column. Finally, the separation reaches a steady state value which is of opposite direction from the initial separation. It should be noted that such cases would probably show instability in operation and rather small separations.

Debye (8) has developed an interesting modification of the thermal diffusion column. Acting on the assumption that

a total reflux column would perform better separations if the convection velocities were decreased, he constructed a column in which the separating space was packed with a fibrous or porous material, such as glass wool. It developed that the packing did not materially diminish the lateral thermal diffusion so that greater separations were possible for a given set of column dimensions. Debye used his column to fractionate solutions of high molecular weight polymers in suitable low molecular weight solvents. It is interesting to note that the polymer was always more concentrated than the solvent at the bottom of the column. This points out that, when the ratio of molecular weights is very great (100 or more), the molecular weight controls the direction of separation. In addition, a fractionation occurred between the various molecular weights of polymer, with the higher molecular weight polymer being more concentrated than the lower molecular weight polymer at the bottom of the column. This points out that, for molecules of similar shape, the molecular weight controls the direction of separation. Debye and Beuche (9) have also discussed the theory of the operation of thermal diffusion columns, with some modifications of the theory applicable to the separation of polymers.

Trevoy and Drickamer (35) have studied thermal diffusion in binary mixtures of paraffin hydrocarbons with each other and with benzene. They used a total reflux column with a feed composition of 50 mol percent. In addition, they used small temperature differences so they could study the effect

of temperature on the thermal diffusion coefficient. The results of their investigation showed that the molecular weight was important in determining the magnitude of separation by thermal diffusion of the members of a homologous series from some other compound or some member of the series. In addition, they found that the thermal diffusion coefficient was only slightly affected by temperature.

Jones and Milberger (23) have reported the results of their study of a great many systems composed of organic liquids. Their results were obtained for binary and a few ternary systems at total reflux with the column design and operating conditions being held constant so they could study the separation obtained from different systems. The materials used were such that the ratio of molecular weights of the components was less than three. They found that the shape of the molecules was the controlling factor in determining the direction of separation. In general, structurally more compact molecules diffused toward the cold wall of the column and thus concentrated at the bottom, regardless of molecular weight. However, if the molecules had similar shapes, the higher molecular weight molecules diffused toward the cold wall and concentrated at the bottom. They also found that some systems failed to separate despite differences in molecular weight and shape. As a guide to determining which component diffuses toward the hot wall, Jones and Milberger state that the component having the greater specific heat per unit volume is the hot wall product. This relationship

was found to hold true in nearly all the cases they studied. They also suggest that some of the cases for which the specific heat relationship fails may be situations in which the forgotten effect plays an important role. In addition, they determined that the maximum separation normally occurred when the composition of the feed was 50 percent by volume. It is significant that the volume composition determines the maximum separation rather than the molecular composition.

Jones and Hughes (22) have patented a variety of thermal diffusion columns for liquids as well as methods for using thermal diffusion on a continuous basis. They also point out the possibility of using thermal diffusion for such processes as improvement of the viscosity index of lubricating oil, purification of castor oil, purification of oleic acid, and purification of fish oil. Jones and Foreman (21) have demonstrated that the fatty acids and rosin acids in a tall oil can be separated easily by thermal diffusion.

A number of other investigators have studied thermal diffusion in liquids. These investigations were made in columns operating at total reflux for the purpose of establishing that thermal diffusion would occur in the systems studied and of determining the direction of the separation. In some cases, the magnitude of the thermal diffusion effect was also determined. Among these investigators are Carr (2), Clusius and Dickel (7), Fournier (15), Korsching (26,27), Prigogine et al (31), van Dranen and Bergsma (36), van Velden et al (37), and Wirtz (39).

An excellent summary on thermal diffusion as well as ordinary diffusion may be found in a book (25) by Jost, who includes a comprehensive list of references complete through 1950. Jones and Furry (24) also include a long list of annotated references in their article on isotope separation by thermal diffusion.

THEORY OF THE THERMAL DIFFUSION COLUMN

It is important to know the theoretical work of Furry, Jones, and Onsager (16,17,18,24) to be able to understand the operation of the thermal diffusion column. The essence of the procedure involved is to combine the basic mass transfer equation for thermal and ordinary diffusion with the hydrodynamic equations describing the velocity profile and with the heat transfer equation describing the temperature profile in a thermal diffusion column. In the following pages, the total reflux case will first be considered, and then the total reflux results will be adapted to the case of continuous operation.

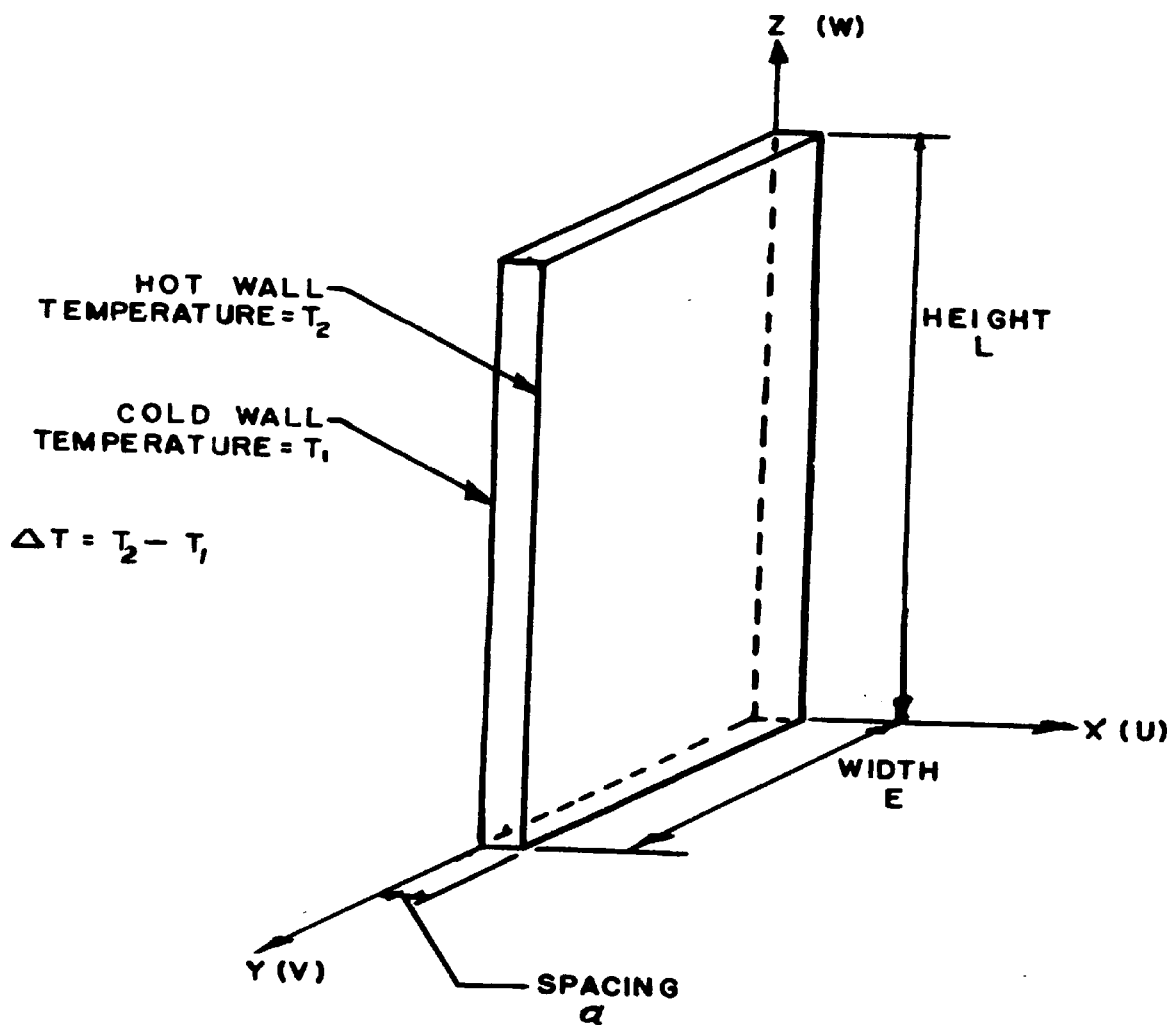
Total Reflux

Before proceeding with the derivation of the equations, it is necessary to have an idea of the physical situation to be described. Figure I, page 13, is a diagram of the essential features of a thermal diffusion column, showing the dimensions and operating variables involved. It may be seen that the column treated in the theory consists of two flat parallel plates, one heated and the other cooled. The material comprising the system is between the two plates. Since the concentric tube columns used for this study have rather large circumferences, it is believed that their behavior can be described by the parallel plate theory.

A number of assumptions are necessary in the derivation of the equations. Some of the more important of these assumptions are stated below, and a few others will be given at appropriate points in the solution.

FIGURE 1

COLUMN DESCRIBED BY THEORY



VALUES IN PARENTHESES SHOW DIRECTION
OF VELOCITY COMPONENTS.

1. The steady state has been attained.
2. The column is operating at total reflux. (This assumption is removed at a later stage.)
3. The system consists of two components.
4. Heat transfer is by conduction only, and takes place in the x direction alone.
5. The convection velocity is in the z direction only, and is a function of x alone.
6. The physical properties of the system are independent of concentration and are therefore independent of z.
7. End and edge effects are neglected. (The finite column is assumed to behave like a portion of an infinite column in the y and z directions.)
8. Nothing varies in the y direction.
9. Diffusion is neglected in the z direction.

Heat Transfer

With the above assumptions in mind, it is possible to set up the heat transfer equation. Since heat is transferred by conduction in the x direction, the following equation relates the temperature gradient dT/dx to the heat flux Q and the thermal conductivity k :

$$\frac{dT}{dx} = -\frac{Q}{k} \quad (1)$$

Thus, assuming k to be a constant:

$$\frac{dT}{dx} = \frac{\Delta T}{a} \quad (2)$$

Hydrodynamics

The hydrodynamic problem is next to be considered. The basic equation is the Navier-Stokes vector equation, which relates the density s , velocity $\bar{V}$, time t , pressure P , and viscosity m for a system which is in laminar flow.

$$\begin{aligned}
s \left[\frac{\partial \bar{V}}{\partial t} + (\bar{V} \cdot \text{grad}) \bar{V} \right] = & \bar{g}s - g_c \text{ grad } P - \frac{2}{3} \text{ grad } m \text{ div } \bar{V} \\
& + (\text{div } m \text{ grad}) \bar{V} + \text{div } m \frac{\partial \bar{V}}{\partial x} \bar{i} \\
& + \text{div } m \frac{\partial \bar{V}}{\partial y} \bar{j} + \text{div } m \frac{\partial \bar{V}}{\partial z} \bar{k} \quad (3)
\end{aligned}$$

Utilizing assumption 5, the velocity vector reduces to:

$$\bar{V} = w(x) \bar{k} \quad (4)$$

Thus:

$$\text{div } \bar{V} = \frac{\partial w}{\partial z} = 0 \quad (5)$$

and,

$$\text{div } m \frac{\partial \bar{V}}{\partial x} = \text{div } m \frac{\partial \bar{V}}{\partial y} = \text{div } m \frac{\partial \bar{V}}{\partial z} = 0 \quad (6)$$

and,

$$(\bar{V} \cdot \text{grad}) \bar{V} = 0 \quad (7)$$

Because of assumption 1:

$$\frac{\partial \bar{V}}{\partial t} = 0 \quad (8)$$

Thus, equation 3 reduces to:

$$\frac{d}{dx} m \frac{dw}{dx} = g_c \frac{dP}{dz} - g_s \quad (9)$$

Also, since ds/dz is a constant, it is permissible to use the value of dP/dz when $\Delta T = 0$, namely:

$$\frac{dP}{dz} = - \frac{g s_0}{g_c} \quad (10)$$

where s_0 is the average density in the column. Thus:

$$\frac{d}{dx} m \frac{dw}{dx} = g(s - s_0) \quad (11)$$

The boundary conditions on w are as follows:

$$w(0) = w(a) = 0 \quad (12)$$

No boundary conditions are needed for the y and z direc-

tions because of assumption 7 regarding end and edge effects. The following equation is assumed to represent the variation of density with temperature T , and expansion coefficient β :

$$s = s_0 - \beta (T - T_0) \quad (13)$$

Combining equations 11 and 13:

$$\frac{d}{dx} m \frac{dw}{dx} = -g \beta (T - T_0) \quad (14)$$

Define $X = x/a$, assume the viscosity can be represented by an average value, and substitute $T - T_0 = \Delta T (X - \frac{1}{2})$, derived from equation 2 with the definition of X . Thus:

$$\frac{d^2 w}{dX^2} = -\frac{ga^2 \beta \Delta T}{m} (X - \frac{1}{2}) \quad (15)$$

With the boundary conditions:

$$w(0) = w(1) = 0 \quad (16)$$

The solution to equations 15 and 16 is then:

$$w = -\frac{ga^2 \beta \Delta T}{6m} X(X - \frac{1}{2})(X - 1) \quad (17)$$

Equation 17 is the desired solution to the hydrodynamic problem.

Mass Transfer

The continuity equation is the basic equation for the mass transfer.

$$\frac{\partial s_i}{\partial t} = -\text{div } s_i \bar{V}_i \quad (18)$$

where s_i is defined from the density s and mass fraction C by,

$$s_i = Cs \quad (19)$$

The diffusion flux vector J_i is defined as follows:

$$J_i = s_i (\bar{V}_i - \bar{V}) \quad (20)$$

where,

$$\bar{V} = \sum_k C_k \bar{V}_k \quad (21)$$

Combining equations 18 and 20:

$$s \left[\frac{\partial C}{\partial t} + \mathbf{V} \cdot \text{grad } C \right] = - \text{div } \mathbf{J}_1 \quad (22)$$

The diffusion flux vector $\mathbf{J}_1$, neglecting diffusion in the z direction, is given by de Groot(10) as:

$$\mathbf{J}_1 = - D_L s \left[\frac{\partial C}{\partial x} - \frac{\alpha C(1-C)}{T_0} \frac{\partial T}{\partial x} \right] \quad (23)$$

where D_L is the ordinary diffusivity and α is the thermal diffusion coefficient. According to assumption 1 regarding the steady state:

$$\frac{\partial C}{\partial t} = 0 \quad (24)$$

Combining equations 4, 22, 23, and 24:

$$ws \frac{\partial C}{\partial z} = \frac{\partial}{\partial x} \left[D_L s \frac{\partial C}{\partial x} - \alpha D_L s \frac{C(1-C)}{T_0} \frac{dT}{dx} \right] \quad (25)$$

Substituting $X = x/a$, $Z = z/L$, and $dT/dx = \Delta T/a$:

$$\frac{ws}{L} \frac{\partial C}{\partial Z} = \frac{1}{a^2} \frac{\partial}{\partial X} \left[D_L s \frac{\partial C}{\partial X} - \alpha D_L s \frac{C(1-C)}{T_0} \Delta T \right] \quad (26)$$

Rearranging and assuming that the physical properties are constant:

$$\frac{wa^2}{D_L L} \frac{\partial C}{\partial Z} = \frac{\partial}{\partial X} \left[\frac{\partial C}{\partial X} - \frac{\alpha \Delta T}{T_0} C(1-C) \right] \quad (27)$$

In order to simplify equation 27, a function G is defined as follows:

$$\frac{\partial C}{\partial Z} G(Z, X) = \frac{\partial C}{\partial X} - \frac{\alpha \Delta T}{T_0} C(1-C) \quad (28)$$

If it is assumed that:

$$\frac{\partial^2 C}{\partial Z \partial X} = 0 \quad (29)$$

combination of equations 27, 28, and 29 results in:

$$\frac{\partial G}{\partial X} = \frac{wa^2}{D_L L} \quad (30)$$

However, $wa^2/D_L L$ is a function of X alone. Therefore, $\partial G/\partial X$ must also be a function of X alone. Thus:

$$G(Z, X) = G_1(X) + G_{II}(Z) \quad (31)$$

Since there can be no diffusive transport through the boundary, the boundary conditions on C are as follows:

$$\frac{\partial C}{\partial X} = \frac{\alpha \Delta T}{T_0} C(1 - C) \quad \text{at } X = 0, 1 \quad (32)$$

Combination of equations 28 and 32 results in:

$$G(Z, 0) = G(Z, 1) = 0 \quad (33)$$

Substitution of equation 33 in equation 31 produces:

$$G_1(0) + G_{II}(Z) = G_1(1) + G_{II}(Z) = 0 \quad (34)$$

Rearranging:

$$-G_1(1) = G_{II}(Z) = -G_1(0) = \text{a constant} \quad (35)$$

There is no loss of generality in including this constant in $G_1(X)$. Therefore,

$$G(Z, X) = G(X) \quad (36)$$

a function of X alone. Combining the result of equation 36 with equation 30 gives:

$$\frac{dG}{dX} = \frac{wa^2}{D_L L} \quad (37)$$

Substituting for w from equation 17:

$$\frac{dG}{dX} = \frac{ga^4 \beta \Delta T}{6mD_L L} X(X - \frac{1}{2})(1 - X) \quad (38)$$

Integrating:

$$G(X) = -\frac{ga^4 \beta \Delta T}{6mD_L L} \left[\frac{X^4}{4} - \frac{X^3}{3} + \frac{X^2}{4} \right] + c \quad (39)$$

However:

$$G(0) = c = 0 \quad (40)$$

Thus, rearranging equation 39:

$$G(X) = \frac{ga^4\beta\Delta T}{24mD_L L} X^2(X-1)^2 \quad (41)$$

Now, define W_1 , the transport of component 1 up the column:

$$W_1 = \int_0^1 EaswC \, dX \quad (42)$$

Substituting for w from equation 37:

$$W_1 = \frac{EsLD_L}{a} \int_0^1 C \frac{dG}{dX} \, dX \quad (43)$$

Integrating by parts, and using $G(0) = G(1) = 0$:

$$W_1 = \frac{EsLD_L}{a} \int_0^1 G \frac{\partial C}{\partial X} \, dX \quad (44)$$

Substituting for $\partial C/\partial X$ from equation 28:

$$W_1 = \frac{EsLD_L}{a} \int_0^1 \left[G^2 \frac{\partial C}{\partial Z} + \frac{\alpha \Delta T}{T_0} C(1-C)G \right] \, dX \quad (45)$$

Assuming that $C(1-C)$ does not vary appreciably with X , and that the variation of C with X is negligible with respect to its variation with Z :

$$W_1 = \frac{EsLD_L}{a} \frac{\partial C}{\partial Z} \int_0^1 G^2 \, dX + \frac{ELs\alpha\Delta TC(1-C)D_L}{aT_0} \int_0^1 G \, dX \quad (46)$$

Substituting for G from equation 41 and integrating:

$$W_1 = \frac{\alpha g \beta s E a^3 (\Delta T)^2}{6!m} C(1-C) - \frac{sg^2 \beta^2 E a^7 (\Delta T)^2}{9!m D_L} \frac{dC}{dz} \quad (47)$$

Defining transport coefficients H and K as follows:

$$H = \frac{\alpha g \beta E a^3 (\Delta T)^2}{6!m} \quad (48)$$

and,

$$K = \frac{sg^2 \beta^2 E a^7 (\Delta T)^2}{9!m D_L} \quad (49)$$

results in the basic transport equation for a thermal diffusion column operating at total reflux:

$$W_1 = HC(1 - C) - \frac{K}{L} \frac{dC}{dz} \quad (50)$$

In equation 50, it should be remembered that the values of C are averaged with respect to the variable X . Since the system is in the steady state and the column is operating at total reflux, $W_1 = 0$. Defining q :

$$q = \frac{C_D/1 - C_D}{C_B/1 - C_B} \quad (51)$$

Thus, equation 50 may be integrated to yield:

$$\ln q = \frac{HL}{K} \quad (52)$$

which gives the desired result for the separation attainable in a thermal diffusion column operating at total reflux.

Continuous Operation

It is possible to adapt the transport equation (50) to the case of continuous operation, in which products are removed from the top and bottom of the column and a feed is introduced in the middle. A flow sheet showing the streams and their nomenclature is presented in Figure II, page 21. If it is assumed that the transport coefficients H and K do not change from the total reflux case, the transport equation can be modified as follows:

$$W_1 = \int_0^1 Easw''C \, dX \quad (53)$$

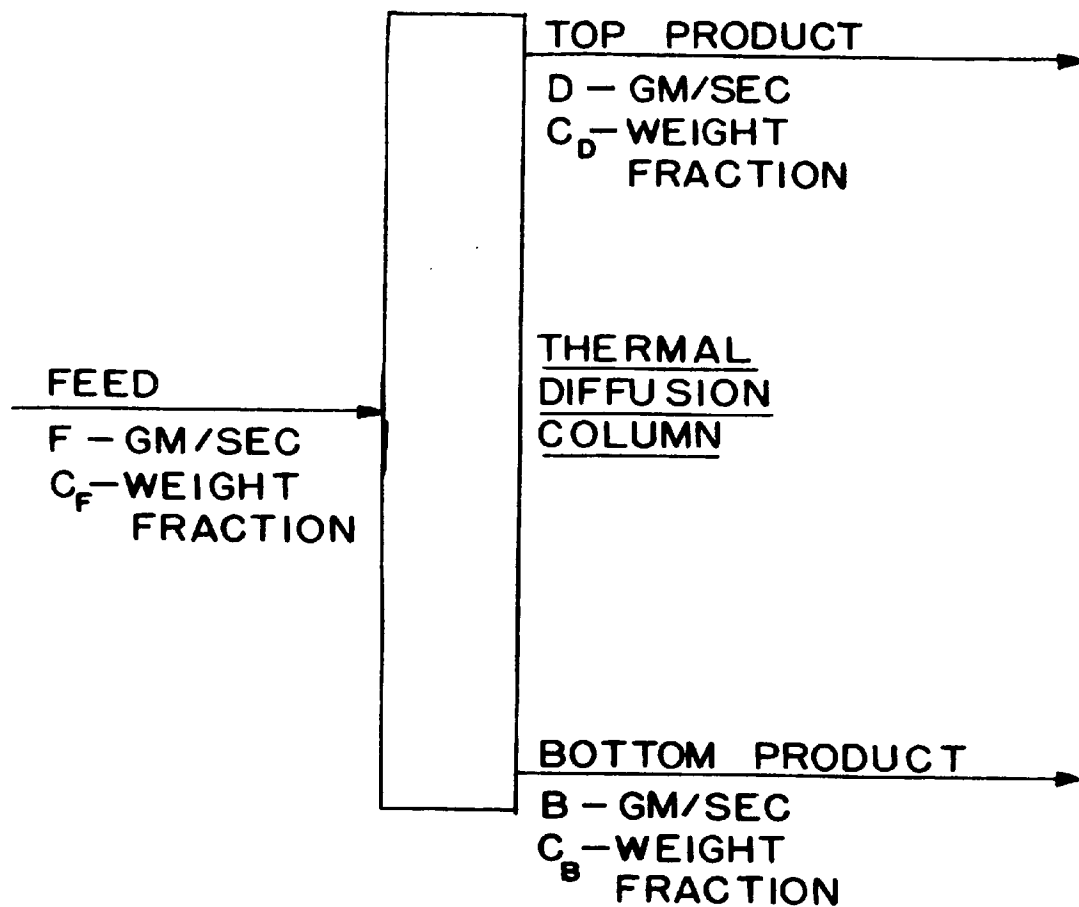
where it is assumed that:

$$w'' = w_0 + w \quad (54)$$

The w_0 is the average velocity of removal of material from the column, and w is taken from the previous section for total reflux. Thus:

FIGURE II FLOW DIAGRAM FOR CONTINUOUS OPERATION

WEIGHT FRACTIONS ARE GIVEN FOR THE
COMPONENT WHICH CONCENTRATES AT THE
TOP



$$S = \text{SEPARATION} = C_D - C_B$$

$$W_1 = \int_0^1 Easw_0C \, dX + \int_0^1 EaswC \, dX \quad (55)$$

W_1 is the amount of material removed from the column, so that a material balance for the top section of the column requires that:

$$W_1 = DC_D \quad (56)$$

The first integral in equation 55 reduces to:

$$\int_0^1 Easw_0C \, dX = DC \quad (57)$$

where C is averaged with respect to X . The second integral in equation 55 is the same as in the total reflux case:

$$\int_0^1 EaswC \, dX = HC(1 - C) - K \frac{dC}{dz} \quad (58)$$

Thus, equation 55 reduces to:

$$D(C_D - C) = HC(1 - C) - K \frac{dC}{dz} \quad (59)$$

A similar procedure for the bottom section of the column leads to:

$$B(C - C_B) = HC(1 - C) - K \frac{dC}{dz} \quad (60)$$

Although equations 59 and 60 may be integrated exactly, the result is too complex to be of much value. However, if it is assumed that $C(1 - C)$ is constant with respect to variations in z , a simple result is obtained. Rearranging equation 59 and integrating:

$$\int_0^{L_D} dz = \int_{C_F}^{C_D} \frac{K \, dC}{HC(1 - C) - D(C_D - C)} \quad (61)$$

With the restriction that $C(1 - C)$ is constant:

$$L_D = \frac{K}{D} \ln \frac{HC(1-C)}{HC(1-C) - D(C_D - C_F)} \quad (62)$$

Correspondingly, for the bottom section of the column, integration of equation 60 results in:

$$L_B = \frac{K}{B} \ln \frac{HC(1-C)}{HC(1-C) - B(C_F - C_B)} \quad (63)$$

Combining equations 62 and 63 and utilizing material balance relationships results in:

$$L = L_D + L_B = \frac{K}{D} + \frac{K}{B} \ln \frac{HC(1-C)}{HC(1-C) - (BD/F)(C_D - C_B)} \quad (64)$$

It should also be noted that for the case in which $C(1-C)$ is constant, the total reflux separation S' ($= C_D - C_B$ For total reflux) is given by:

$$S' = \frac{HL}{K} C(1-C) \quad (65)$$

In addition, division of equation 62 by equation 63 results in:

$$DL_D = BL_B \quad (66)$$

Since $L_D = L_B$ for the columns used in this study, $D = B = F/2$ should be substituted in equation 64. Combination of equations 64 and 65 gives the following relation for separation S ($= C_D - C_B$):

$$\frac{S}{S'} = \frac{1 - \exp(-FL/4K)}{FL/4K} \quad (67)$$

which describes the variation of the separation between top and bottom products from a thermal diffusion column as a function of the feed and product rates, as well as the variables contained in the transport coefficients H and K .

In summary, the theory predicts that the total reflux separation is determined by:

$$\ln q = HL/K$$

The ratio of the separation to the total reflux separation is determined by the following relation:

$$\frac{S}{S_r} = \frac{1 - \exp(-FL/4K)}{FL/4K}$$

EXPERIMENTAL WORK

The experimental work for this study consisted of a series of runs made at different values of the variables considered. The following sections describe the equipment used to perform these runs, the experimental procedure, the calibration of instruments used, the system used, and the measurement and correlation of the physical properties of the n-heptane - benzene system.

Description of the Equipment

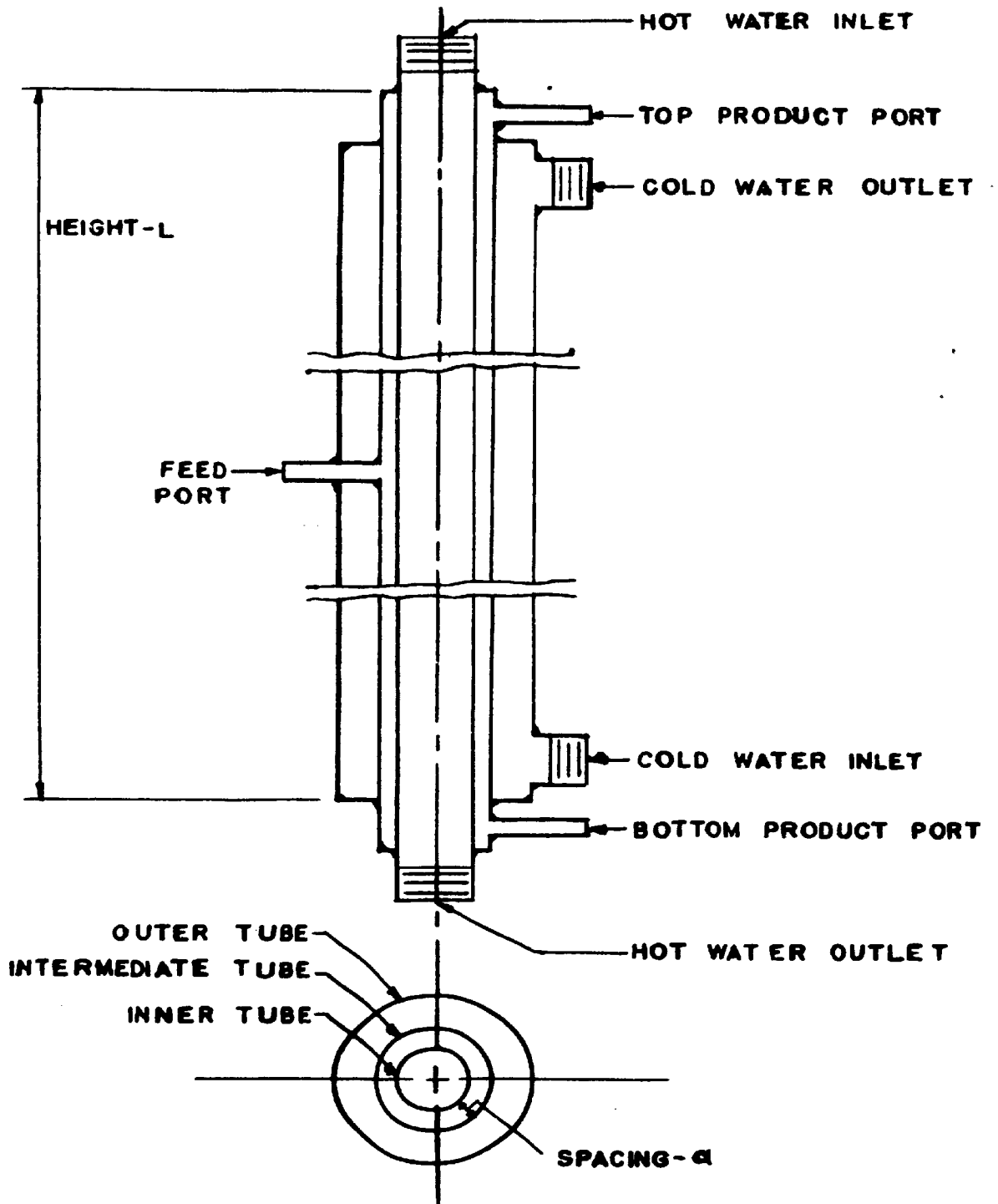
Concentric-tube thermal diffusion columns were used for this study. The construction of the columns and the assembly of the columns with the auxiliary equipment are described below.

Column Construction

The basic apparatus for this work consisted of four thermal diffusion columns. A schematic diagram of the columns is presented in Figure III, page 26. Each column was constructed of three pieces of aluminum tubing arranged concentrically, with suitable end pieces and piping connections welded in place. The space inside the inner tube contained circulating hot water; the space between the intermediate and inner tubes contained the system to be separated; and the space between the outer and intermediate tubes contained circulating cold water. The inside wall of the intermediate tube was termed the cold wall, and the outside wall of the inner tube was termed the hot wall of the column. A feed

FIGURE III

DIAGRAM OF A THERMAL DIFFUSION COLUMN



port was located exactly half way up each column, and product removal ports were located at the top and bottom. The height of each column was considered to be the length of the outer tube, while the spacing was defined as the distance between the hot and cold walls. The circumference was the average of the hot and cold wall circumferences. The dimensions of each column are given in Table I, page 28. Also included are the dimensions of a column used by Trevoy and Drickamer (35) with the n-heptane - benzene system.

The chief reason for selection of the concentric tube design, in preference to a design in which the hot and cold walls were parallel flat plates, was to achieve a more uniform temperature distribution. It is acknowledged that the parallel plate construction could give somewhat better control over the spacing, but it would be rather difficult to achieve a uniform temperature distribution across the plate. Any lack of uniformity in the temperature distribution across the plate would cause additional convection currents perpendicular to the main convection pattern. These additional convection currents would tend to destroy the effectiveness of the separation by remixing the concentrated materials from the top and bottom of the column.

In the concentric tube columns used in this study, the spacing was maintained constant in the following manner. When the columns were being built, a number of wooden blocks about one eighth of an inch square and of the proper thickness to maintain the spacing correctly in each column were

TABLE I
Column Dimensions

Column	Length L cm	Spacing a cm	Circumference E cm
1	306	0.1052	14.3
2	206	0.1648	14.5
3	153	0.1082	14.3
4	153	0.2621	13.8
Trevoy and Drickamer	10.2	0.1016	2.01

impregnated with phenolic resin and dried. These materials were used to provide a hard nonconducting spacer which would resist the heptane and benzene. A small sharp projection was raised with a cold chisel on the hot wall where each spacer was to be located. A spacer was forced onto each of these projections so that, when the inner tube was inserted into the column, the spacer was held in place between the inner and intermediate tubes. Three spacers were installed circumferentially 120 degrees apart about every two feet along the length of the column.

Assembly of Columns with Auxiliary Equipment

A flow sheet demonstrating how each column was assembled with the auxiliary equipment is presented in Figure IV, page 30, and a photograph of the assembled equipment is presented in Figure V, page 31. A gear pump was used to circulate the hot water, which contained a pint of radiator compound to prevent rust. The water was heated with low pressure steam in a small steam jacket located downstream from the pump. Cold water was taken from the city water lines and drained to the sewer after one pass through the column. The flow rates of the hot and cold water streams, measured by Fisher and Porter size 8 rotameters, were maintained at about fifteen gallons per minute. The hot water was introduced at the top of the column and the cold water at the bottom. By this arrangement, the hotter material in the separating space was at the top of the column. Therefore, the less dense material at the top of the column rendered the convection

FIGURE IV FLOW SHEET OF EQUIPMENT

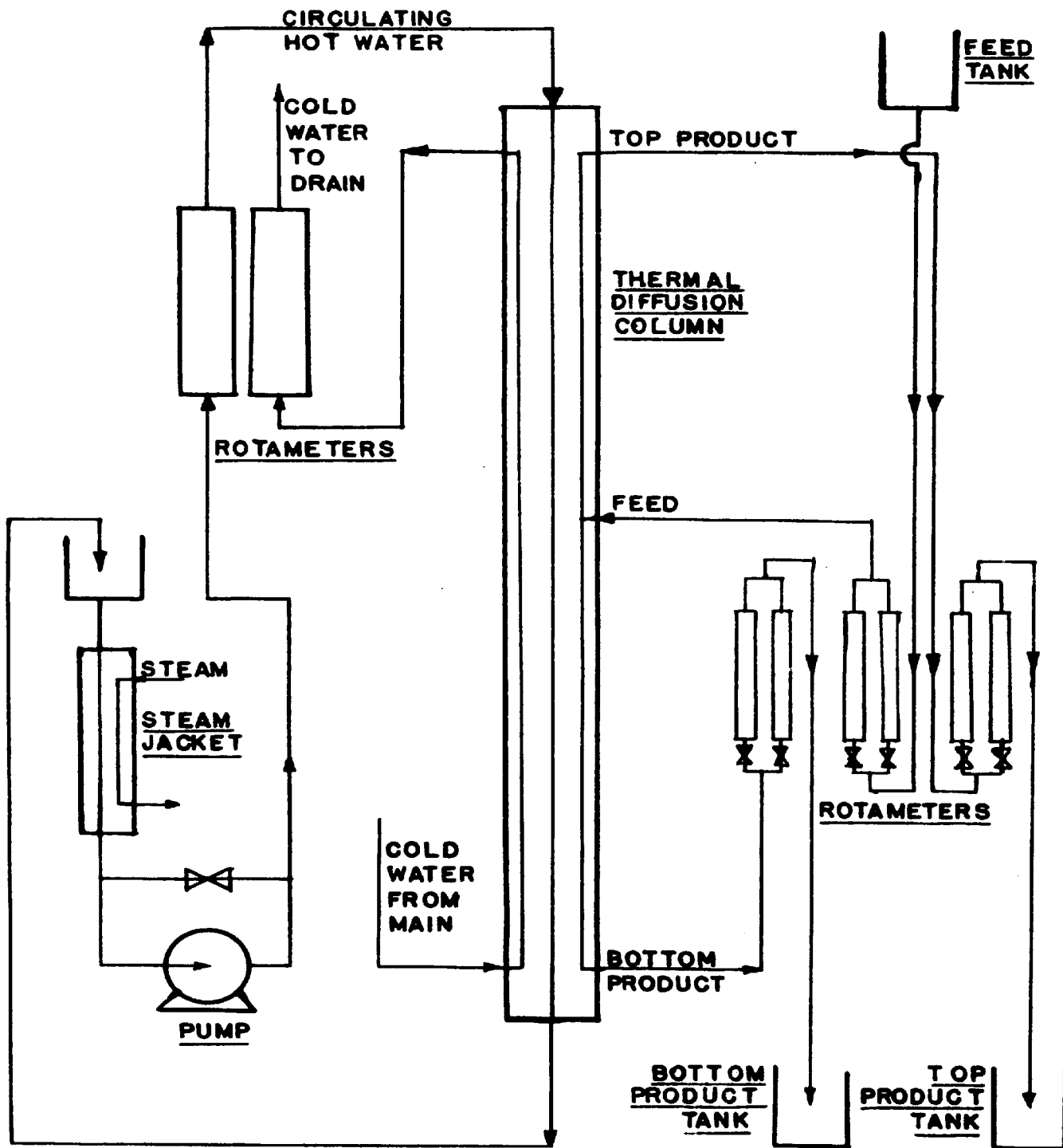
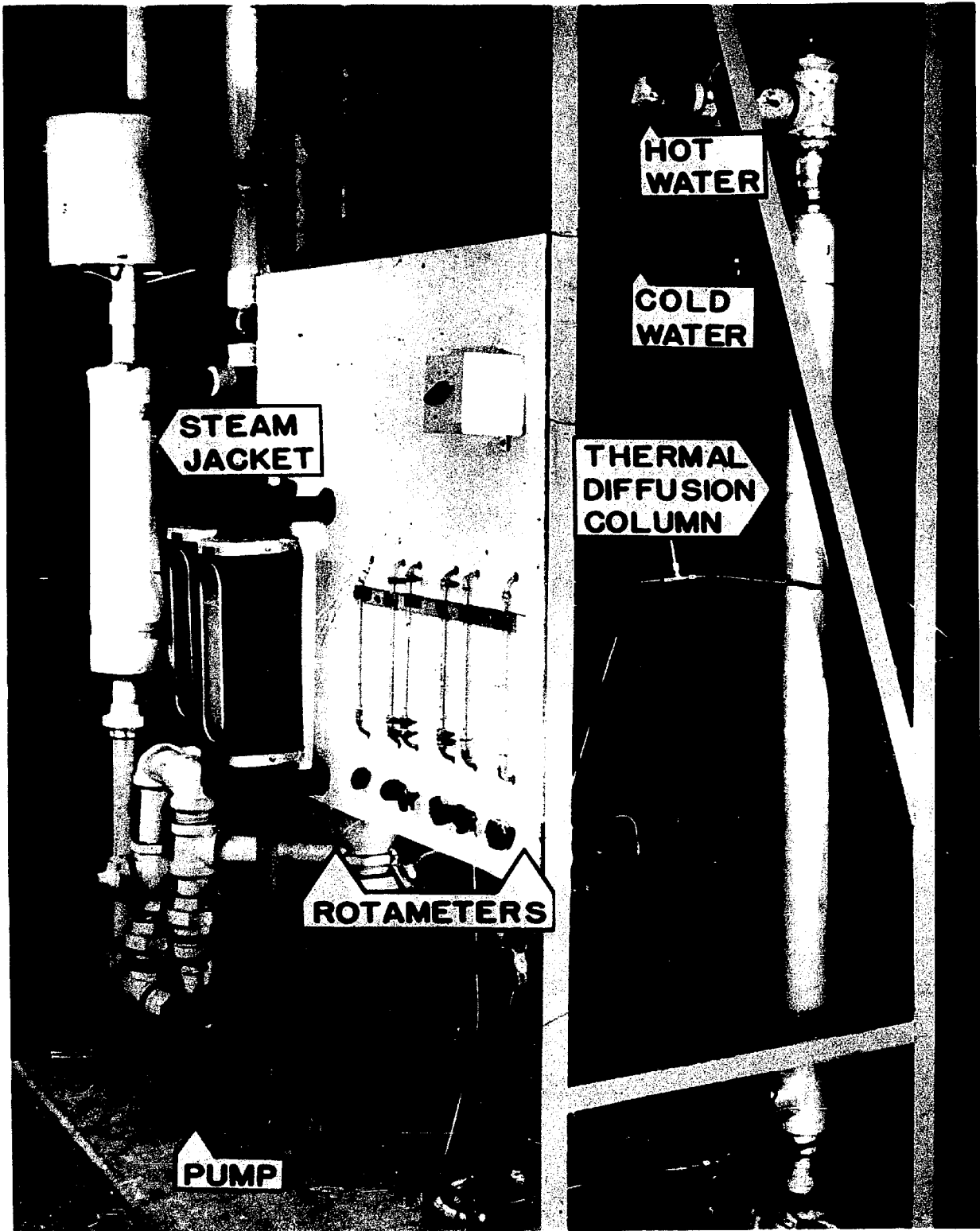


FIGURE V EXPERIMENTAL EQUIPMENT



pattern stable.

The feed was supplied by gravity to the center of the column from a one gallon can located above the column, and the products were collected in half-gallon containers on the floor. The flow rates of the feed and product streams were measured with Fisher and Porter size 07 or 08 rotameters. These flow rates were controlled with one-eighth inch needle valves.

Copper-constantan thermocouples were placed at the inlets and outlets of the hot and cold water streams, both in the streams and on the hot or cold walls. The thermocouples on the walls were made of 30 gage wire and were welded to the surface with a small flash welder. The thermocouples in the streams were made of 24 gage wire and were held in the centers of the streams with heavy copper wires. The EMF's developed by the thermocouples were measured with a Leeds and Northrup Portable Precision Potentiometer. The cold junction for the thermocouples was at room temperature, the cold junction correction being made by the compensator on the potentiometer.

Experimental Procedure

The following sections describe the operation of the equipment, the criterion used to determine the end of a run, the variation of operating conditions, the data taken, and the analysis of the feed and products.

Operation of Equipment

The equipment was started up in the following way.

First, the hot and cold water streams were turned on and adjusted to flow rates of approximately 15 gallons per minute. Then the steam was turned on so that the hot water would heat up to any desired temperature. It was found that the hot water temperature would reach a steady state in two or three hours. At the same time the water streams were started, the feed and product streams were also turned on and set at any desired flow rate. Control of these flow rates was accomplished by adjusting the valves on the two product streams, the valve on the feed being left open. By this procedure, the product flow rates were kept constant, and fluctuations in flow were assimilated in the feed stream. These fluctuations, which were believed to have been caused by small variations in the average temperature of the column, generally amounted to less than 20 percent of the feed rate. The rotameters in the feed stream were read by averaging the fluctuations.

At the beginning of this study, it was found that the apparatus required a long enough time to reach a steady state that the column would have to be operated without shutting down between runs. A run was considered to be the period of time beginning when the operating conditions were adjusted to new values and ending when the column had run in a steady state for at least four hours, thus including the transient period. No noticeable decrease in the length of a run was detected by running at total reflux during part of the transient period. However, the length of the transient period

was reduced by changing operating conditions between runs without shutting down the apparatus. Thus, only a small change in separation had to be made during any run as compared with the previous run.

Criterion for the End of a Run

It was necessary to develop a criterion to determine when the end of a run had been reached. For the operating conditions used, it was found that, if the separation changed less than 0.1 weight percent in four hours, the column had reached as nearly a steady state as possible. In addition, a secondary condition was developed which was somewhat easier to use. It was found that the primary criterion was always satisfied when a total of two column volumes of liquid had been fed to the column. In order to be on the safe side, a total of four column volumes were fed to the column before a run was ended. With columns 1, 2, and 4, a run took approximately one day, and with column 3 approximately half a day.

Variation of Operating Conditions

The run conditions were varied according to the following kind of schedule. For each column and feed composition, a set of runs was made for some particular temperature difference at different feed rates. After that set had been completed, the temperature was changed and another similar set of runs was made. This procedure was repeated for at least one more temperature difference, and then the whole series was begun again for other feed compositions. After

enough feed compositions had been tested, another column was put in place and the preceding process was repeated. The range of operating conditions covered in each column is listed in Table II, page 36.

Data Taken

The data taken at the end of each run consisted of the following:

1. Room temperature
2. Rotameter readings from the hot and cold water streams
3. Rotameter readings from the feed and product streams
4. EMF's of the thermocouples in the hot and cold water streams and on the hot and cold walls

In addition, samples were taken for analysis of the feed and products. The experimental data for this study may be found in Table IV, pages 86 to 94. The numbers assigned to each run are the number of the column and a serial number. Thus, run 1-60 is the sixtieth run made in column 1.

Analysis

The feed and products were analyzed by measurement of their refractive indices. For the samples from columns 1, 2, and 3, the analysis was accomplished at 25°C in a Zeiss-Abbe refractometer capable of measuring refractive indices to plus or minus one part in the fourth decimal place. The samples from column 4, along with samples of pure n-heptane and benzene, were analyzed at room temperature in a Zeiss precision refractometer, which measured refractive indices to plus or minus three parts in the fifth decimal place.

TABLE II
Variation in Operating Conditions

Column	1	2	3	4
Feed	0.100	0.594	0.261	0.489
Composition	0.260		0.462	
Weight	0.452		0.598	
Fraction	0.572			
n-heptane	0.818			
Temperature	7.1	21.5	8.9	30.8
Difference	to	to	to	to
°C	42.3	46.6	47.8	57.2
Feed	0.0048	0.0045	0.0049	0.0048
Rate	to	to	to	to
gm/sec	0.153	0.039	0.128	0.071
Separation	0.046	0.024	0.011	0.0091
Weight	to	to	to	to
Fraction	0.150	0.036	0.077	0.0131
n-heptane				
Average	20.6	31.8	21.0	29.0
Temperature	to	to	to	to
°C	42.0	42.7	42.6	41.8
Top to	0.33	0.96	0.17	0.58
Bottom	to	to	to	to
Ratio	12.5	1.75	14.4	1.76

Calibration

The equipment calibrated consisted of the rotameters in the hot and cold water streams, the rotameters in the feed and product streams, and the thermocouples. In addition, the pertinent dimensions of the columns were measured.

Rotameters in the Water Streams

The rotameters in the hot and cold water streams were calibrated by passing water through them and weighing the amount of water collected during a measured time. It was found that the two meters had the same calibration, and that this calibration agreed closely enough with the scale readings put on by the manufacturer.

Rotameters in the Feed and Product Streams

The rotameters in the feed and product streams were calibrated in a similar manner. However, since the flow rates were so slow, these rotameters were affected markedly by the viscosity of the material passing through them. Calibration of these meters was accomplished by passing liquids of various viscosities through them and measuring the volume of liquid collected during a measured time. The liquids used for calibration were ethanol, benzene, ethyl acetate, and acetone. Correlation of these measurements was accomplished by the method proposed by Martin (30) to account for the effect of the viscosity. These calibrations are presented in Figures XVIIa and XVIIb, pages 102 and 103. In these curves, the group $s (s_f - s)/m^2$ is plotted against W/m .

for various rotameter readings, where s is the density of the fluid, s_f is the density of the float, m is the viscosity of the fluid, and W is the flow rate. The float density for these meters is 2.28. Examination of these curves shows that for a given rotameter reading the flow rate is roughly proportional to the viscosity, as might be expected if there were laminar flow in the meters. These calibrations were spot checked from time to time, and the check calibrations agreed with the original calibration within the accuracy of the latter. It was estimated that this calibration gave flow rates accurate to about plus or minus 15 percent.

Thermocouples

The thermocouples were calibrated by running cold water through the apparatus and circulating the hot water stream without turning on the steam, so that both streams would be at very close to the same temperature. The stream temperatures were measured with a calibrated thermometer. The EMF's developed by the thermocouples were converted to temperatures with the standard calibration (19) for copper-constantan thermocouples. If the latter temperatures did not agree with the measured temperature to within 0.1°C, the readings from the thermocouple giving poor agreement were discarded. This calibration was made after each column was set up and just prior to taking it down.

Column Dimensions

The following dimensions were measured for each column

used in this study:

1. The diameter of the hot wall
2. The diameter of the cold wall
3. The height of the column

The diameter of the hot wall for each column was measured with a micrometer before the column was assembled. Twenty measurements were made at various points along the column and the results were averaged. Care was taken to measure the diameters at different points around the column so that the effect of any eccentricity would be accounted for. The diameter of the cold wall was measured in a similar manner, except that a telescope gage was used to determine the diameter. The diameter settings on this gage were measured with the same micrometer that was used to measure the hot wall diameters. It is believed that the average diameters measured by this method are accurate to within plus or minus 0.2 percent. The average diameter was calculated as the average of the hot and cold wall diameters, and the spacing was calculated as the difference between the hot and cold wall diameters. The spacings derived by this method are believed to be accurate to plus or minus 0.002 cm. This accuracy gives the spacing for columns 1 and 3 to 2 percent, for column 2 to $1\frac{1}{4}$ percent, and for column 4 to $\frac{3}{4}$ percent. The height of each column was measured with an ordinary steel tape. The heights are believed to be accurate to 0.2 percent. The dimensions of each column were given previously in Table I.

System Used

The system used for this study was chosen primarily to give a separation large enough that the feed and products from the column could be analyzed easily. A binary system was considered most suitable for ease of analysis. In addition, since determination of compositions by refractive index would provide a very convenient method of analysis, it was desirable that the two pure components have a large difference in refractive index.

Ethanol - Benzene System

An attempt was made to use the ethanol - benzene system. It was apparent after several runs in column 1 that this system would not separate very well. To eliminate the possibility that the poor separation was caused by some feature of the column, an effort was made to remove possible errors in the column. The assembly was checked to insure that the column was vertical and was not vibrating appreciably. The column was also run with the direction of the hot and cold water streams reversed. This procedure made little if any difference in the separation obtained. In addition, runs were made at several different feed compositions. These runs showed that at different relative concentrations in the feed the direction of separation changed. At a feed composition of 13 weight percent ethanol, the benzene concentrated at the top of the column. When the feed composition was 50 weight percent ethanol, the column would not separate

ethanol and benzene. With feed compositions of 69 and 94 weight percent ethanol, the ethanol concentrated at the top of the column. The differences in composition between top and bottom products were always less than 4 weight percent. The reversal in separation could have been caused either by the forgotten effect or by a reversal in the direction of thermal diffusion. In any case, it was decided that the ethanol - benzene system would not be suitable to study the performance of the columns.

n-Heptane - Benzene System

The next system tried was the n-heptane - benzene system. It was discovered that this system separated to a much greater extent and that the direction of separation did not depend on the feed composition. It was decided that this system would be suitable for studying the behavior of the columns.

Physical Properties of the System Used

The physical properties of the n-heptane and benzene used are given below as an indication of their purity. A number of physical properties of n-heptane - benzene mixtures were needed for correlation of the experimental data. The required properties were:

1. Refractive index
2. Density and coefficient of expansion
3. Viscosity
4. Diffusivity

These properties had to be known as functions of temperature

and composition, with the exception of refractive index, which had to be determined as a function of composition at a single temperature.

Pure Components

The heptane used in this study was Pure Grade n-heptane purchased from the Phillips Petroleum Company. It had a minimum purity listed as 99 mol percent n-heptane. This material was used without further purification. A comparison of the physical properties of this n-heptane with the properties listed in the literature is given in Table III, page 43.

The benzene used was reagent-grade thiophene-free benzene supplied by the University of Michigan Chemistry Stores. This material was used without further purification. A comparison of the properties of this benzene with the properties listed in the literature may be found in Table III, page 43.

Refractive Index

The refractive indices in the n-heptane - benzene system were needed for analysis of the feed and products. The refractive indices were measured at 25.00C plus or minus 0.03C. Standard samples were prepared by mixing weighed amounts of n-heptane and benzene. The refractive indices of these samples were measured in a Zeiss-Abbe refractometer capable of determining refractive index to within plus or minus one part in the fourth decimal place. Since the difference in refractive index between n-heptane and benzene amounted to 0.1120,

TABLE III
Physical Properties of Pure Materials
at 25C

		Density gm/cm ³	Refractive Index	Viscosity cp
Heptane:	Measured	0.6794	1.3852	0.394
	Literature*	0.6794	1.3854	0.386
Benzene:	Measured	0.8725	1.4972	0.607
	Literature	0.8735	1.4974	0.606

* Literature values are from the "International Critical Tables."

compositions determined from the refractive indices were accurate to approximately 0.1 weight percent.

To facilitate correlation of the refractive index data, the following procedure was used. First, an ideal refractive index n_i was calculated for each standard sample on the basis of a linear relation between refractive index and weight fraction n-heptane. Then the difference between the ideal refractive index and the experimental index was calculated for each standard sample. This difference, termed the refractive index deviation, was plotted against refractive index as in Figure XVIII, page 104. The composition of any unknown mixture could be calculated by the following relation:

$$C = \frac{n_b - n - (n_i - n)}{n_b - n_h} \quad (68)$$

where C is weight fraction n-heptane, n_b is the refractive index of pure benzene, n_h is the refractive index of pure heptane, and n is the refractive index of the unknown mixture.

Density and Coefficient of Expansion

The densities of n-heptane - benzene mixtures were also measured at 25.00C plus or minus 0.03C, using the same standard samples that were used for the refractive index measurements. The density of each sample was determined in a calibrated density pipette, which was found to be accurate by measuring the density of distilled water. The densities

determined by this method are believed to be accurate to better than 0.1 percent.

In addition, the densities of pure n-heptane and benzene as functions of temperature were taken from the International Critical Tables (19). These densities were differentiated with respect to temperature to determine the coefficients of expansion for pure n-heptane and benzene. It was assumed that the coefficient of expansion for a mixture was a linear function of the composition in weight fraction units. The densities of mixtures were determined using the measured densities of mixtures at 25°C, the densities of the pure compounds as functions of temperature, and the assumed values for the coefficients of expansion of mixtures. The densities of n-heptane - benzene mixtures as a function of temperature and composition are presented in Figure XIX, page 105, and the coefficients of expansion are shown in Figure XX, page 106.

Viscosity

The viscosities of n-heptane - benzene mixtures were determined at 25.00°C plus or minus 0.03°C, using the same standard samples described above. The kinematic viscosity of each sample was measured in a modified Ostwald viscosimeter, which had a Bureau of Standards calibration. The kinematic viscosities determined by this instrument are believed to be accurate to 0.2 percent. The absolute viscosities of the standard samples were computed by dividing the kinematic vis-

cosities by the corresponding densities. The absolute viscosities of the two pure components as functions of temperature were taken from the International Critical Tables. To determine the viscosities of mixtures as a function of temperature, the viscosities of the pure components were plotted as $\log \eta$ versus $1/T$, so that a linear graph would be obtained. In addition, the point which corresponded to the viscosity of each standard mixture at 25°C was plotted on the same graph. The viscosity of each mixture as a function of temperature was interpolated by drawing a straight line on the $\log \eta$ versus $1/T$ plot through the experimental point and with a slope intermediate to the slopes of the lines for the pure components. The results of this interpolation are presented in Figure XXI, page 107, which is a graph of viscosity against composition with temperature as a parameter.

Diffusivity

The only experimental values of diffusivity in the n-heptane - benzene system were those of Trevoy and Drickamer (35) for a 50 mol percent mixture. It was necessary to extend these data throughout the entire range of composition. Wilke (38) recommended that the group D_m/T should be independent of temperature. It was found that the data of Trevoy and Drickamer corroborated this relation within the accuracy of their experimental measurements. Wilke also recommended that the group $(D_m/T)/(d \ln a'/d \ln N)$ should be a linear function of the composition in mol fraction units. The func-

tion $(d \ln a'/d \ln N)$ was evaluated by calculating activity coefficients at the normal boiling points from the vapor-liquid equilibrium data of Clark (5). These activity coefficients are presented in Figure XXII, page 108. VanLaar equations were fitted to these activity coefficients. Differentiation of the VanLaar equations provided the function $(d \ln a'/d \ln N)$, which was assumed to be independent of temperature. Wilke and Arnold (1) have both presented methods for predicting the limiting values of (D_m/T) for dilute solutions. Using the values of (D_m/T) from Wilke in conjunction with the function $(d \ln a'/d \ln N)$ gave rather poor agreement with the experimental values of Trevoy and Drickamer. On the other hand, the equation of Arnold:

$$D_L = \frac{0.01(1/M_1 + 1/M_2)^{\frac{1}{2}}}{A_1 A_2 m_2^{1/2} (V_1^{1/3} + V_2^{1/3})^2} \quad (69)$$

with $A_1 = 1.05$ for heptane and 1.05 for benzene, and $A_2 = 0.66$ for heptane and 1.00 for benzene gave good agreement with the data of Trevoy and Drickamer. The values of (D_m/T) thus determined are presented in Figure XXIII, page 109.

RESOLUTION OF OBSERVED DATA

The following sections describe the resolution of the observed data into values of the basic variables describing the operation of thermal diffusion columns. The observed refractive indices, rotameter readings, and thermocouple EMF's were converted into compositions, flow rates, and temperatures. From this information for each run, values could be computed for separation, feed composition, feed rate, top to bottom product ratio, temperature difference, and average temperature in the column. In addition, the spacing was corrected for thermal expansion of the column in each run. The transport coefficients and dimensionless groups from the theory were also computed. A sample calculation demonstrating resolution of the observed data for one run may be found in the Appendix, page 82.

Compositions

The conversion of refractive indices of the feed and product streams to weight fractions of n-heptane was accomplished with the previously described calibration, using the following relation:

$$C = \frac{n_b - n - (n_1 - n)}{n_b - n_h} \quad (68)$$

where the values of $(n_1 - n)$ were taken from Figure XVIII, page 104. The separation was then calculated as the difference in weight fraction between the top and bottom products. In addition, the ratio of top to bottom product flow rates could

be calculated from the weight fractions by the following material balance relation:

$$\frac{D}{B} = \frac{C_F - C_B}{C_D - C_F} \quad (70)$$

Flow Rates

The flow rates of the feed and product streams were calculated from the rotameter readings with the calibration curves presented in Figures XVIIa and XVIIb, pages 102 and 103. It was found that the material in these streams was essentially at room temperature. Thus, the required viscosities and densities for these streams were evaluated at room temperature and at the compositions calculated as above. Then the sum of the product rates was compared with the feed rate to check the material balance. In case the two figures did not agree, the sum of the product rates was considered to be the feed rate to the column. This choice was made because the rotameters in the feed stream were noted to be fluctuating, whereas the product rates seemed to be steady. The fluctuations in the feed stream were believed to have been caused by density variations, probably the result of fluctuations of the average temperature in the column. The ratio of top to bottom product rates was computed directly and compared with the ratio computed from the compositions to serve as another check on the material balance. The ratio of top to bottom product rates usually agreed to within plus or minus 20 percent.

Temperatures

Conversion of the thermocouple EMF's to temperatures was done with the standard calibration (19) for copper-constantan thermocouples. It was found that some of the thermocouples on the walls became detached or gave inaccurate readings due to other causes. However, it was discovered that the readings of the good thermocouples on the walls could have been calculated accurately enough from the stream temperatures, using the heat transfer coefficients from MacAdams (29, chapter VII, equations 9c and 25). These calculations also tended to confirm the assumption used in the theoretical treatment that heat was transferred by conduction alone through the n-heptane - benzene mixture in the column. Wherever possible, the temperature differences between the streams and the walls were computed by ratio from experimental temperature differences. In any case, the temperature differences through the water films were less than 10 percent of the overall temperature differences, so that relatively large errors in the water film temperature differences could cause only relatively small errors in the calculated wall temperatures. The average temperature in the column was computed as the average of the hot and cold water temperatures, and the temperature difference as the difference between the hot and cold wall temperatures.

Correction of Spacing for Thermal Expansion

It was necessary to correct the spacing of each column for the thermal expansion or contraction of the hot and cold

walls during a run. It was assumed that the tubes comprising these walls behaved like thin cylindrical shells so that the dimensions would change linearly with temperature. Thus, the following relation was derived for correction of the spacing:

$$\frac{a}{a_r} = 1 - \beta \Delta T \left[\frac{R_{rH}}{a_r} + \frac{T_r - T_C}{\Delta T} \right] \quad (71)$$

where a is the spacing corresponding to the temperature difference ΔT , a_r is the spacing measured at temperature T_r , R_{rH} is the radius of the hot wall at T_r , and β is the expansion coefficient for aluminum. The correction involved amounted to less than 2 percent of the total spacing. However, this resulted in corrections of as much as 15 percent in the spacing to the seventh power, which was used to compute the transport coefficient K .

Calculation of Transport Coefficients and Dimensionless Groups

The transport coefficient K was calculated for each run by the relation:

$$K = \frac{sg^2 a^7 \beta^2 E (\Delta T)^2}{9! m^2 D_L} \quad (49)$$

The dimensionless group $FL/4K$ derived from the theory was also computed for each run. The transport coefficient H , given by the relation:

$$H = \frac{\alpha s g a^3 \beta E (\Delta T)^2}{6! m T_0} \quad (48)$$

could not be calculated for each run because the value of the thermal diffusion coefficient α was not known. However, it was discovered that the physical properties contained in

the dimensionless group HL/K were very nearly independent of temperature. Thus, the group $HL/\alpha K$ could be determined for each set of runs at a given feed composition.

Summary of Data Resolution

The following information was available for each run:

1. Separation
2. Feed Composition
3. Feed Rate
4. Top to Bottom Product Ratio
5. Temperature Difference
6. Average Temperature
7. Spacing
8. Height
9. Circumference
10. Transport Coefficient K
11. Dimensionless Group FL/LK

In addition, the group $HL/\alpha K$ was known for each set of runs made at a given feed composition. A summary of the calculations for each run may be found in Table V, page 95, and a summary of the total reflux calculations for each set of runs made at a given feed composition may be found in Table VI, page 101.

RESULTS

The results of this study are presented in the following sections, first for the case of continuous operation and then for the total reflux case. The results are compared with the theoretical equations developed by Furry, Jones, and Onsager. Since this comparison shows the theory to be inadequate for both cases, empirical correlations are developed to fit the data.

Continuous Operation

The results from continuous operation of the columns are presented below in terms of the effect on the separation of the group $FL/4K$ and of the top to bottom product ratio D/B . An empirical correlation of the data is also derived.

Effect of $FL/4K$

The group $FL/4K$, given by the relation:

$$\frac{FL}{4K} = \frac{9!FLm^2D_L}{sg^2aT\beta^2E(\Delta T)^2} \quad (72)$$

may be seen to include the variables; feed rate, spacing, height, circumference, and temperature difference. The variables, feed composition and average temperature, are also included through their effect on the physical properties in $FL/4K$.

The effect of $FL/4K$ on the separation can be seen in Figures VIa to VIe, pages 54 to 58, which are graphs of the logarithm of the separation versus $FL/4K$. The semi-logarithmic plot is used because the theoretical relation, given by:

FIGURE VI a

LOG SEPARATION VS $\frac{FL}{4K}$

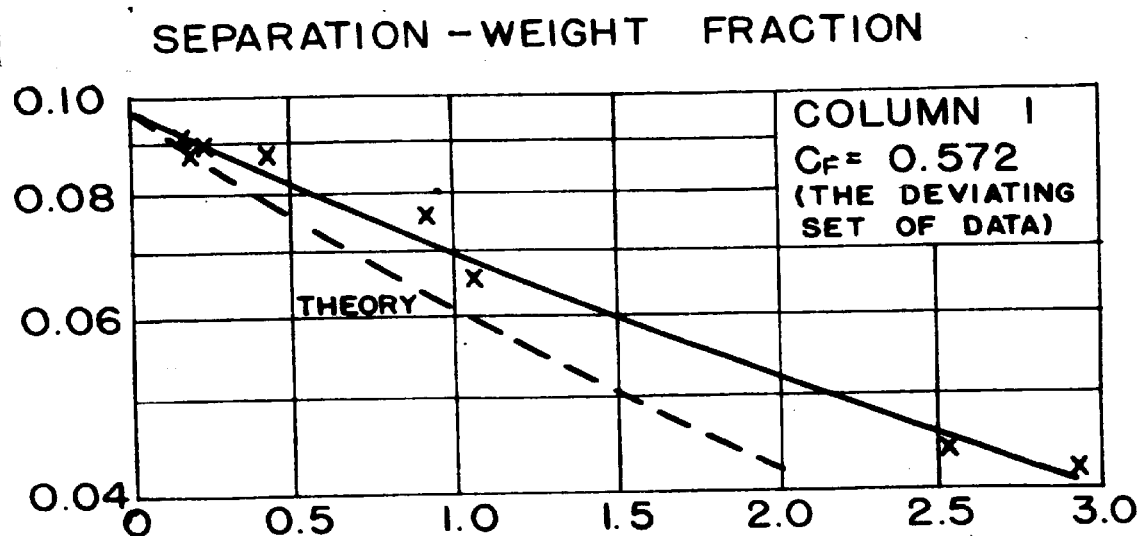
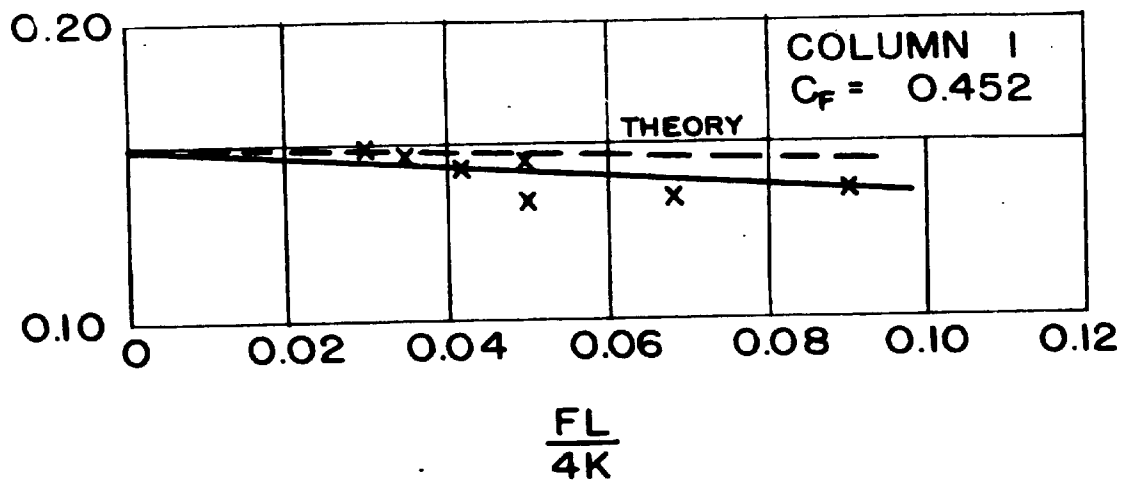


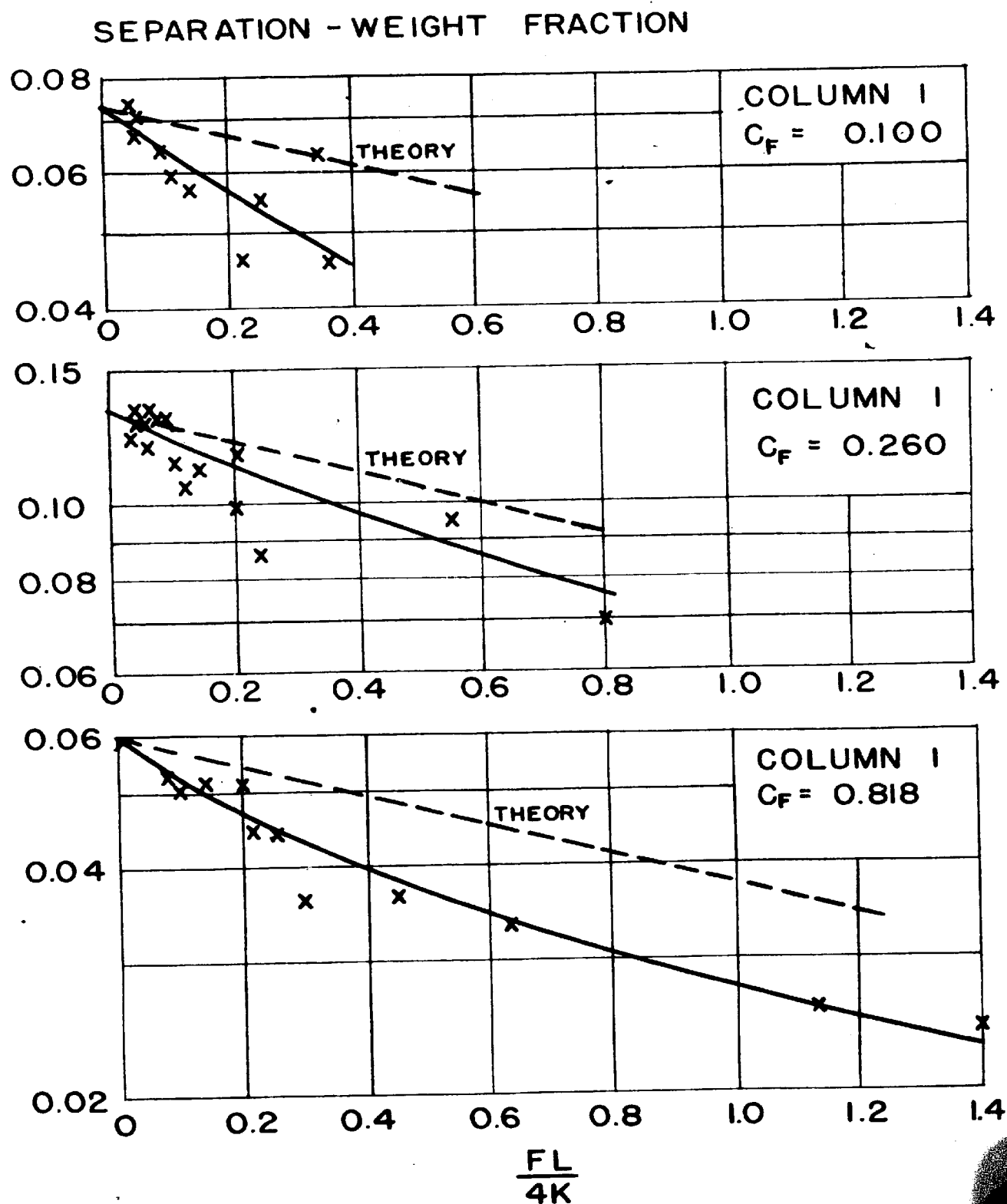
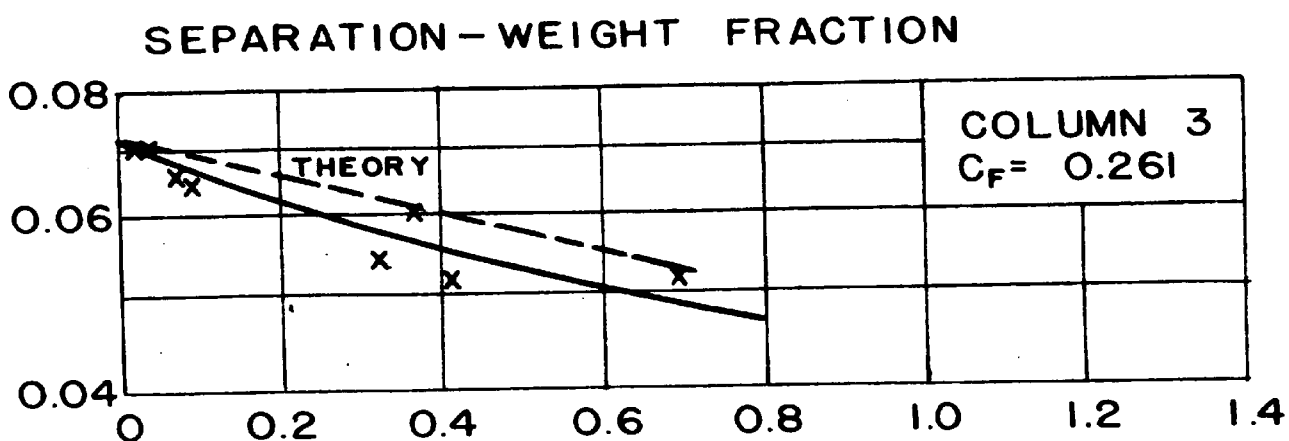
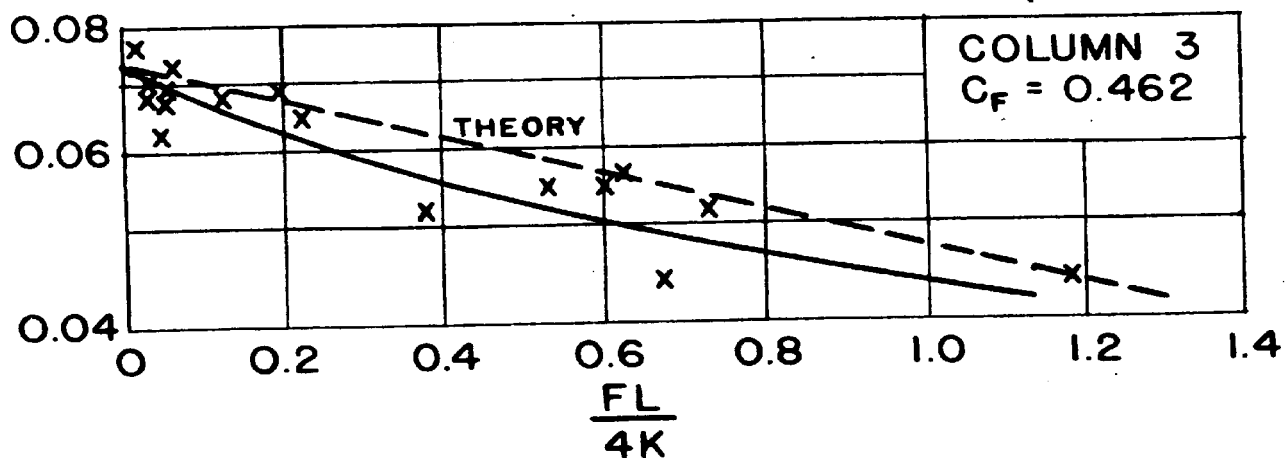
FIGURE VI_bLOG SEPARATION VS $\frac{FL}{4K}$ 

FIGURE VI_c LOG SEPARATION VS $\frac{FL}{4K}$



LOG SEPARATION VS $\frac{FL}{4K}$ FIGURE VI_d

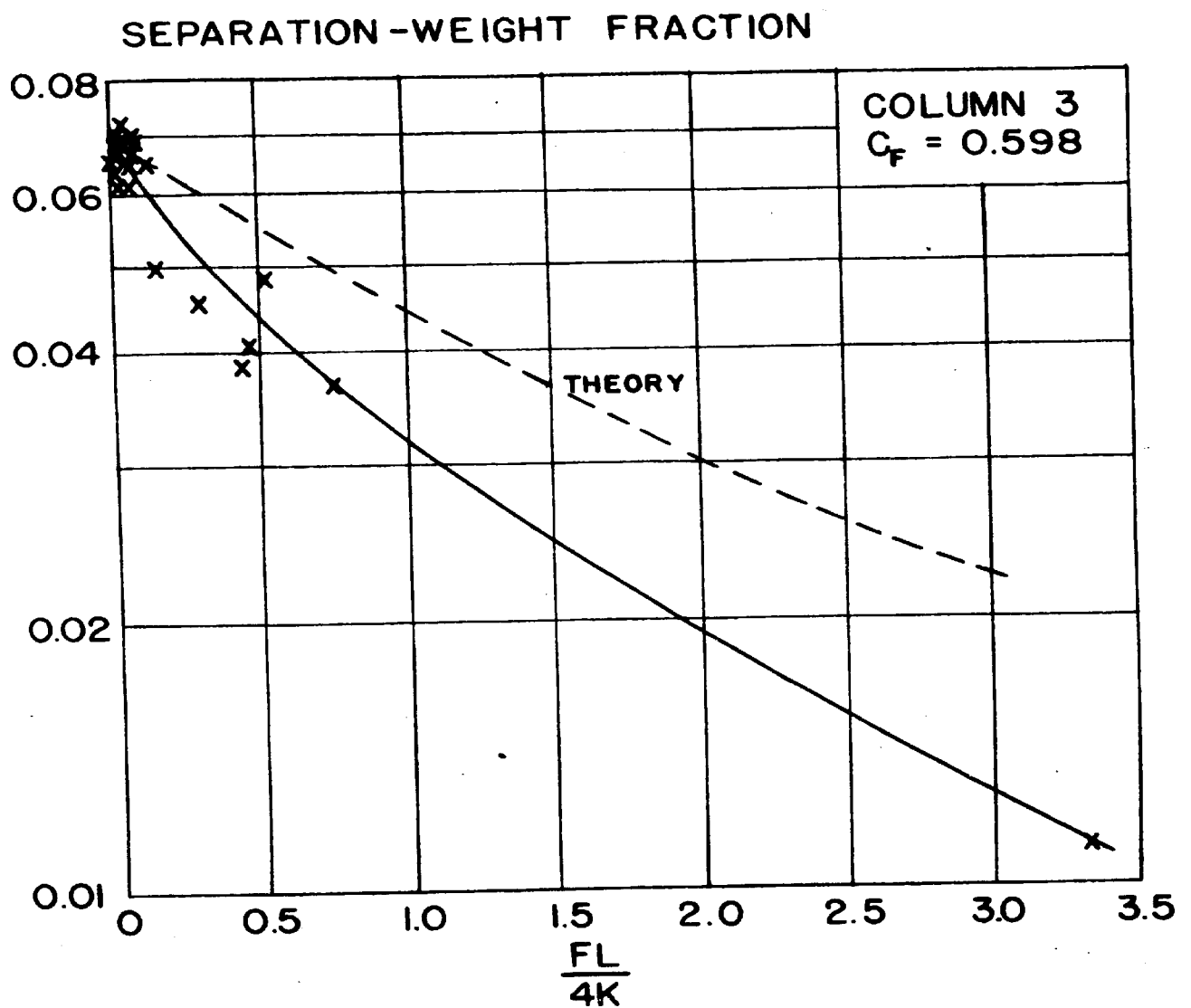
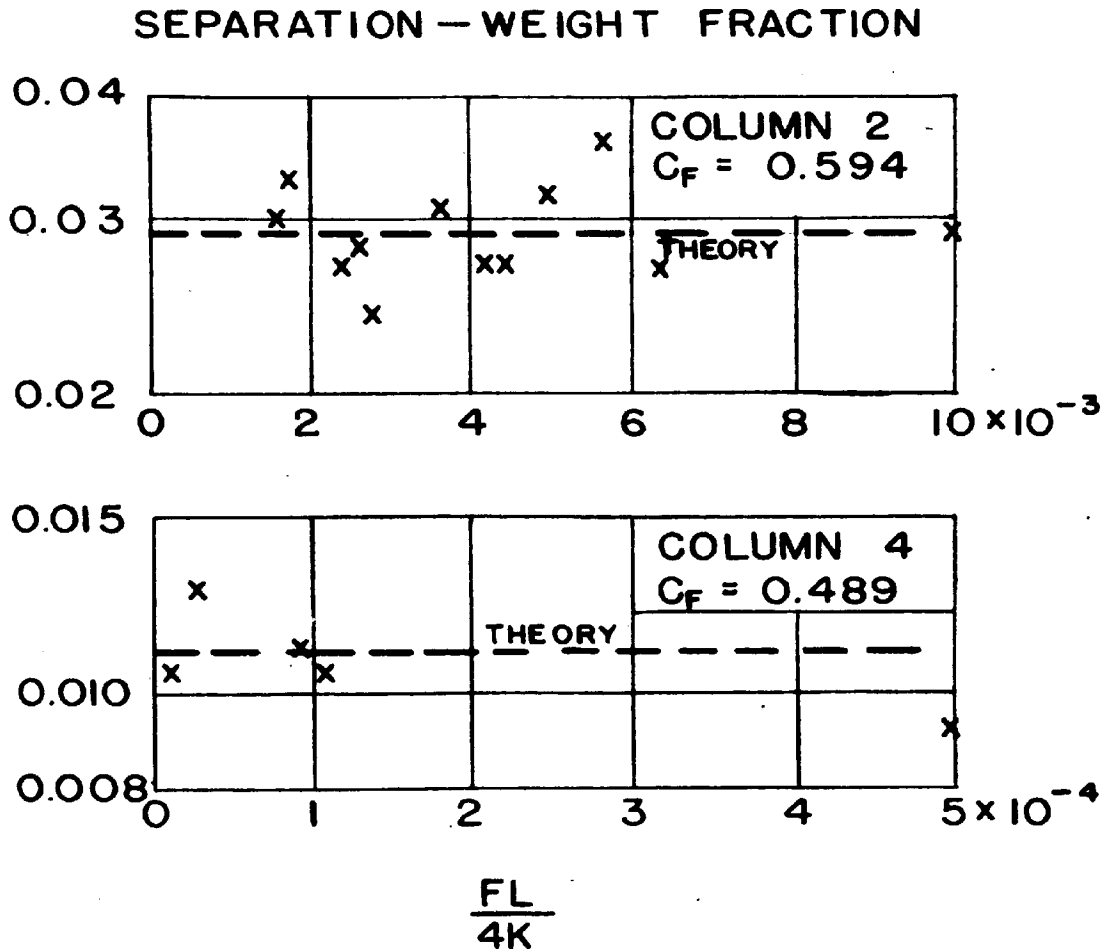


FIGURE VI_e LOG SEPARATION VS $\frac{FL}{4K}$



$$\frac{S}{S_1} = \frac{1 - \exp(-FL/4K)}{FL/4K} \quad (67)$$

can be approximated by a straight line on this type of graph for values of $FL/4K$ less than 1.5.

The data from columns 1 and 3 are seen to be rather well correlated by the group $FL/4K$. However, the theoretical curve (dashed line) lies above the curve drawn through the data in every case but one (Figure VIa). It is believed that this set of data is inaccurate because, as will be seen later, the thermal diffusion coefficient calculated from this set of data also shows deviations from the rest of the thermal diffusion coefficients. It is believed that the deviations in this set of data are caused either by failure to allow the column to reach a steady state or by gross errors in the temperature differences or feed rates used for some of the runs in the set. However, neglecting this one set of data, the separations are less than those predicted by theory.

The data from columns 2 and 4 show that the values of $FL/4K$ are so small that the separation is practically independent of $FL/4K$, indicating that these columns are operating at essentially total reflux. The scattering of these data is believed to have been caused by experimental errors in the measurements, because no definite trend can be noted in the variation of separation with temperature difference for a given value of $FL/4K$.

Effect of D/B

The effect of the top to bottom product ratio D/B may be seen in Figure VII , page 61 , in which separation is plotted against D/B for a single temperature difference and for two different feed rates. These data indicate that the separation is independent of D/B. This fact is corroborated by Jones (20). With the remainder of the data, D/B was kept at values near 1.0, although there was some variation from 0.5 to 1.5. The independence of separation and D/B implies that these variations can be neglected in correlation of the data.

Empirical Correlation

The data for continuous operation were seen to be correlated by the group $FL/4K$, but the theoretical function was not adequate to relate the separation to $FL/4K$. Examination of the shape of the curves in Figures VIa to VI d , pages 54 to 57 , suggests that the data might be correlated by a function of the form:

$$\log S/S' = -A(FL/4K)^p \quad (73)$$

where A is a function of feed composition and p is some number less than 1. To test this assumption, some of the data were plotted as $\log \log S/S'$ against $\log FL/4K$, as in Figure VIII , page 62 . The slope of this graph gives the value of p. The data show that p should be equal to approximately 0.75. Since the scattering of the data is magnified on this type of graph, the value of p cannot be determined more precisely.

FIGURE VII
SEPARATION VS. TOP TO
BOTTOM PRODUCT RATIO

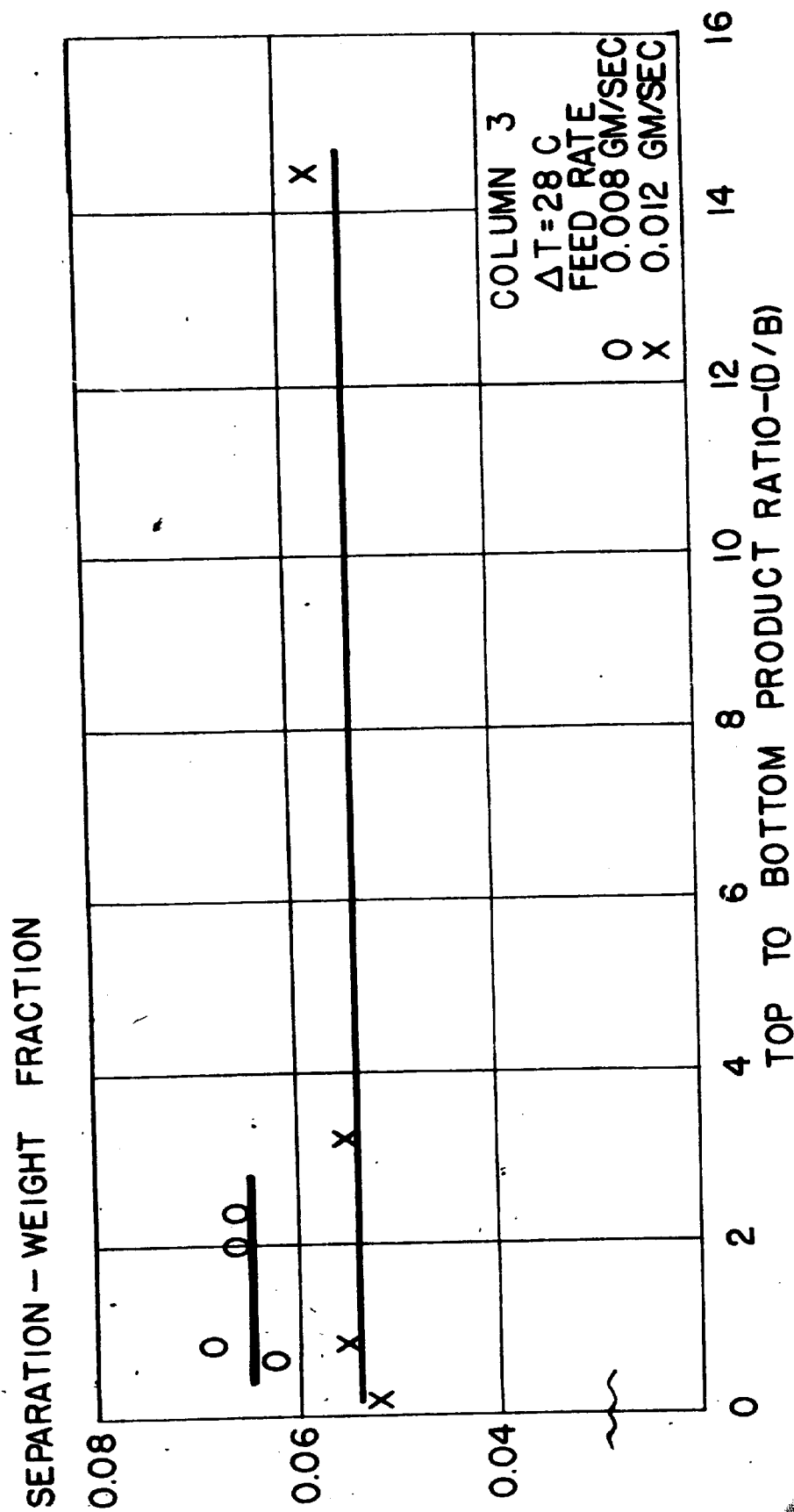
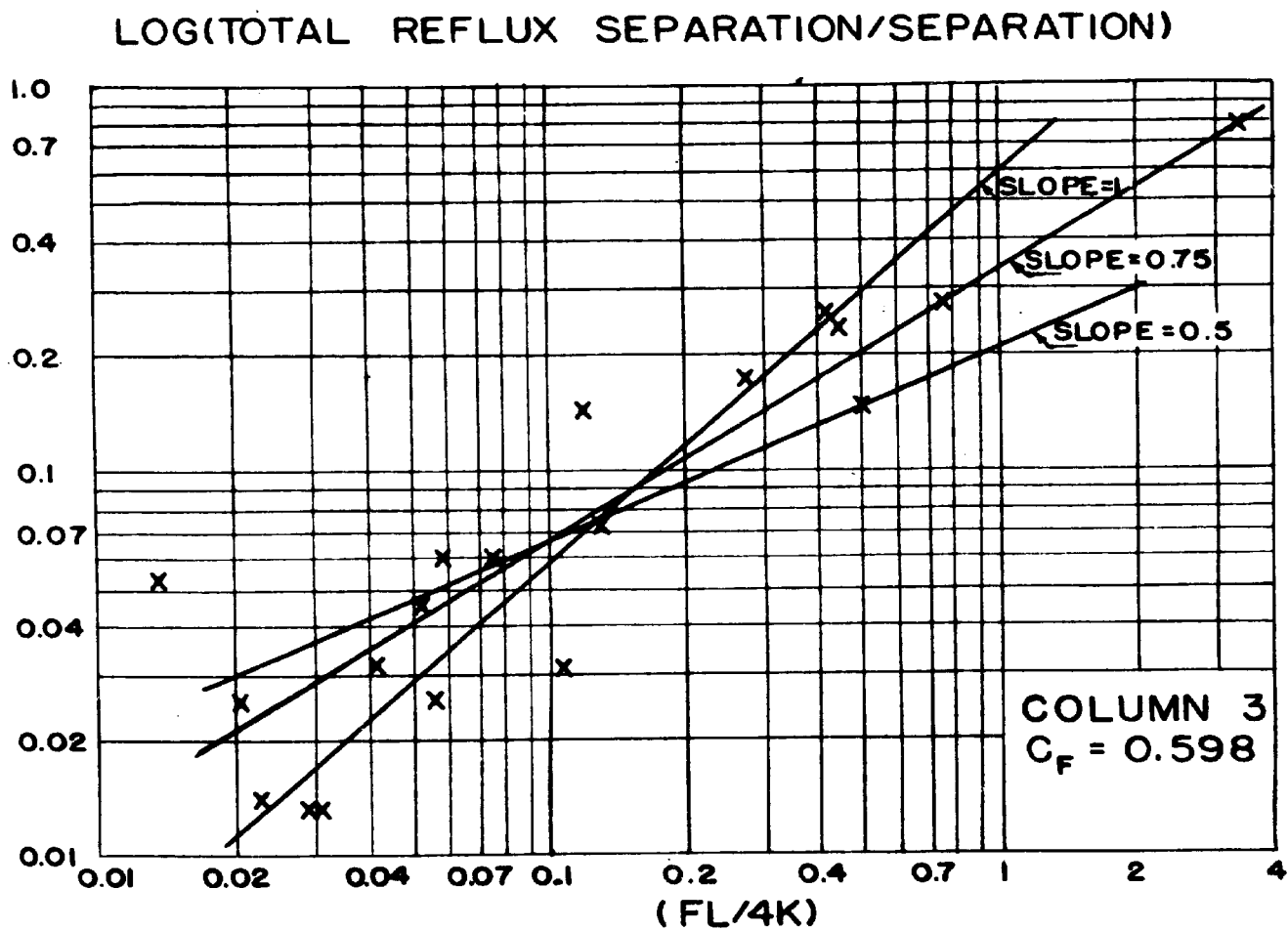


FIGURE VIII DETERMINATION OF EXPONENT OF (FL/4K)



Graphs of the logarithm of the separation against $(FL/4K)^{0.75}$ for columns 1 and 3 are presented in Figures IXa to IXc , pages 64 to 66 . The data give rather good straight lines on these graphs. The values of A were determined as the slopes of these lines. A was found to be a function of composition, as in Figure X , page 67 . The data from columns 1 and 3 were combined by plotting $\log S/S'$ against $A(FL/4K)^{0.75}$. This graph is presented in Figure XI , page 68. This method of correlation reproduces the values of S/S' with an average error of 6.5 percent, not including the one set of data which gave poor agreement with the rest.

Total Reflux

The results for the total reflux case are presented in terms of the effect on separation of the group HL/K and of temperature difference. An empirical function is derived to correlate the data.

Effect of HL/K

The total reflux separations for columns 1 and 3 were obtained from the curves of the logarithm of the separation versus $FL/4K$ by extrapolation to $FL/4K$ equals zero. The total reflux separations for columns 2 and 4 were obtained by averaging all the values of separation obtained experimentally, since these columns were operating at essentially total reflux. The separations were converted to separation factors q by the equation:

FIGURE IX a

LOG SEPARATION VS $\left(\frac{FL}{4K}\right)^{0.75}$

SEPARATION - WEIGHT FRACTION

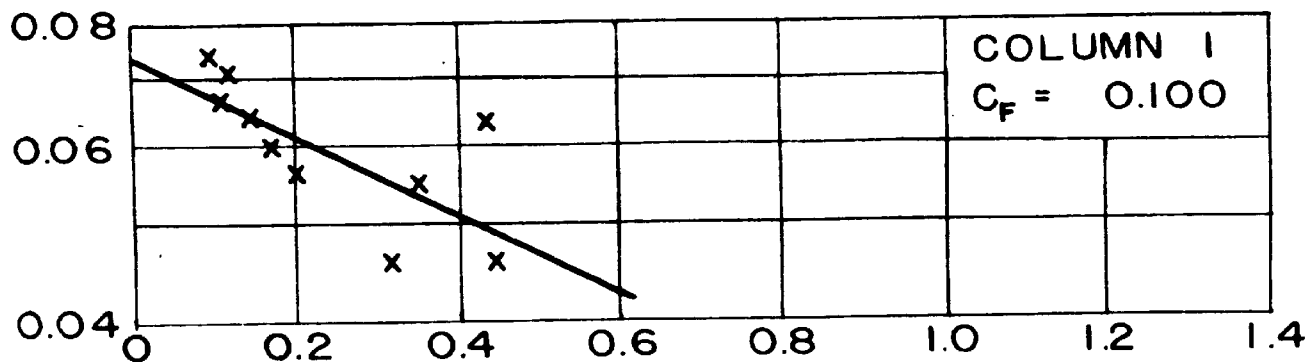
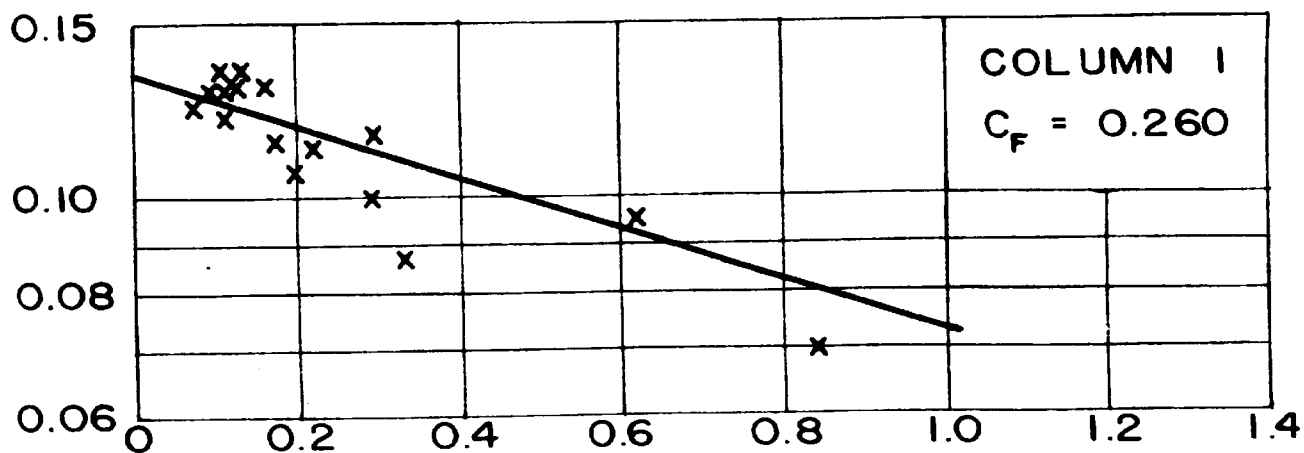
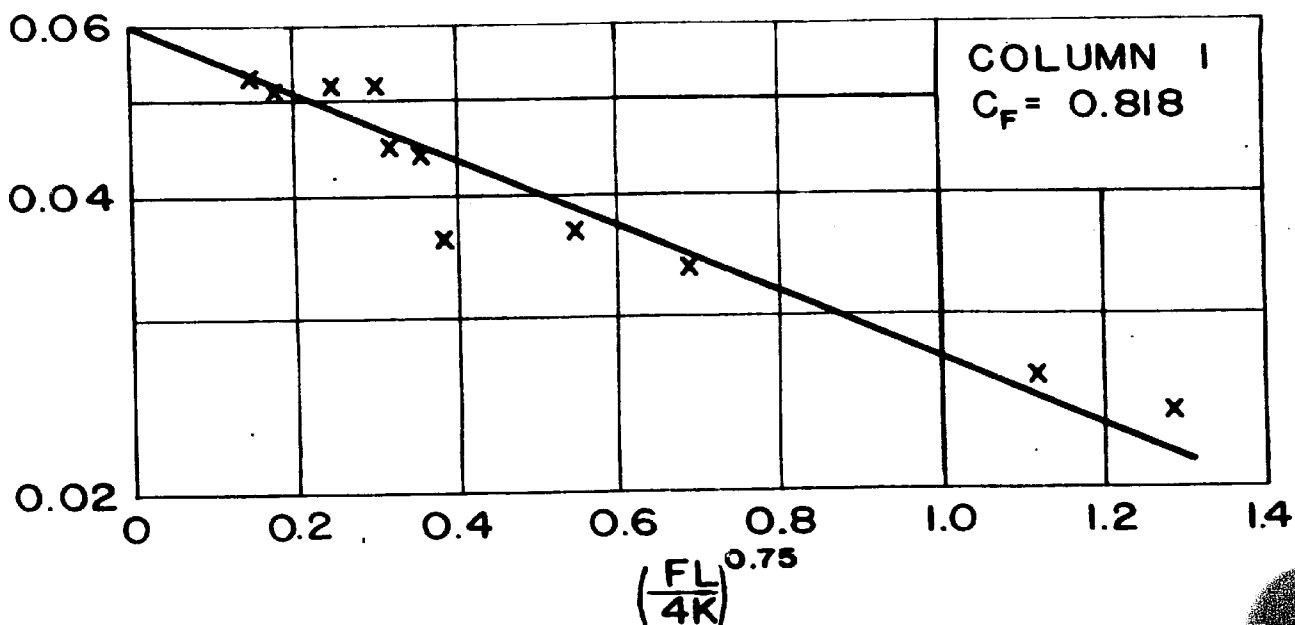


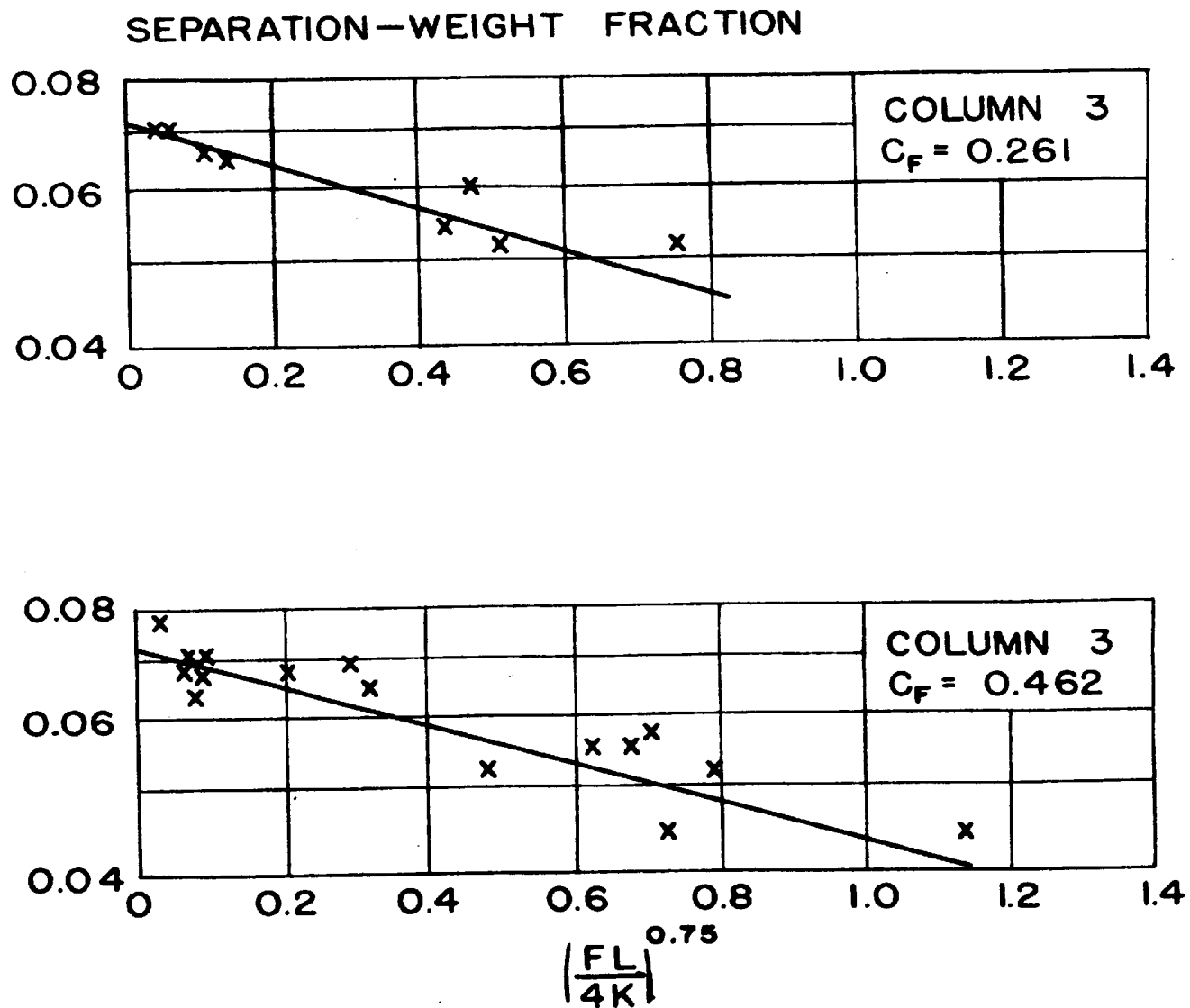
FIGURE IX_bLOG SEPARATION VS $\left(\frac{FL}{4K}\right)^{0.75}$ 



FIGURE X CORRECTION FACTOR—A — FOR CONTINUOUS OPERATION

EMPIRICAL CORRECTION FACTOR — A

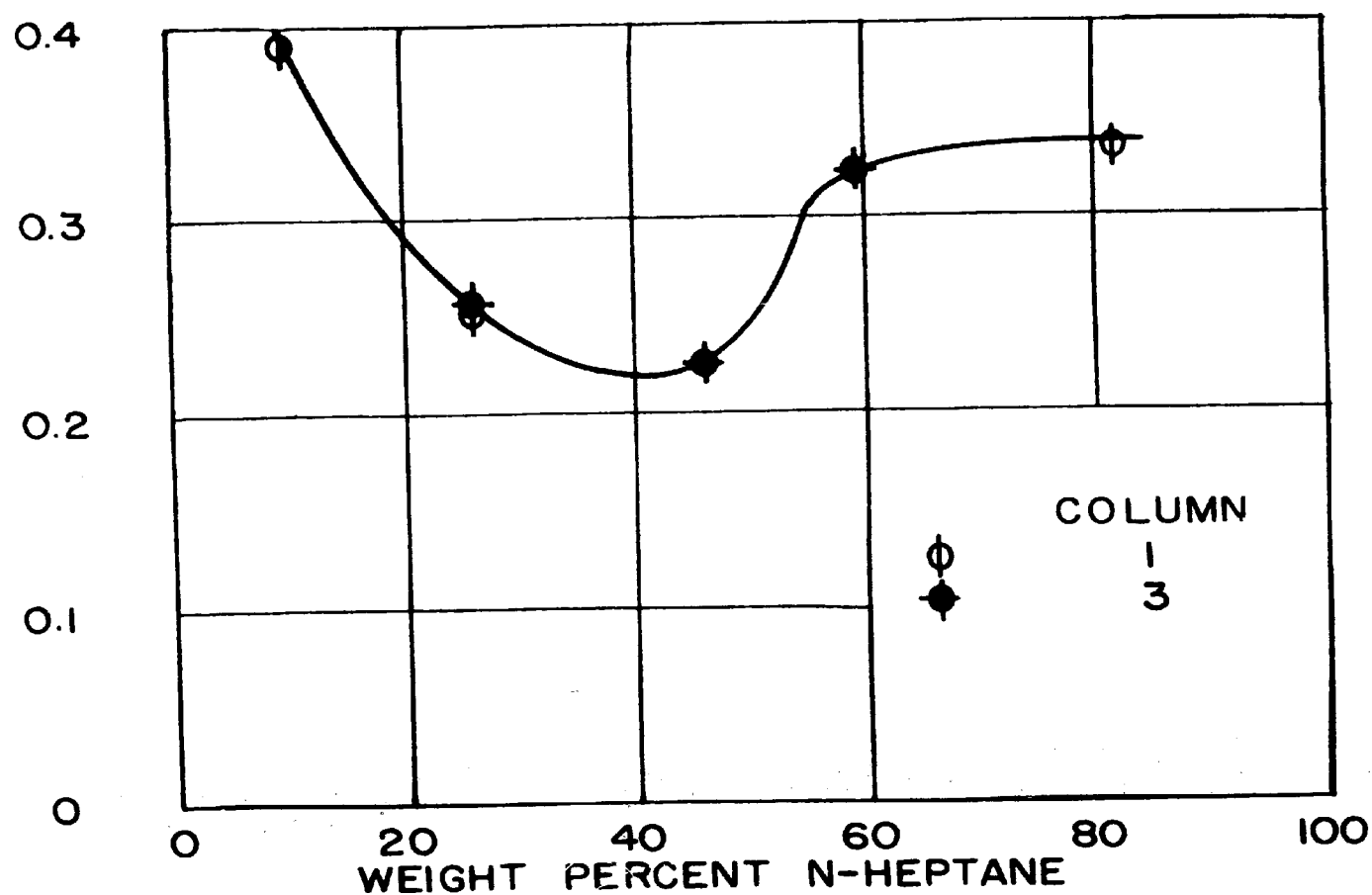
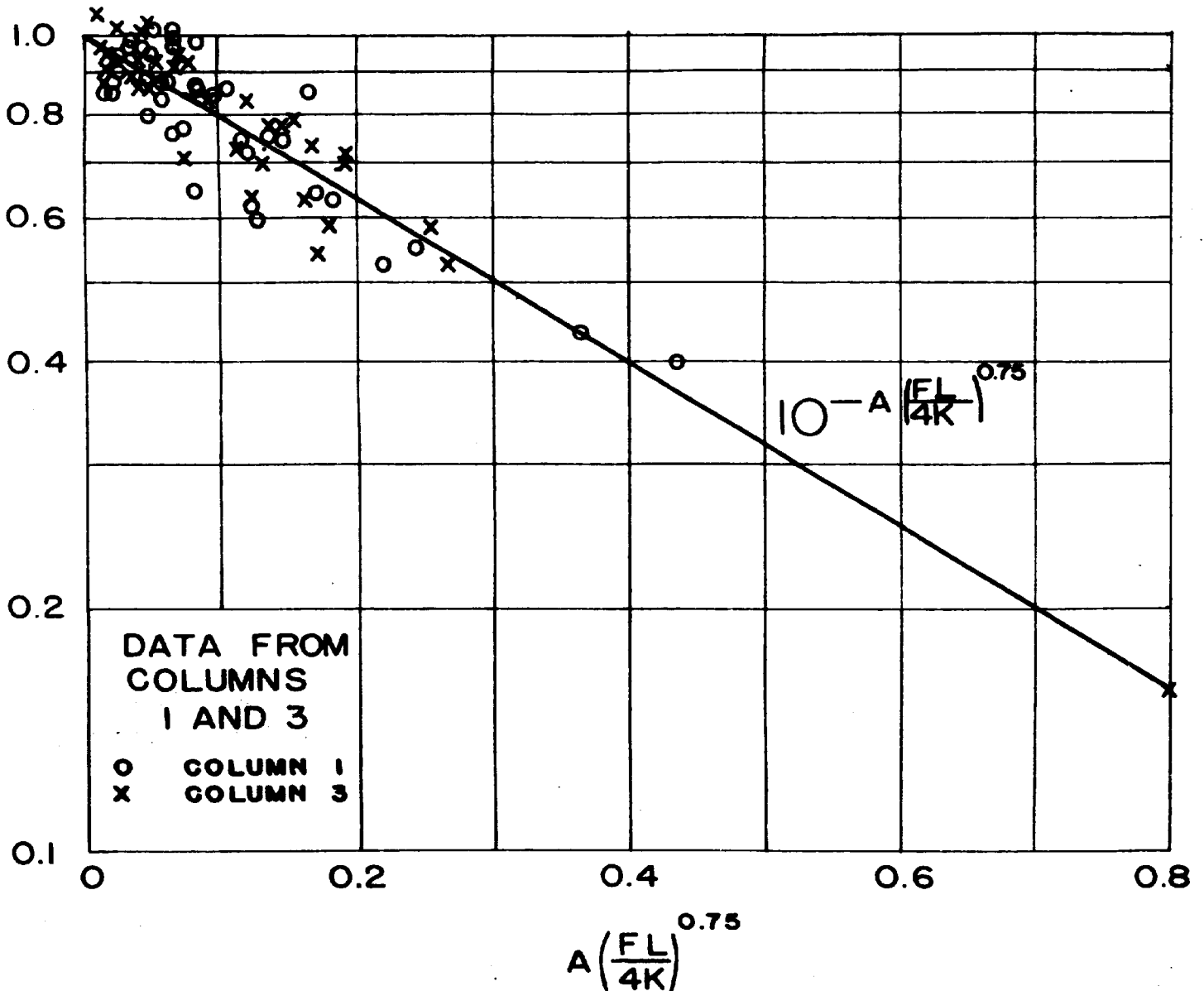


FIGURE XI

CORRELATION OF SEPARATION FOR CONTINUOUS OPERATION

(SEPARATION / TOTAL REFLUX SEPARATION)



$$q = \frac{C_D/1 - C_D}{C_B/1 - C_B} \quad (51)$$

using the material balance relations:

$$C_D = C_F + S/2 \quad ; \quad C_B = C_F - S/2 \quad (74)$$

valid for the case in which top and bottom product rates are equal. It should be noted that the values of q are the same whether weight, mol, or volume fractions are used to express the compositions. Therefore, the results obtained do not depend on the units chosen for composition.

Thermal diffusion coefficients were calculated by the theoretical equation:

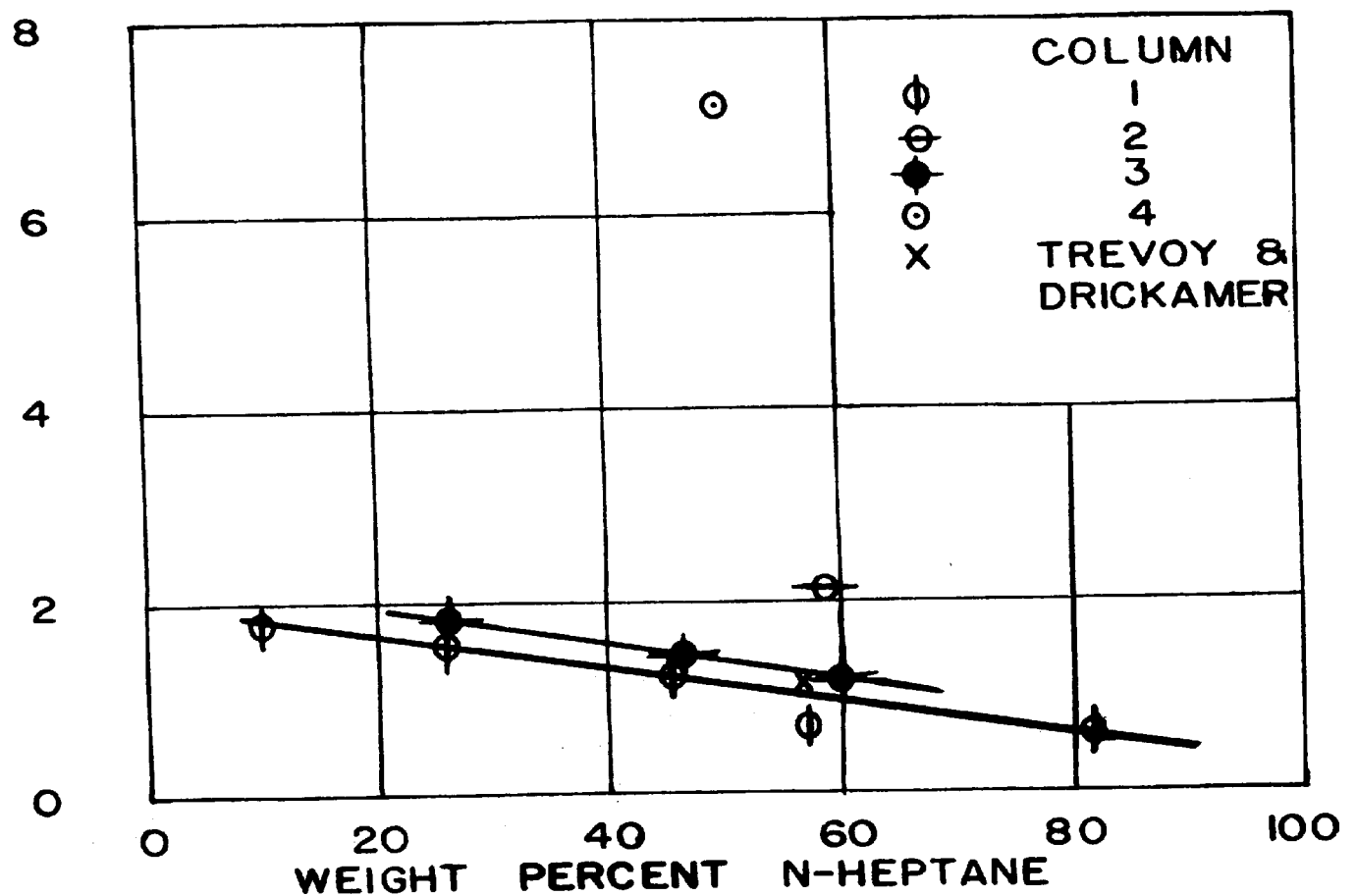
$$\alpha = \frac{\ln q}{HL/\alpha K} \quad (75)$$

The values of α thus determined are presented as a function of composition in Figure XII, page 70. Also plotted on the same graph is the average of the values of α determined by Trevoy and Drickamer (35) in a column operating only at total reflux. Examination of this graph reveals that, although the values of α from columns 1 and 3 and from Trevoy and Drickamer agree quite well with each other, the values of α from the other two columns are quite different. This indicates that the theory does not predict the correct function to describe the total reflux case.

The exact reasons for the deviation of the experimental data from the theory are not known. It is probable, however, that the assumptions made in the derivation of the theoretical equations do not really represent a true picture of an

FIGURE XII
THEORETICAL THERMAL
DIFFUSION COEFFICIENT
 α

THERMAL DIFFUSION COEFFICIENT- α



actual column. However, relaxation of any of the assumptions made in the derivation of the equations results in extremely complicated equations, if a solution can be obtained at all.

Effect of Temperature Difference

The theoretical relation for the total reflux case predicts that the separations for this case are independent of temperature difference. Some data demonstrating this point may be seen in Figures XIIIa and XIIIb, pages 72 and 73, which are graphs of separation versus feed rate with temperature difference as a parameter. Extrapolation of these curves to zero feed rate tends to corroborate the theory. It is acknowledged that the data on this point are not completely conclusive, but the effect of temperature difference on the total reflux separation should be relatively slight.

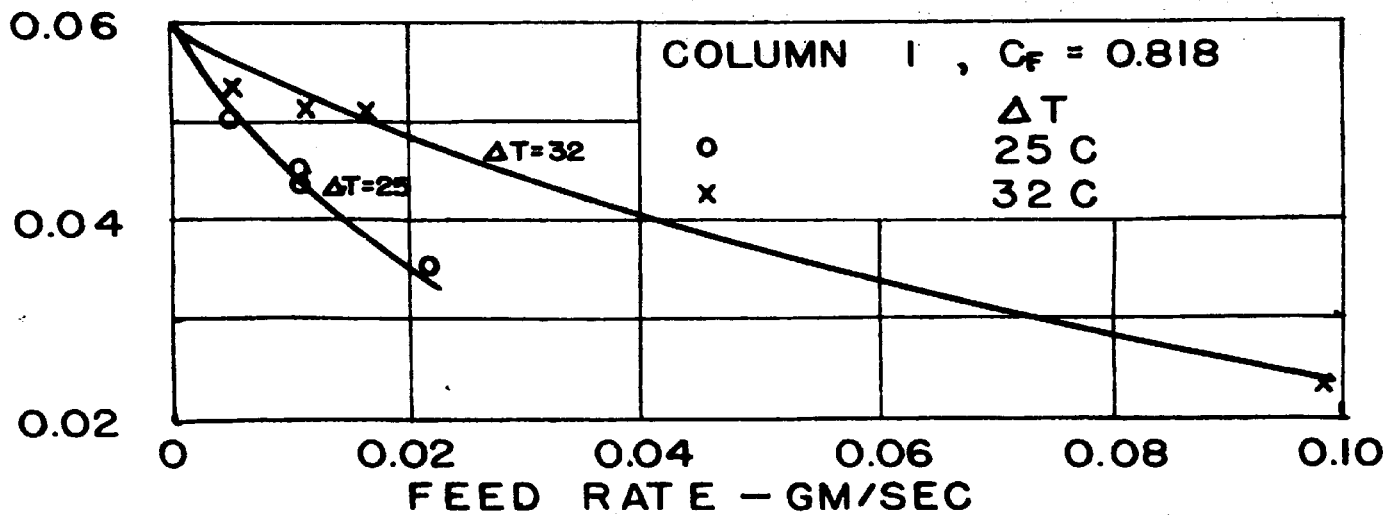
Empirical Correlation

The values of α determined from the total reflux separations show considerable variation. The variation does not seem to be a function of the height or circumference because of the agreement between the thermal diffusion coefficient from Trevoy and Drickamer with those from columns 1 and 3, all these columns having approximately the same spacing but different heights and circumferences. Comparison of the coefficients from Trevoy and Drickamer and from columns 1 and 3 with the coefficients from columns 2 and 4 indicates that the thermal diffusion coefficient seems to increase with larger spacings. This shows that the wrong function has been

FIGURE XIII a

SEPARATION VS FEED RATE AND TEMPERATURE DIFFERENCE

SEPARATION - WEIGHT FRACTION



SEPARATION - WEIGHT FRACTION

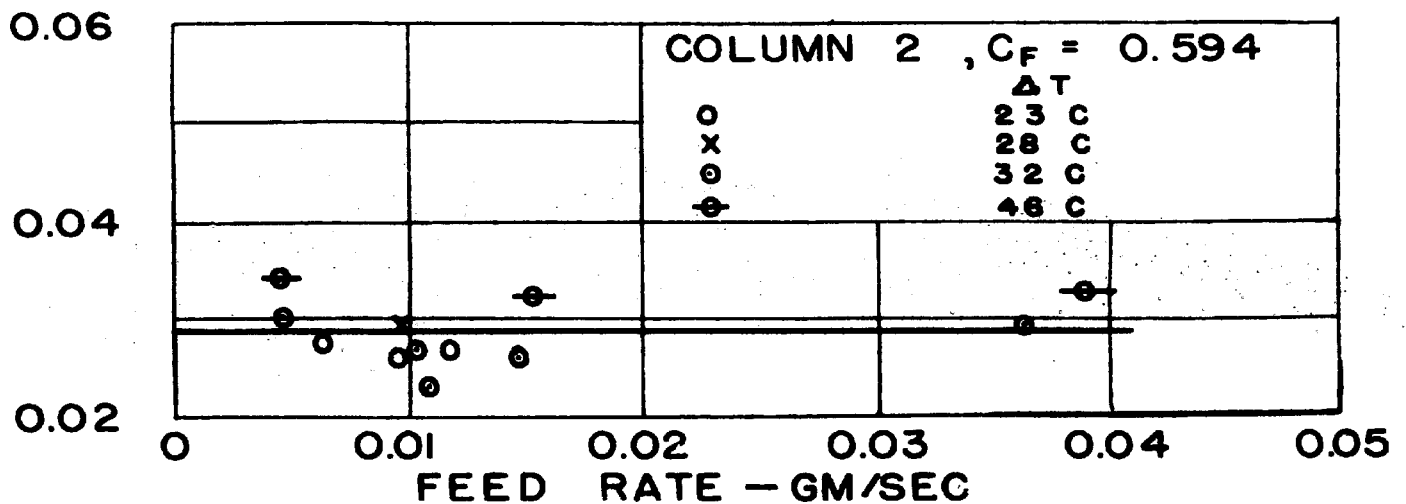
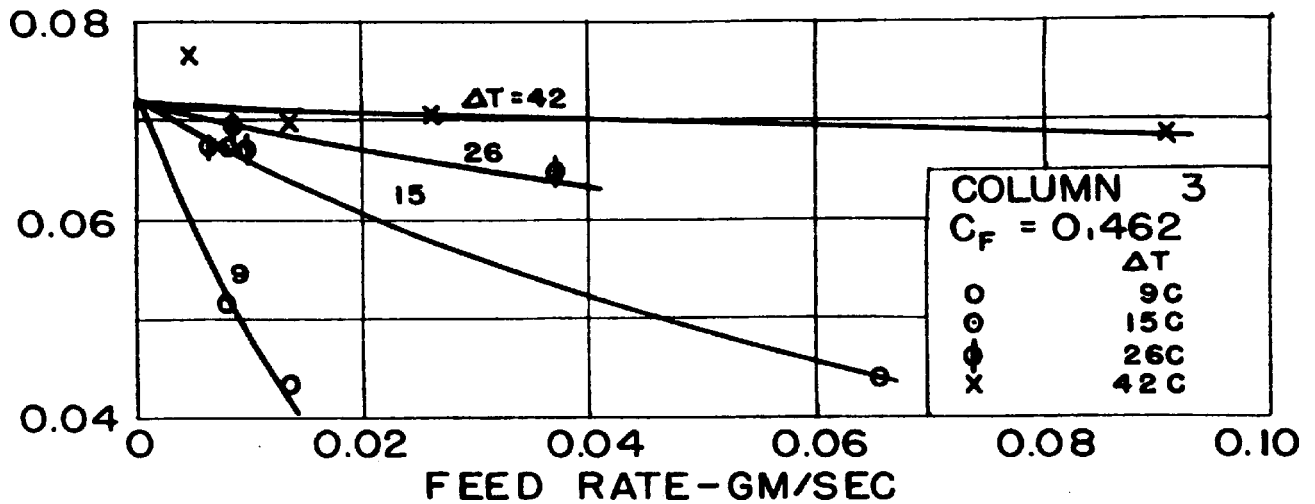


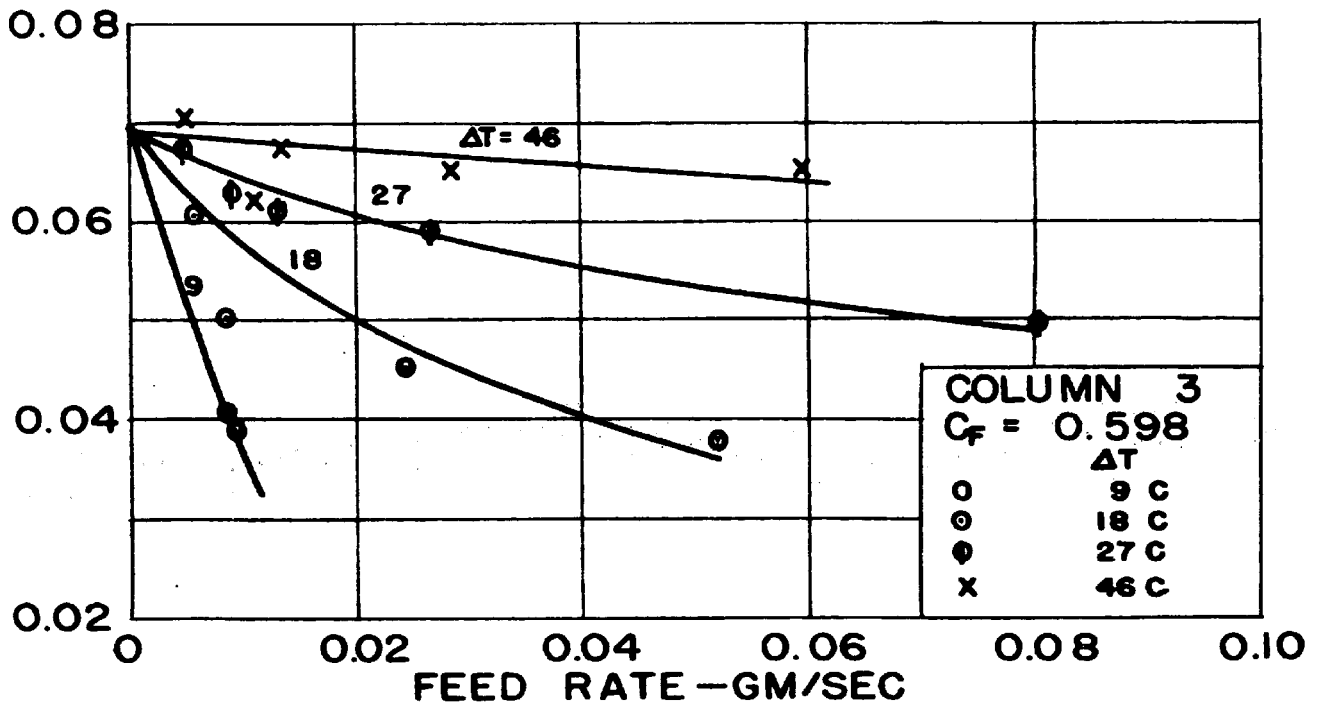
FIGURE XIII b

SEPARATION VS FEED RATE AND TEMPERATURE DIFFERENCE

SEPARATION-WEIGHT FRACTION



SEPARATION-WEIGHT FRACTION



used to calculate the thermal diffusion coefficients, which should be a property of the fluid alone.

Since no one of the thermal diffusion coefficients determined is more reliable than any other, it is not possible to find absolute values for the thermal diffusion coefficients. Relative values can be found as properties of the fluid alone, if the following functions are defined:

$$\alpha' = \alpha / f \quad (76)$$

where α' is a property of the fluid, and f is a function of the spacing. It should be noted that there is an infinity of choices for α' and f . In addition, it should be emphasized that the values of α' thus determined can only be used in conjunction with the function f to correlate the separation in thermal diffusion columns and not in any application requiring absolute values of thermal diffusion coefficients. A set of values for α' and f can be found in Figures XIV and XV, pages 75 and 76. These values of α' and f were determined so that the column having the smallest spacing also had f equal to 1.

The graph of f versus spacing is on logarithmic coordinates to demonstrate an additional point. It may be seen that a line of slope equal to 2 drawn on this graph would approximate the function f , so that f is nearly proportional to the spacing squared. Recalling that the group of physical properties involved in HL/K is nearly independent of temperature, the function $(\ln q)/(L/a^2)$ should correlate the data and be a function of composition only. Figure XVI,

FIGURE XIV

EMPIRICAL RELATIVE THERMAL

DIFFUSION COEFFICIENT

α'

THERMAL DIFFUSION COEFFICIENT — α'

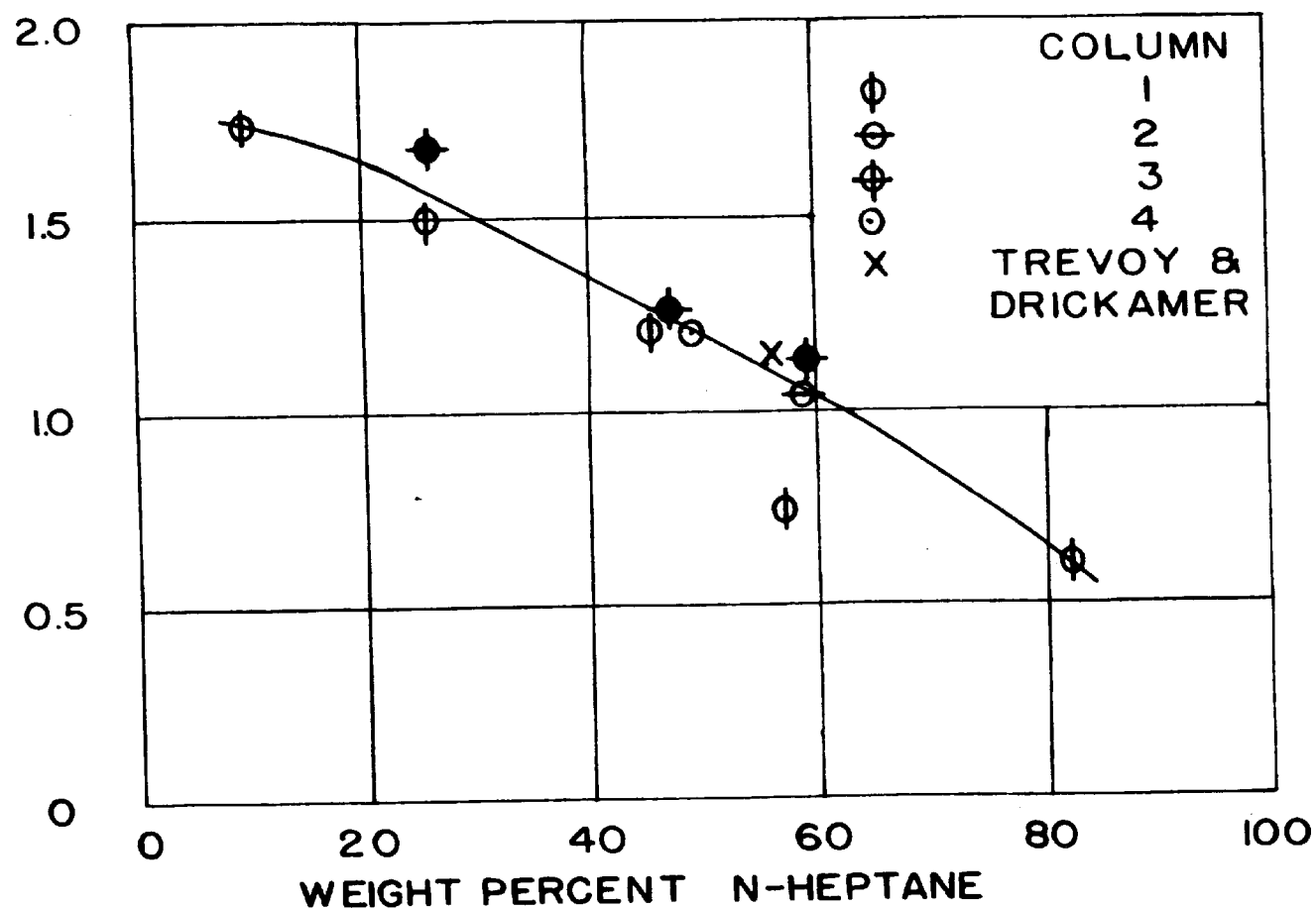
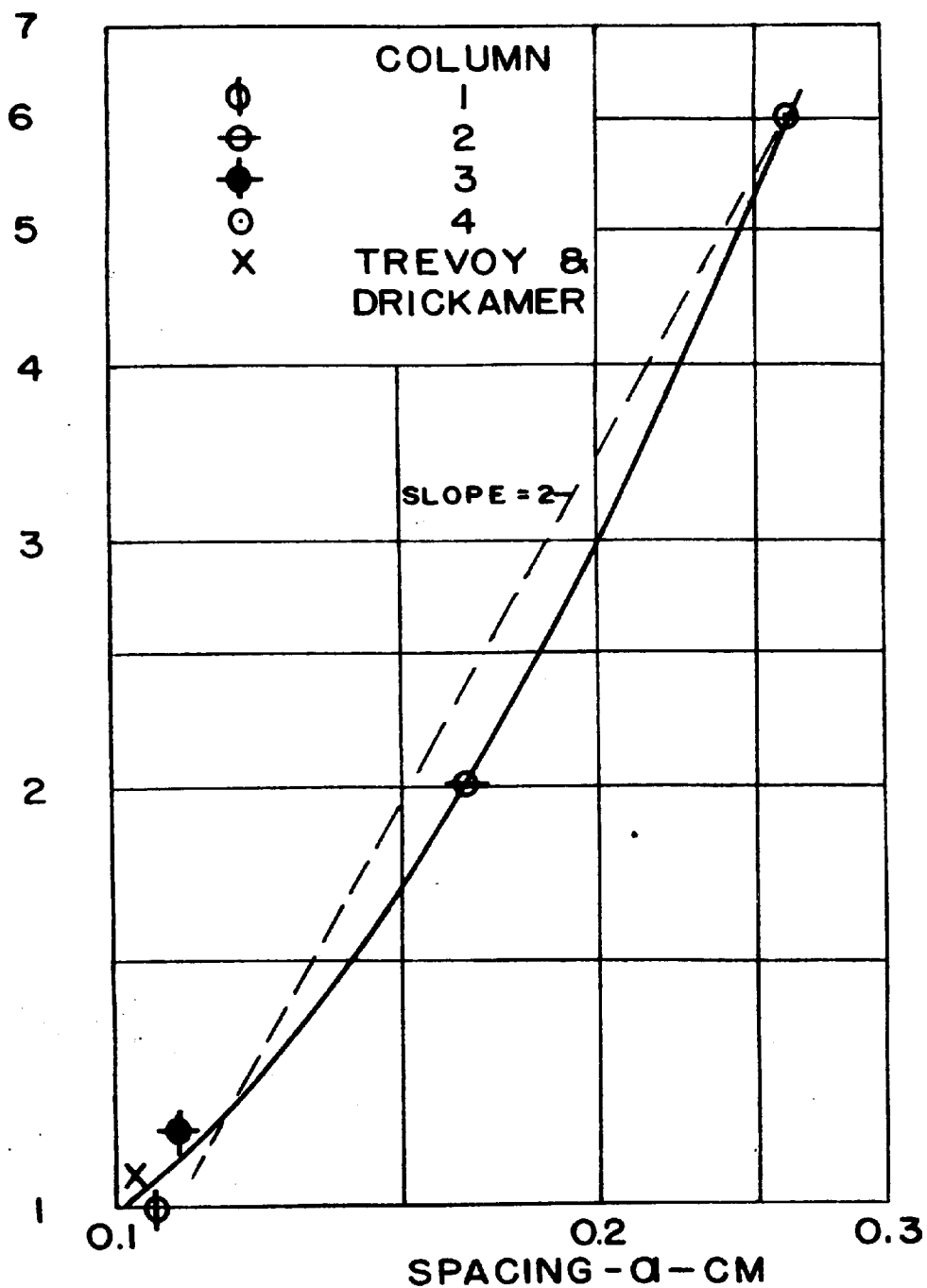


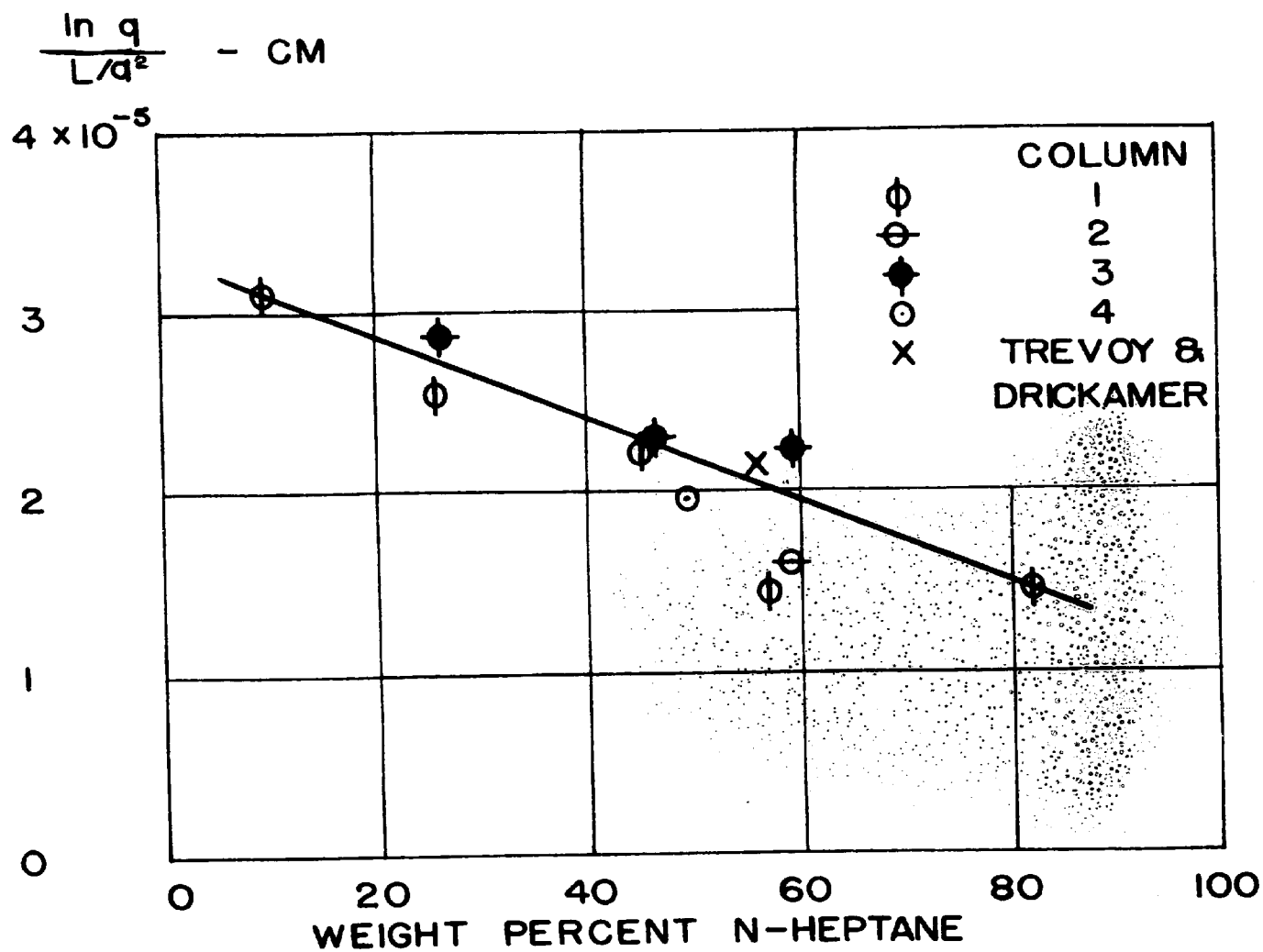
FIGURE XV TOTAL REFLUX CORRECTION FACTOR - f

CORRECTION FACTOR - f 

page 78, is a graph of $(\ln q)/(L/a^2)$ versus composition. This function correlates the data quite well although not as well as f .

It should be noted in Figure XIV that the value of α' determined from column 1 at 57.2 weight percent n-heptane lies quite far below the rest of the data. This is the value taken from the set of data mentioned previously which showed poor agreement in other respects. Excluding this one value of α' , the correlation based on the function f reproduces the data with an average error of 3.5 percent.

FIGURE XVI EMPIRICAL TOTAL REFLUX CORRELATION



CONCLUSIONS AND RECOMMENDATIONS

The separation of n-heptane and benzene in thermal diffusion columns is not well correlated by the equations of Furry, Jones, and Onsager. For the total reflux case, the theory produces thermal diffusion coefficients that are a function of the column dimensions. This demonstrates that the theory does not give the correct function to account for variations in column dimensions. For the case of continuous operation, the theory predicts separations that are too high. In addition, the theoretical function does not have the proper shape to correlate the experimental data.

The total reflux separation factor in the n-heptane - benzene system can be correlated by the relation:

$$\ln q = \frac{504L \alpha'_m D_L f}{ga^3 \beta T_0}$$

where α' is a relative thermal diffusion coefficient which is a function of composition and f is a correction factor which is a function of the spacing. This correlation includes the results of this study and of Trevoy and Drickamer (35). The values of α' and f must be used together. In particular, the values of α' must not be used for any application requiring absolute values of the thermal diffusion coefficient. Graphs of α' and f are presented in Figures XIV and XV, pages 75 and 76. It should be pointed out that the total reflux separation factor is independent of temperature difference, a result predicted by theory. However, the nature of the correction factor f is such that $\ln q$ is approximately

inversely proportional to the square of the spacing rather than the fourth power predicted by theory.

The separation for continuous operation can be correlated by the relation:

$$\log S/S' = -A(FL/4K)^{0.75}$$

where A is a function of composition presented in Figure X , page 67. In this relation, the dimensionless group $FL/4K$ correlates the data quite well, as predicted by theory. However, the theoretical function does not correlate the separation satisfactorily with $FL/4K$.

There is a great deal of additional work that could be done on thermal diffusion. The empirical relations developed in this study should be tested with other systems to see if they are more generally applicable. Moreover, it would be desirable to develop a method for determining absolute values for thermal diffusion coefficients from the behavior of thermal diffusion columns. Further studies on thermal diffusion should be made to extend knowledge of the relationship of the thermal diffusion coefficient to the other physical properties of the system or to molecular configuration. In addition, it would be interesting to determine the effect of thermal diffusion on mass transfer rates for the case of simultaneous heat and mass transfer.

APPENDIX

SAMPLE CALCULATION

The following sample calculation is presented for run 1-60. The experimental data used in this calculation may be found in Table IV, and the results of the calculation may be found in Table V. The experimental data for run 1-60 are as follows:

1. Refractive indices of feed and products; $n_F = 1.4386$, $n_D = 1.4285$, $n_B = 1.4451$
2. Thermocouple EMF's; hot water outlet 2.369 mv, hot wall outlet 2.305 mv, cold water inlet 0.447 mv, cold water outlet 0.477 mv
3. Rotameter readings; hot water 83.0, cold water 74.5, top product (5) 5.20, bottom product (6) 7.05, feed (1) 2.20
4. Room temperature; 26.1C

The refractive indices are converted to compositions using equation 68 and the values of $n_1 - n$ from Figure XVIII.

$$C_F = \frac{1.4972 - 1.4386 - 0.0101}{1.4972 - 1.3852} = 0.433$$

$$C_D = \frac{1.4972 - 1.4285 - 0.0101}{1.4972 - 1.3852} = 0.523$$

$$C_B = \frac{1.4972 - 1.4451 - 0.0099}{1.4972 - 1.3852} = 0.376$$

The separation is calculated as:

$$S = 0.523 - 0.376 = 0.147$$

The top to bottom product ratio is given by:

$$\frac{D}{B} = \frac{0.433 - 0.376}{0.523 - 0.433} = 0.63$$

The thermocouple EMF's were converted to temperatures by using the standard calibration (19) for copper-constantan thermocouples. The temperatures thus found are: hot water

outlet T_H'' 57.8C, hot wall outlet T_{WH}'' 56.3C, cold water inlet T_C' 11.5C, cold water outlet T_C'' 12.3C. The hot water inlet temperature T_H' can be calculated, using the ratio of the flow rates (rotameter readings) of the hot and cold water streams:

$$T_H' = 57.8 + (12.3 - 11.5)(74.5/83.0) = 58.6C$$

The temperature drop through the hot water film is:

$$T_H'' - T_{WH}'' = 57.8 - 56.3 = 1.5C$$

The temperature drop through the cold water film is calculated, using heat transfer coefficients from MacAdams (29).

For the hot water, using MacAdams' nomenclature:

$$h = 150(1 + 0.011t)(V')^{0.8}/(D')^{0.2}$$

and for the cold water:

$$(h/C_p G)(C_p \mu/k)^{2/3} = 0.020(D_2/D_1)^{0.53}(D_e G/\mu)^{-0.2}$$

The thermal conductivity of aluminum is large enough that the temperature drop through the wall of the column can be neglected. The ratio of the temperature drops through the cold and hot water films calculated from the above heat transfer coefficients is 1.83. Thus:

$$T_{WC} - T_C = 1.83(1.5) = 2.7C$$

The average hot water temperature is 58.2C and the average cold water temperature is 11.9C. The average hot wall temperature is 56.9C and the average cold wall temperature is 14.6C. Thus, the average temperature in the column is:

$$T_o = (58.2 + 11.9)/2 = 36.1C$$

and the temperature difference is:

$$\Delta T = 56.9 - 14.6 = 42.3C$$

The rotameter readings were converted to flow rates using the calibration curves of Figure XVII. The densities and viscosities used to calculate these flow rates were evaluated at 26.1°C, room temperature, and were taken from Figures XIX and XXI. The values of $s(s_f - s)/m^2$ are: feed 6.20, top product 6.60, and bottom product 5.95 ($\text{gm/cm}^3\text{cp}$)². The values of viscosity are: feed 0.433 cp, top product 0.417 cp, and bottom product 0.445 cp. The flow rates are calculated as: feed 0.010 gm/sec, top product 0.0040 gm/sec, and bottom product 0.0058 gm/sec. The sum of top and bottom product rates is 0.0098, which compares to 0.010 from the rotameter in the feed. The former value is considered to be the feed rate to the column. The ratio of top to bottom product rates is:

$$D/B = 0.0040/0.0058 = 0.68$$

This compares with the value of D/B equal to 0.63 calculated from the compositions.

The spacing is corrected for thermal expansion of the column by equation 71. Thus:

$$\begin{aligned} a/a_r &= 1 - (23.6 \times 10^{-6})(42.3)(21.2 + 20.1/42.3) \\ &= 0.978 \end{aligned}$$

where $23.6 \times 10^{-6} \text{ } 1/^{\circ}\text{C}$ is the expansion coefficient of aluminum, 21.2 is the ratio R_{RH}/a_r , and 20.1 is the difference between the reference temperature 32.0°C and the cold water temperature 11.9°C.

The transport coefficient K can be calculated as:

$$K = \frac{sg^2 \rho^2 a^7 E (\Delta T)^2}{9! m^2 D_L}$$

$$= \frac{(0.762)(980)^2 (9.7 \times 10^{-4})^2 (0.1052)^7 (0.978)^7 (14.3)(42.3)^2}{(9!)(3.86 \times 10^{-3})^2 (2.72 \times 10^{-5})}$$

$$= 14.6 \text{ gm cm/sec}$$

where the physical properties are evaluated at the feed composition and at the average temperature in the column.

Finally, the dimensionless group $FL/4K$ can be calculated:

$$FL/4K = (0.0098)(306)/(4)(14.6) = 0.050$$

TABLE IV

Experimental Data

(Numbers in parentheses denote rotameter used in the run.)

Run	Rotameter Readings				
	Hot Water	Cold Water	Top Product	Bottom Product	Feed
1-60	83.0	74.5	5.20 (5)	7.05 (6)	2.20 (1)
1-61	74.5	75.0	3.80 (5)	3.90 (6)	1.10 (1)
1-62	77.5	79.0	7.95 (5)	7.40 (6)	2.90 (1)
1-63	78.0	81.5	3.90 (5)	6.40 (6)	2.60 (1)
1-65	78.0	77.0	4.25 (5)	3.50 (6)	1.60 (1)
1-66	76.0	85.0	4.35 (5)	4.45 (6)	1.75 (1)
1-67	77.0	83.0	3.20 (5)	3.20 (6)	1.50 (1)
1-68	69.0	68.5	4.65 (5)	5.00 (6)	7.00 (4)
1-69	69.5	69.0	3.10 (5)	2.90 (6)	6.20 (4)
1-70	73.5	79.0	3.70 (3)	6.40 (2)	7.35 (1)
1-71	74.0	79.0	7.10 (5)	5.35 (6)	11.50 (4)
1-72	74.5	80.5	8.05 (5)	4.00 (6)	10.90 (4)
1-73	74.5	81.0	11.40 (5)	4.45 (6)	3.50 (1)
1-74	73.0	78.0	4.00 (5)	4.20 (6)	8.20 (4)
1-75	73.0	77.5	3.90 (5)	6.90 (6)	10.40 (4)
1-76	73.0	75.0	3.90 (5)	10.00 (6)	12.55 (4)
1-77	73.0	75.0	6.20 (5)	9.80 (6)	12.60 (4)
1-78	74.0	76.5	3.65 (3)	3.80 (2)	5.00 (1)
1-79	75.0	72.0	4.60 (5)	5.30 (6)	10.90 (4)
1-80	75.0	70.0	2.60 (5)	3.30 (6)	6.50 (4)
1-81	73.5	74.5	7.50 (5)	6.70 (6)	12.00 (4)
1-82	76.0	77.0	7.60 (5)	5.85 (6)	12.10 (4)
1-83	76.5	76.0	7.35 (5)	4.70 (6)	10.75 (4)
1-84	78.5	76.5	7.50 (5)	5.60 (6)	11.85 (4)
1-85	71.5	71.0	4.65 (5)	4.65 (6)	8.00 (4)
1-86	72.0	75.0	7.90 (5)	6.80 (6)	12.50 (4)
1-87	72.5	73.0	4.45 (5)	3.40 (6)	8.30 (4)
1-88	72.5	74.0	7.50 (5)	3.25 (6)	9.90 (4)
1-89	73.0	74.5	11.10 (5)	2.70 (6)	13.80 (4)
1-90	66.0	70.0	4.70 (3)	4.60 (2)	6.50 (1)
1-91	71.0	71.0	11.35 (5)	3.60 (6)	3.40 (1)
1-92	71.5	71.5	5.80 (3)	3.60 (6)	5.40 (1)
1-93	71.5	70.5	6.65 (5)	3.35 (6)	9.40 (4)
1-94	72.0	69.5	3.40 (5)	3.20 (6)	7.00 (4)
1-95	69.5	69.0	5.75 (5)	8.60 (6)	11.40 (4)
1-96	69.5	69.0	3.50 (5)	3.70 (6)	---
1-97	80.0	76.0	3.70 (5)	3.95 (6)	8.10 (4)
1-98	71.5	72.0	4.20 (5)	3.80 (6)	8.00 (4)
1-99	74.0	71.0	7.20 (5)	6.20 (6)	11.50 (4)
1-100	75.0	72.0	10.40 (5)	10.40 (6)	3.80 (1)
1-101	75.0	72.0	6.25 (5)	6.25 (6)	9.85 (4)
1-102	71.5	71.0	9.00 (5)	9.00 (6)	3.35 (1)

TABLE IV - cont.
Experimental Data

Run	Thermocouple EMF's - mv				
	Hot Water Outlet	Hot Water Inlet	Hot Wall Outlet	Cold Water Inlet	Cold Water Outlet
1-60	2.369	2.275	2.305	0.447	0.477
1-61	2.297	2.242	2.248	0.476	0.508
1-62	2.099	2.026	2.046	0.444	0.468
1-63	2.010	1.932	1.962	0.448	0.473
1-65	2.003	1.895	1.955	0.549	0.572
1-66	2.328	2.165	2.282	0.607	0.635
1-67	2.494	2.343	2.443	0.615	0.639
1-68	2.258	2.198	2.197	0.628	0.656
1-69	2.131	2.062	2.072	0.624	0.645
1-70	2.150	2.083	2.096	0.652	0.679
1-71	1.815	1.750	1.768	0.660	0.680
1-72	1.849	1.790	1.805	0.634	0.650
1-73	1.877	1.812	1.832	0.658	0.674
1-74	2.262	2.156	2.212	0.675	0.698
1-75	2.368	2.272	2.309	0.682	0.707
1-76	2.453	2.340	2.393	0.708	0.732
1-77	2.374	2.242	2.318	0.708	0.736
1-78	2.431	2.283	2.375	0.710	0.739
1-79	0.880	0.880	0.875	0.733	0.738
1-80	1.067	1.064	1.051	0.733	0.737
1-81	2.154	2.053	2.110	0.720	0.742
1-82	2.428	2.310	2.373	0.713	0.738
1-83	2.677	2.540	2.617	0.735	0.762
1-84	1.570	1.535	1.540	0.732	0.745
1-85	1.518	1.473	1.483	0.751	0.758
1-86	1.559	1.512	1.531	0.769	0.786
1-87	2.273	2.210	2.208	0.768	0.792
1-88	2.200	2.132	2.138	0.818	0.838
1-89	2.218	2.050	2.052	0.772	0.808
1-90	2.398	2.240	2.348	0.702	0.732
1-91	2.363	2.250	2.310	0.699	0.730
1-92	2.410	2.324	2.355	0.740	0.768
1-93	2.358	2.279	2.300	0.741	0.768
1-94	2.288	2.212	2.233	0.742	0.758
1-95	1.456	1.428	1.436	0.742	0.753
1-96	1.456	1.428	1.436	0.742	0.753
1-97	1.027	1.028	1.018	0.717	0.722
1-98	2.004	1.952	1.965	0.724	0.742
1-99	1.962	1.882	1.923	0.883	0.804
1-100	1.857	1.776	1.830	0.746	0.762
1-101	1.768	1.692	1.732	0.787	0.803
1-102	2.290	2.195	2.239	0.752	0.778

TABLE IV - cont.

Experimental Data

Run	Refractive Indices			Room Temp. Deg. C
	Top Product	Bottom Product	Feed	
1-60	1.4285	1.4451	1.4386	26.1
1-61	1.4298	1.4466	1.4380	26.1
1-62	1.4300	1.4452	1.4377	25.0
1-63	1.4285	1.4432	1.4375	25.5
1-65	1.4275	1.4420	1.4342	25.0
1-66	1.4262	1.4420	1.4339	26.1
1-67	1.4246	1.4413	1.4347	27.2
1-68	1.4512	1.4676	1.4608	26.7
1-69	1.4522	1.4684	1.4607	26.1
1-70	1.4518	1.4640	1.4607	28.3
1-71	1.4532	1.4678	1.4600	26.7
1-72	1.4550	1.4687	1.4600	25.6
1-73	1.4563	1.4695	1.4596	27.2
1-74	1.4518	1.4682	1.4596	27.8
1-75	1.4495	1.4651	1.4597	28.9
1-76	1.4479	1.4649	1.4599	29.4
1-77	1.4493	1.4660	1.4597	29.4
1-78	1.4510	1.4660	1.4592	30.0
1-79	1.4580	1.4598	1.4590	26.7
1-80	1.4552	1.4642	1.4589	27.8
1-81	1.4506	1.4653	1.4578	28.9
1-82	1.4494	1.4660	1.4578	30.0
1-83	1.4497	1.4671	1.4573	29.4
1-84	1.4522	1.4633	1.4575	30.6
1-85	1.4778	1.4848	1.4818	30.6
1-86	1.4783	1.4852	1.4818	31.1
1-87	1.4772	1.4874	1.4815	31.7
1-88	1.4783	1.4880	1.4815	33.3
1-89	1.4799	1.4886	1.4812	32.2
1-90	1.4762	1.4858	1.4816	30.6
1-91	1.4792	1.4885	1.4815	31.7
1-92	1.4880	1.4885	1.4815	32.2
1-93	1.4772	1.4879	1.4810	31.7
1-94	1.4756	1.4867	1.4810	32.8
1-95	1.3995	1.4025	1.4014	28.9
1-96	1.3997	1.4030	1.4013	27.2
1-97	1.3999	1.4022	1.4013	26.7
1-98	1.3982	1.4028	1.4005	31.1
1-99	1.3982	1.4022	1.4003	30.0
1-100	1.3984	1.4018	1.4000	28.0
1-101	1.3975	1.4014	1.3996	28.0
1-102	1.3973	1.4020	1.3997	26.7

TABLE IV - cont.

Experimental Data

Run	Rotameter Readings					Feed
	Hot Water	Cold Water	Top Product	Bottom Product		
1-103	71.5	71.0	6.20 (3)	6.50 (2)		10.00 (1)
1-104	72.5	71.0	3.70 (5)	3.80 (6)		8.00 (4)
1-105	71.0	70.0	6.50 (5)	7.80 (6)		12.60 (4)
1-106	70.0	73.0	5.75 (5)	4.95 (6)		9.95 (4)
1-107	70.5	73.0	2.65 (3)	2.40 (2)		3.65 (1)
1-108	71.5	73.0	5.25 (3)	4.75 (2)		7.60 (1)
1-109	71.5	72.0	5.45 (5)	6.75 (6)		10.40 (4)
1-110	71.5	73.0	4.35 (3)	4.10 (2)		5.70 (1)
1-111	71.5	71.0	6.80 (5)	6.40 (6)		2.80 (1)
1-112	72.0	71.0	8.00 (3)	8.00 (2)		13.10 (1)
1-113	72.0	71.0	8.00 (3)	8.00 (2)		13.10 (1)
2-1	74.0	73.0	5.75 (5)	5.90 (6)		8.75 (4)
2-2	72.5	76.0	3.25 (5)	3.15 (6)		7.15 (4)
2-3	72.5	77.0	6.40 (5)	5.60 (6)		9.30 (4)
2-4	72.5	77.0	5.95 (5)	4.80 (6)		8.80 (4)
2-5	77.5	72.5	6.00 (5)	5.70 (6)		8.50 (4)
2-6	73.5	72.5	5.95 (5)	5.85 (6)		9.00 (4)
2-7	74.0	73.5	---	8.45 (6)		2.75 (1)
2-8	72.5	73.0	4.00 (3)	3.20 (2)		5.30 (1)
2-9	70.5	73.0	2.50 (5)	2.70 (6)		6.30 (4)
2-10	73.5	73.5	3.10 (5)	3.70 (6)		7.70 (4)
2-11	74.0	73.0	8.30 (5)	8.15 (6)		2.85 (1)
2-12	74.0	74.0	4.10 (3)	2.75 (2)		4.70 (1)
3-1	71.5	72.5	5.80 (5)	6.30 (6)		9.30 (4)
3-1a	71.5	72.5	5.85 (5)	6.35 (6)		9.20 (4)
3-2	71.5	72.5	2.90 (5)	3.00 (6)		7.30 (4)
3-2a	71.0	68.0	3.05 (5)	3.45 (6)		7.40 (4)
3-3	71.5	70.0	2.90 (5)	2.90 (6)		6.80 (4)
3-4	71.5	67.0	5.30 (3)	5.70 (2)		8.30 (1)
3-5	71.5	70.0	5.85 (5)	5.85 (6)		8.20 (4)
3-6	71.5	70.0	2.95 (3)	2.95 (2)		3.60 (1)
3-7	71.5	72.0	7.60 (5)	7.60 (6)		2.70 (1)
3-8	70.0	70.0	4.40 (3)	4.60 (2)		6.10 (1)
3-9	69.5	73.5	6.50 (5)	6.50 (6)		10.00 (4)
3-10	69.5	71.5	3.00 (3)	3.00 (2)		---
3-11	69.5	73.0	7.75 (5)	7.75 (6)		11.50 (4)
3-12	72.5	72.5	3.00 (5)	3.00 (6)		6.90 (4)
3-12a	74.5	72.5	3.40 (5)	3.50 (6)		7.20 (4)
3-13	75.0	75.0	6.05 (5)	5.80 (6)		1.90 (1)
3-14	74.5	76.0	5.20 (3)	5.70 (2)		8.35 (1)
3-15	74.5	76.0	6.20 (5)	6.20 (6)		1.60 (1)
3-16	74.5	73.5	4.10 (3)	4.50 (2)		6.10 (1)

TABLE IV - cont.
Experimental Data

Run	Thermocouple EMF's - mv				
	Hot Water Outlet	Hot Water Inlet	Hot Wall Outlet	Cold Water Inlet	Cold Water Outlet
1-103	2.147	2.058	2.092	0.724	0.745
1-104	2.175	2.098	2.124	0.695	0.719
1-105	2.205	2.125	2.143	0.698	0.720
1-106	1.758	1.698	1.715	0.688	0.703
1-107	1.745	1.683	1.704	0.682	0.702
1-108	1.840	1.780	1.797	0.685	0.702
1-109	1.710	1.648	1.668	0.712	0.728
1-110	1.798	1.758	1.757	0.712	0.728
1-111	1.708	1.658	1.668	0.711	0.728
1-112	1.776	1.730	1.733	0.740	0.755
1-113	1.815	1.765	1.772	0.711	0.728
			Inlet		
2-1	1.928	1.963	1.959	0.765	0.796
2-2	1.857	1.888	1.878	0.773	0.816
2-3	1.718	1.750	1.738	0.810	0.835
2-4	1.868	1.908	1.898	0.825	0.858
2-5	2.173	2.238	2.212	0.818	0.850
2-6	1.765	1.840	1.792	0.745	0.754
2-7	2.715	2.785	2.740	0.718	0.725
2-8	2.708	2.765	2.715	0.689	0.709
2-9	2.736	2.808	2.762	0.721	0.729
2-10	2.015	2.082	2.058	0.708	0.722
2-11	2.033	2.093	2.070	0.692	0.717
2-12	2.042	2.097	2.068	0.668	0.682
3-1	2.127	2.141	---	0.682	0.695
3-1a	2.060	2.074	---	0.635	0.648
3-2	2.029	2.040	---	0.657	0.668
3-2a	2.008	2.020	---	0.650	0.662
3-3	1.809	1.818	---	0.671	0.677
3-4	1.830	1.840	---	0.637	0.645
3-5	1.908	1.918	---	0.654	0.664
3-6	1.952	1.962	---	0.663	0.669
3-7	1.898	1.906	---	0.652	0.661
3-8	2.834	2.854	---	0.612	0.628
3-9	2.842	2.862	---	0.652	0.667
3-10	2.817	2.835	---	0.657	0.672
3-11	2.734	2.755	---	0.642	0.654
3-12	2.802	2.822	---	0.644	0.664
3-12a	2.578	2.597	---	0.660	0.674
3-13	1.039	1.042	---	0.642	0.648
3-14	1.086	1.090	---	0.635	0.639
3-15	1.116	1.118	---	0.662	0.665
3-16	1.398	1.403	---	0.622	0.630

TABLE IV - cont.
Experimental Data

Run	Refractive Indices			Room Temp. Deg. C
	Top Product	Bottom Product	Feed	
1-103	1.3984	1.4006	1.3995	27.8
1-104	1.3970	1.4018	1.3996	28.9
1-105	1.3967	1.4012	1.3993	25.6
1-106	1.4190	1.4282	1.4237	23.9
1-107	1.4191	1.4280	1.4236	25.6
1-108	1.4202	1.4269	1.4232	29.2
1-109	1.4186	1.4275	1.4234	25.8
1-110	1.4193	1.4269	1.4233	31.1
1-111	1.4188	1.4277	1.4233	26.1
1-112	1.4209	1.4250	1.4231	30.3
1-113	1.4208	1.4252	1.4232	30.9
2-1	1.4200	1.4230	1.4219	34.2
2-2	1.4187	1.4212	1.4199	35.0
2-3	1.4188	1.4212	1.4199	33.1
2-4	1.4188	1.4212	1.4199	30.9
2-5	1.4182	1.4209	1.4197	31.7
2-6	1.4214	1.4245	1.4228	24.7
2-7	1.4210	1.4242	1.4227	28.6
2-8	1.4209	1.4240	1.4222	28.6
2-9	1.4206	1.4240	1.4217	24.4
2-10	1.4199	1.4228	1.4217	26.4
2-11	1.4202	1.4229	1.4213	26.1
2-12	1.4200	1.4228	1.4211	27.5
3-1	1.4213	1.4279	1.4251	25.3
3-1a	1.4205	1.4275	1.4242	26.8
3-2	1.4202	1.4270	1.4240	25.2
3-2a	1.4200	1.4273	1.4240	27.8
3-3	1.4201	1.4268	1.4242	25.2
3-4	1.4206	1.4254	1.4233	28.6
3-5	1.4198	1.4260	1.4230	26.7
3-6	1.4195	1.4253	1.4230	28.8
3-7	1.4198	1.4258	1.4222	25.0
3-8	1.4178	1.4241	1.4212	30.1
3-9	1.4180	1.4240	1.4215	28.3
3-10	1.4174	1.4238	1.4205	32.8
3-11	1.4172	1.4238	1.4205	29.4
3-12	1.4161	1.4230	1.4196	25.6
3-12a	1.4158	1.4218	1.4187	29.4
3-13	1.4160	1.4200	1.4181	20.7
3-14	1.4172	1.4182	1.4177	23.0
3-15	1.4160	1.4198	1.4179	21.7
3-16	1.4157	1.4192	1.4177	24.7

TABLE IV - cont.
Experimental Data

Run	Rotameter Readings				
	Hot Water	Cold Water	Top Product	Bottom Product	Feed
3-17	75.0	75.5	5.50 (5)	5.50 (6)	8.50 (4)
3-18	75.0	72.5	2.60 (3)	3.00 (2)	4.10 (1)
3-19	76.0	73.5	3.50 (5)	3.50 (6)	7.30 (4)
3-20	72.5	71.5	---	5.80 (6)	8.20 (4)
3-21	72.5	72.5	4.80 (5)	5.10 (6)	7.20 (4)
3-22	72.5	69.0	5.45 (3)	5.60 (2)	8.40 (1)
3-23	72.0	72.0	7.00 (5)	8.70 (6)	11.50 (4)
3-24	71.5	71.0	7.50 (3)	7.25 (2)	12.20 (1)
3-25	71.0	74.5	---	6.55 (6)	9.20 (4)
3-26	71.0	72.0	8.10 (3)	8.50 (2)	13.10 (1)
3-27	71.5	74.0	---	4.40 (6)	7.50 (4)
3-28	71.5	72.5	4.10 (3)	5.30 (2)	7.00 (1)
3-29	72.0	72.0	---	5.90 (6)	9.00 (4)
3-30	72.0	72.5	---	5.70 (6)	9.10 (4)
3-31	72.5	73.0	---	8.70 (6)	12.10 (4)
3-32	70.0	71.5	5.90 (3)	5.90 (2)	8.85 (1)
3-33	70.5	73.0	7.40 (5)	8.20 (6)	11.50 (4)
3-34	70.0	72.0	3.10 (3)	2.90 (2)	---
3-35	69.5	72.5	3.00 (5)	3.00 (6)	6.85 (4)
3-36	70.5	67.5	8.60 (3)	4.10 (2)	12.10 (1)
3-37	71.0	67.0	8.00 (5)	3.40 (6)	10.90 (4)
3-38	71.0	67.0	5.20 (3)	5.30 (2)	11.50 (1)
3-39	70.0	67.0	5.10 (5)	5.80 (6)	9.20 (4)
3-40	70.0	64.0	12.40 (3)	2.10 (2)	12.10 (1)
3-41	70.0	65.5	---	2.75 (6)	8.00 (4)
3-42	67.0	66.0	3.90 (3)	10.50 (2)	12.00 (1)
3-43	64.5	65.5	---	5.55 (6)	8.05 (4)
3-44	72.0	66.0	3.55 (3)	3.75 (2)	4.90 (1)
4-1	82.0	79.9	7.00 (5)	7.45 (6)	12.00 (4)
4-2	81.5	79.0	4.55 (3)	5.70 (2)	7.70 (1)
4-3	80.5	75.0	---	6.55 (6)	2.50 (1)
4-4	73.0	80.0	5.00 (3)	4.50 (2)	6.80 (1)
4-5	71.0	79.5	2.10 (5)	3.10 (6)	4.30 (4)

TABLE IV - cont.
Experimental Data

Run	Thermocouple EMF's - mv			
	Hot Water Outlet	Hot Water Inlet	Cold Water Inlet	Cold Water Outlet
3-17	1.466	1.473	0.669	0.674
3-18	1.523	1.533	0.638	0.642
3-19	1.599	1.607	0.648	0.657
3-20	1.088	1.092	0.639	0.645
3-21	1.552	1.562	0.618	0.629
3-22	1.797	1.810	0.622	0.634
3-23	1.707	1.718	0.628	0.638
3-24	1.810	1.822	0.637	0.646
3-25	2.290	2.308	0.651	0.664
3-26	2.397	2.411	0.630	0.643
3-27	2.447	2.463	0.640	0.653
3-28	1.304	1.313	0.654	0.661
3-29	1.056	1.063	0.643	0.647
3-30	1.392	1.402	0.635	0.640
3-31	1.047	1.048	0.644	0.648
3-32	2.560	2.578	0.622	0.639
3-33	2.468	2.489	0.619	0.633
3-34	2.605	2.625	0.619	0.630
3-35	2.551	2.567	0.626	0.647
3-36	2.052	2.069	0.654	0.667
3-37	1.918	1.928	0.602	0.615
3-38	1.888	1.900	0.619	0.630
3-39	1.898	1.909	0.629	0.642
3-40	1.823	1.833	0.601	0.611
3-41	1.918	1.922	0.631	0.638
3-42	1.775	1.781	0.573	0.584
3-43	1.801	1.808	0.591	0.597
3-44	1.769	1.778	0.574	0.587
4-1	1.819	1.828	0.495	0.508
4-2	1.901	1.911	0.502	0.511
4-3	2.864	2.879	0.498	0.517
4-4	2.974	2.995	0.460	0.477
4-5	2.764	2.784	0.478	0.498

TABLE IV - cont.
Experimental Data

Run	Refractive Indices			Room Temp. Deg. C
	Top Product	Bottom Product	Feed	
3-17	1.4151	1.4200	1.4175	22.8
3-18	1.4148	1.4192	1.4175	25.6
3-19	1.4142	1.4200	1.4169	27.0
3-20	1.4552	1.4622	1.4597	25.3
3-21	1.4545	1.4630	1.4593	25.0
3-22	1.4555	1.4622	1.4592	30.0
3-23	1.4545	1.4629	1.4592	26.4
3-24	1.4553	1.4620	1.4591	29.4
3-25	1.4535	1.4626	1.4590	23.9
3-26	1.4542	1.4619	1.4589	28.3
3-27	1.4542	1.4632	1.4589	26.7
3-28	1.4340	1.4390	1.4370	31.7
3-29	1.4339	1.4398	1.4365	28.6
3-30	1.4329	1.4406	1.4370	31.4
3-31	1.4340	1.4390	1.4368	27.8
3-32	1.4320	1.4398	1.4362	30.8
3-33	1.4320	1.4400	1.4364	26.1
3-34	1.4319	1.4400	1.4360	29.4
3-35	1.4312	1.4400	1.4358	25.6
3-36	1.4330	1.4393	1.4349	26.7
3-37	1.4319	1.4395	1.4342	24.7
3-38	1.4309	1.4372	1.4341	25.6
3-39	1.4300	1.4378	1.4342	24.4
3-40	1.4333	1.4398	1.4341	23.1
3-41	1.4308	1.4385	1.4340	25.6
3-42	1.4290	1.4348	1.4340	24.7
3-43	1.4300	1.4371	1.4340	24.1
3-44	1.4292	1.4365	1.4335	25.3
4-1	1.43065	1.43190	1.43121	26.0
4-2	1.43075	1.43177	1.43132	27.2
4-3	1.42993	1.43140	1.43052	27.2
4-4	1.43041	1.43160	1.43055	28.3
4-5	1.43007	1.43126	1.43044	25.8

TABLE V

Summary of Calculations

Run	F <u>gm</u> sec	D/B from rota- meters	compo- sition	S wt frac	C _P wt frac
1-60	0.0098	0.68	0.63	0.147	0.433
1-61	0.0062	1.00	1.03	0.148	0.438
1-62	0.0128	1.08	0.97	0.134	0.441
1-63	0.0083	0.60	0.64	0.131	0.443
1-65	0.0062	1.18	1.12	0.129	0.471
1-66	0.0069	0.97	1.01	0.141	0.474
1-67	0.0053	1.03	0.63	0.150	0.467
1-68	0.0072	0.95	0.68	0.128	0.249
1-69	0.0049	1.10	0.87	0.125	0.250
1-70	0.0655	0.29	0.35	0.096	0.250
1-71	0.0093	1.33	1.09	0.113	0.255
1-72	0.0097	2.22	1.69	0.105	0.255
1-73	0.0158	2.96	2.50	0.101	0.258
1-74	0.0062	0.95	1.03	0.128	0.258
1-75	0.0083	0.56	0.50	0.123	0.257
1-76	0.0120	0.33	0.38	0.135	0.255
1-77	0.0139	0.57	0.57	0.132	0.257
1-78	0.0334	0.61	0.79	0.118	0.261
1-79	0.0067	1.00	0.06	0.104	0.262
1-80	0.0048	0.81	1.33	0.070	0.263
1-81	0.0115	1.16	0.98	0.115	0.272
1-82	0.0109	1.38	0.93	0.131	0.272
1-83	0.0096	1.68	1.23	0.136	0.276
1-84	0.0106	1.40	1.07	0.087	0.275
1-85	0.0068	0.97	0.70	0.046	0.097
1-86	0.0113	1.19	0.92	0.046	0.097
1-87	0.0058	1.26	1.31	0.067	0.099
1-88	0.0083	2.34	1.91	0.064	0.099
1-89	0.0128	4.66	5.33	0.057	0.101
1-90	0.0491	0.90	0.73	0.064	0.098
1-91	0.0137	4.12	3.00	0.060	0.099
1-92	0.0360	12.50	4.50	0.055	0.099
1-93	0.0074	1.97	1.84	0.071	0.103
1-94	0.0052	1.07	1.06	0.074	0.103
1-95	0.0133	0.58	0.55	0.034	0.805
1-96	0.0061	0.95	1.00	0.036	0.806
1-97	0.0063	0.94	0.63	0.026	0.806
1-98	0.0067	1.08	0.96	0.051	0.815
1-99	0.0116	1.06	0.88	0.045	0.817
1-100	0.0225	0.97	1.18	0.037	0.821
1-101	0.0107	0.96	0.83	0.044	0.825
1-102	0.0173	0.99	0.93	0.052	0.824

TABLE V - cont.

Summary of Calculations

Run	ΔT °C	T_0 °C	$\frac{a}{a_r}$	K $\frac{\text{gm cm}}{\text{sec}}$	$\frac{FL}{4K}$
1-60	42.3	36.1	0.978	14.6	0.050
1-61	40.9	34.6	0.979	13.5	0.035
1-62	36.9	31.8	0.982	11.0	0.089
1-63	35.1	30.8	0.982	9.86	0.066
1-65	32.4	32.0	0.983	9.26	0.052
1-66	38.7	36.6	0.980	12.5	0.042
1-67	42.2	38.5	0.979	14.5	0.029
1-68	35.3	36.0	0.982	10.8	0.052
1-69	33.4	34.4	0.983	9.59	0.038
1-70	33.1	35.0	0.983	9.43	0.533
1-71	25.3	31.2	0.987	5.57	0.126
1-72	27.1	31.1	0.986	6.31	0.119
1-73	26.9	31.8	0.986	6.27	0.194
1-74	35.0	36.6	0.982	10.7	0.044
1-75	37.2	37.9	0.981	12.2	0.053
1-76	38.5	39.3	0.980	13.2	0.069
1-77	36.7	38.2	0.989	11.9	0.088
1-78	37.9	39.0	0.989	12.8	0.197
1-79	2.7	20.6	0.998	0.067	7.70
1-80	7.3	22.9	0.996	0.467	0.792
1-81	32.0	36.8	0.984	9.00	0.099
1-82	38.0	38.9	0.981	12.8	0.064
1-83	42.2	42.6	0.979	16.1	0.045
1-84	19.7	29.4	0.990	3.44	0.235
1-85	17.0	28.6	0.991	2.35	0.216
1-86	17.8	29.4	0.991	2.58	0.340
1-87	32.1	37.8	0.984	8.58	0.053
1-88	29.8	37.5	0.985	7.45	0.085
1-89	31.7	37.5	0.984	8.35	0.117
1-90	37.7	38.0	0.981	11.6	0.324
1-91	36.9	38.2	0.981	11.2	0.093
1-92	37.0	39.1	0.982	11.3	0.248
1-93	35.3	38.5	0.982	10.2	0.056
1-94	33.7	37.6	0.983	9.33	0.043
1-95	16.5	27.8	0.993	1.65	0.617
1-96	16.5	27.8	0.993	1.65	0.282
1-97	7.1	22.1	0.996	0.415	1.16
1-98	28.7	34.0	0.985	4.89	0.104
1-99	26.1	34.5	0.987	4.05	0.219
1-100	25.1	32.5	0.987	3.72	0.451
1-101	21.8	32.0	0.989	2.82	0.260
1-102	33.8	37.5	0.983	6.72	0.198

TABLE V - cont.

Summary of Calculations

Run	F <u>gm</u> sec	D/B from rota- meters	compo- sition	S wt frac	C _F Wt frac
1-103	0.1045	0.79	1.18	0.024	0.827
1-104	0.0062	0.96	0.86	0.054	0.826
1-105	0.1237	0.74	0.73	0.052	0.829
1-106	0.0082	1.10	0.92	0.092	0.569
1-107	0.0209	0.99	0.94	0.089	0.570
1-108	0.0697	1.02	1.20	0.066	0.574
1-109	0.0093	0.65	0.78	0.089	0.571
1-110	0.0547	0.99	0.86	0.076	0.573
1-111	0.0109	1.07	0.92	0.090	0.573
1-112	0.151	0.83	0.91	0.042	0.575
1-113	0.153	0.84	0.83	0.044	0.574
2-1	0.0103	0.96	0.55	0.031	0.587
2-2	0.0059	1.13	1.15	0.028	0.608
2-3	0.0106	1.13	1.25	0.027	0.608
2-4	0.0092	1.27	1.25	0.027	0.608
2-5	0.0102	1.06	1.18	0.024	0.610
2-6	0.0096	1.01	1.70	0.027	0.578
2-7	0.0151	----	0.94	0.033	0.579
2-8	0.0390	1.32	1.13	0.032	0.582
2-9	0.0045	1.06	2.00	0.036	0.589
2-10	0.0053	1.03	0.58	0.030	0.589
2-11	0.0150	0.99	1.45	0.027	0.593
2-12	0.0358	1.75	1.64	0.029	0.596
3-1	0.0099	0.90	0.63	0.065	0.554
3-1a	0.0097	0.98	0.80	0.070	0.563
3-2	0.0049	0.95	0.70	0.068	0.565
3-2a	0.0056	0.93	0.74	0.073	0.565
3-3	0.0048	0.98	0.58	0.068	0.563
3-4	0.0817	0.78	0.75	0.049	0.573
3-5	0.0097	0.98	0.91	0.063	0.576
3-6	0.0266	0.86	0.64	0.059	0.576
3-7	0.0133	0.94	1.44	0.061	0.584
3-8	0.0600	0.80	0.91	0.065	0.595
3-9	0.0111	0.98	0.70	0.063	0.591
3-10	0.0289	0.85	1.06	0.066	0.602
3-11	0.0141	0.96	1.00	0.068	0.602
3-12	0.0051	1.03	0.97	0.071	0.611
3-12a	0.0059	0.99	1.14	0.062	0.621
3-13	0.0094	1.03	0.95	0.041	0.627
3-14	0.0757	0.74	0.83	0.011	0.630
3-15	0.0100	0.98	1.05	0.039	0.629
3-16	0.0518	0.73	0.68	0.037	0.630

TABLE V - cont.

Summary of Calculations

Run	ΔT °C	T_o °C	$\frac{a}{a_r}$	K $\frac{gm \text{ cm}}{sec}$	$\frac{FL}{4K}$
1-103	31.2	35.8	0.984	5.72	1.40
1-104	32.6	35.8	0.983	6.25	0.077
1-105	32.7	36.1	0.984	6.27	0.151
1-106	23.5	30.7	0.988	4.25	0.149
1-107	23.5	30.6	0.988	4.25	0.378
1-108	25.5	31.6	0.987	4.92	1.08
1-109	22.0	30.4	0.989	3.74	0.191
1-110	23.9	31.4	0.988	4.39	0.954
1-111	22.1	30.4	0.989	3.74	0.223
1-112	22.7	31.6	0.988	3.97	2.90
1-113	24.6	31.6	0.987	4.62	2.53
2-1	28.0	33.9	0.991	144	0.0037
2-2	25.3	33.2	0.992	116	0.0026
2-3	21.5	31.8	0.993	83.5	0.0066
2-4	24.1	33.6	0.992	106	0.0045
2-5	31.8	37.5	0.990	186	0.0028
2-6	33.2	31.8	0.989	194	0.0025
2-7	46.4	42.5	0.985	405	0.0019
2-8	46.4	42.0	0.985	402	0.0050
2-9	46.6	42.7	0.985	404	0.0057
2-10	31.3	34.3	0.990	179	0.0016
2-11	31.7	34.3	0.990	182	0.0042
2-12	32.3	34.0	0.989	189	0.0106
3-1	31.5	35.0	0.983	9.26	0.041
3-1a	31.1	33.6	0.983	8.86	0.042
3-2	29.9	33.5	0.984	8.23	0.023
3-2a	29.6	33.2	0.984	8.67	0.026
3-3	25.0	31.0	0.987	5.82	0.031
3-4	25.9	30.8	0.986	6.19	0.504
3-5	27.5	32.0	0.985	6.95	0.053
3-6	28.2	32.6	0.985	7.29	0.140
3-7	27.3	31.9	0.985	6.75	0.075
3-8	47.8	42.2	0.974	20.3	0.113
3-9	47.4	42.8	0.975	20.3	0.021
3-10	46.6	42.6	0.975	19.4	0.057
3-11	45.2	41.5	0.976	18.2	0.030
3-12	46.5	42.4	0.975	19.1	0.010
3-12a	41.6	42.4	0.978	15.5	0.015
3-13	8.9	39.8	0.995	0.78	0.460
3-14	10.0	21.8	0.994	0.874	3.31
3-15	10.1	22.6	0.994	0.897	0.426
3-16	17.3	25.5	0.991	2.62	0.756

TABLE V - cont.

Summary of Calculations

Run	F <u>gm</u> sec	D/B from rota- meters	compo- sition	S wt frac	C _P wt frac
3-17	0.0087	0.98	1.08	0.050	0.633
3-18	0.0242	0.73	0.64	0.046	0.633
3-19	0.0058	1.02	1.11	0.061	0.639
3-20	0.0089	----	0.53	0.055	0.257
3-21	0.0073	0.93	0.74	0.066	0.260
3-22	0.0743	0.83	0.79	0.052	0.261
3-23	0.0127	0.71	0.76	0.065	0.261
3-24	0.126	0.85	0.77	0.053	0.262
3-25	0.0078	----	0.61	0.071	0.262
3-26	0.148	0.77	0.61	0.061	0.263
3-27	0.0060	----	0.87	0.071	0.263
3-28	0.0652	0.56	0.69	0.044	0.447
3-29	0.0083	----	1.36	0.052	0.452
3-30	0.0089	----	0.89	0.068	0.447
3-31	0.0136	----	0.83	0.044	0.449
3-32	0.0907	0.87	0.87	0.069	0.454
3-33	0.0132	0.79	0.84	0.070	0.453
3-34	0.0266	0.99	0.97	0.071	0.456
3-35	0.0050	1.02	0.93	0.077	0.458
3-36	0.128	3.20	2.23	0.055	0.465
3-37	0.0095	2.44	2.19	0.067	0.471
3-38	0.120	0.84	0.90	0.055	0.472
3-39	0.0085	0.85	0.82	0.069	0.471
3-40	0.114	14.4	7.15	0.057	0.472
3-41	0.0068	----	1.35	0.068	0.473
3-42	0.128	0.17	0.16	0.052	0.473
3-43	0.0068	----	0.75	0.063	0.473
3-44	0.0376	0.79	0.71	0.065	0.478
4-1	0.0121	0.87	1.31	0.0112	0.491
4-2	0.0705	0.58	0.79	0.0091	0.491
4-3	0.0123	----	1.49	0.0131	0.488
4-4	0.0486	1.76	7.50	0.0106	0.487
4-5	0.0048	0.87	2.22	0.0106	0.486

TABLE V - cont.

Summary of Calculations

Run	ΔT °C	T_0 °C	$\frac{a}{a_r}$	K $\frac{gm \text{ cm}}{sec}$	$\frac{FL}{4K}$
3-17	17.6	27.0	0.990	2.71	0.123
3-18	19.7	27.3	0.989	3.36	0.276
3-19	21.0	28.3	0.989	3.83	0.058
3-20	10.0	22.0	0.994	1.04	0.326
3-21	20.6	27.4	0.989	4.46	0.063
3-22	25.7	30.4	0.986	6.92	0.410
3-23	23.6	29.3	0.987	5.83	0.084
3-24	25.6	30.6	0.986	6.87	0.698
3-25	35.8	36.5	0.981	13.3	0.023
3-26	38.2	37.5	0.980	15.4	0.368
3-27	39.3	38.2	0.979	16.3	0.014
3-28	14.4	24.8	0.993	2.11	1.18
3-29	9.2	21.7	0.995	0.85	0.372
3-30	16.6	25.6	0.992	2.81	0.120
3-31	8.9	21.0	0.996	0.791	0.657
3-32	41.8	39.2	0.980	17.7	0.197
3-33	40.2	38.2	0.980	16.5	0.031
3-34	42.9	39.6	0.979	18.7	0.054
3-35	41.5	39.1	0.980	17.5	0.011
3-36	30.5	33.7	0.985	9.30	0.527
3-37	28.7	31.6	0.986	8.20	0.045
3-38	27.6	31.4	0.986	7.57	0.607
3-39	27.6	31.6	0.986	7.55	0.043
3-40	26.4	30.4	0.987	6.95	0.627
3-41	28.0	31.8	0.986	7.80	0.033
3-42	26.2	29.4	0.987	6.76	0.736
3-43	26.3	29.3	0.987	6.82	0.038
3-44	26.1	29.4	0.987	6.66	0.216
4-1	30.8	29.0	0.994	4670	0.0000997
4-2	32.7	30.0	0.994	5290	0.000509
4-3	54.0	41.1	0.990	15100	0.0000312
4-4	57.2	41.8	0.989	16900	0.000110
4-5	52.3	39.8	0.990	14000	0.0000132

TABLE VI

Total Reflux Calculations

Column	Feed Comp wt frac	Separ- ation wt frac	Separ- ation Factor q	$\frac{HL}{aK}$	α
1	0.100	0.074	2.36	0.480	1.79
1	0.260	0.133	2.02	0.452	1.56
1	0.452	0.150	1.841	0.490	1.245
1	0.572	0.097	1.489	0.512	0.778
1	0.818	0.060	1.501	0.625	0.650
2	0.594	0.029	1.128	0.0577	2.08
3	0.261	0.072	1.455	0.202	1.85
3	0.462	0.072	1.337	0.215	1.35
3	0.598	0.070	1.338	0.235	1.24
4	0.489	0.011	1.045	0.00612	7.19
Trevo & Drickamer	0.562	0.00525	1.0216	0.0184	1.16

Column	$\frac{\ln q}{(L/a^2)}$ cm	f	α'
1	3.11×10^{-5}	1.03	1.74
1	2.54	1.03	1.51
1	2.21	1.03	1.21
1	1.44	1.03	0.755
1	1.47	1.03	0.63
2	1.59	2.00	1.04
3	2.88	1.075	1.72
3	2.22	1.075	1.255
3	2.23	1.075	1.15
4	1.965	6.00	1.20
Trevo & Drickamer	2.17	1.00	1.16

FIGURE XVII a ROTAMETER CALIBRATIONS

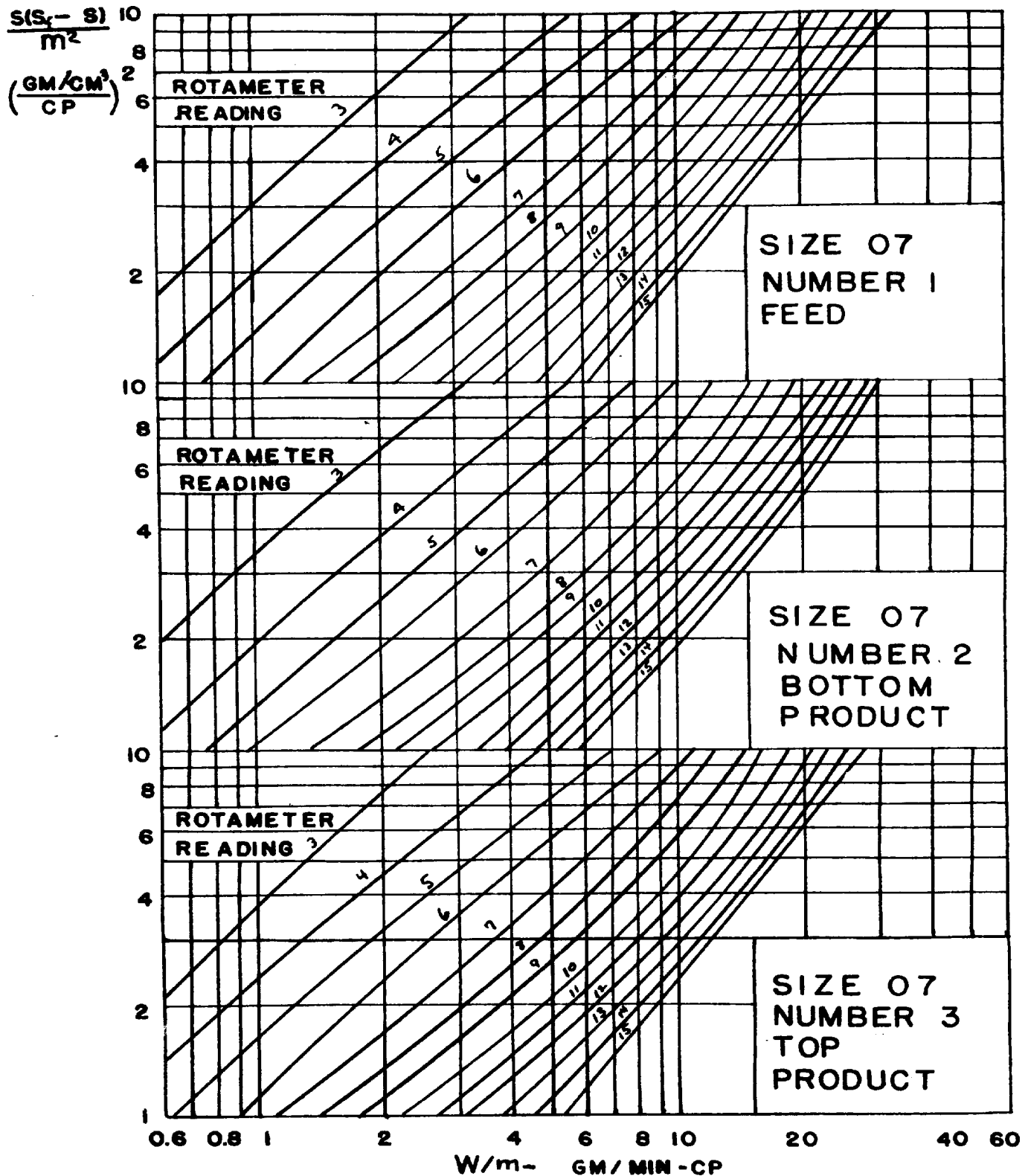


FIGURE XVII b

ROTAMETER CALIBRATIONS

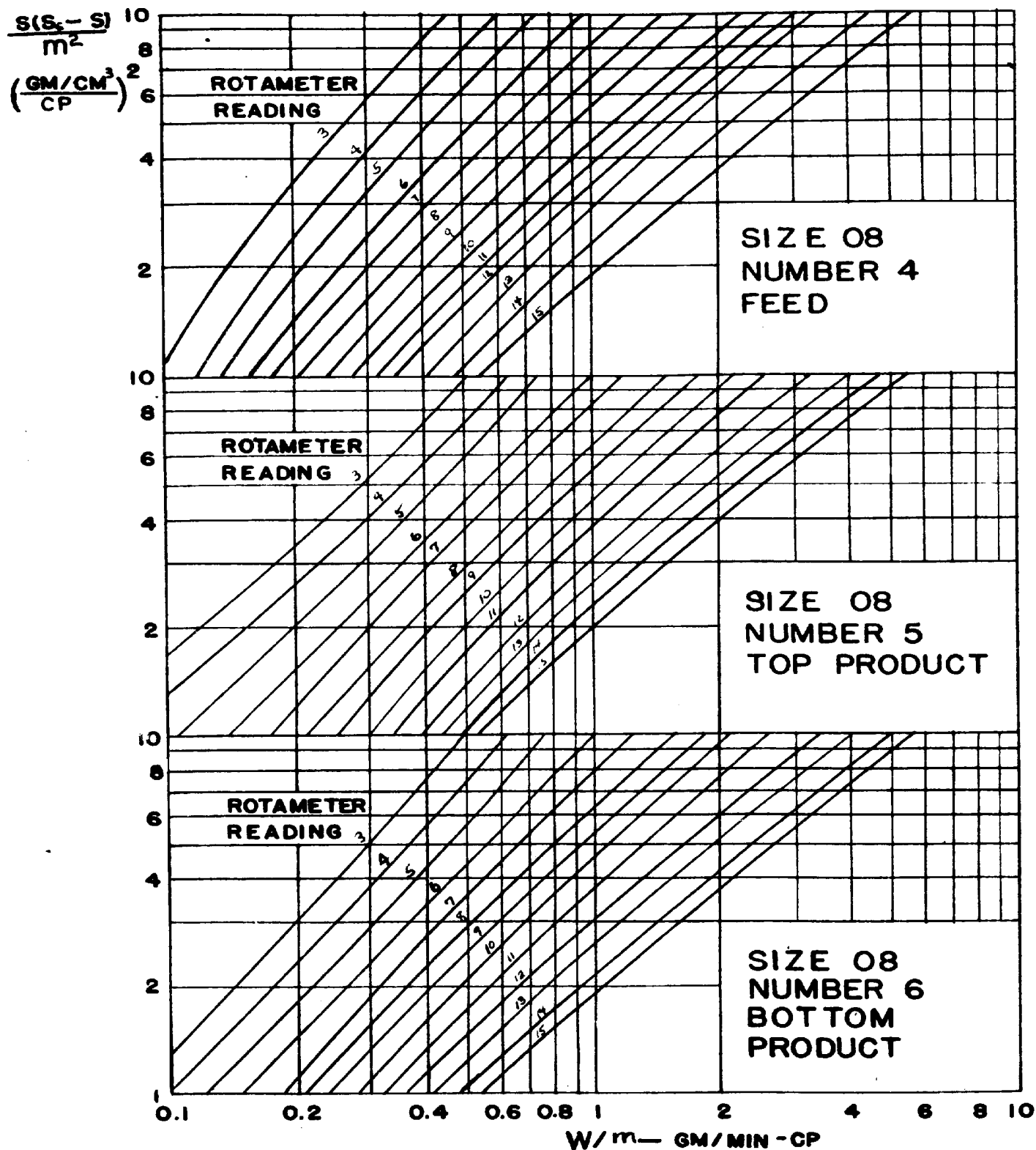


FIGURE XVIII
REFRACTIVE INDEX DEVIATION OF
N-HEPTANE-BENZENE MIXTURES
AT 25 C

REFRACTIVE INDEX
DEVIATION: $(n_i - n)$

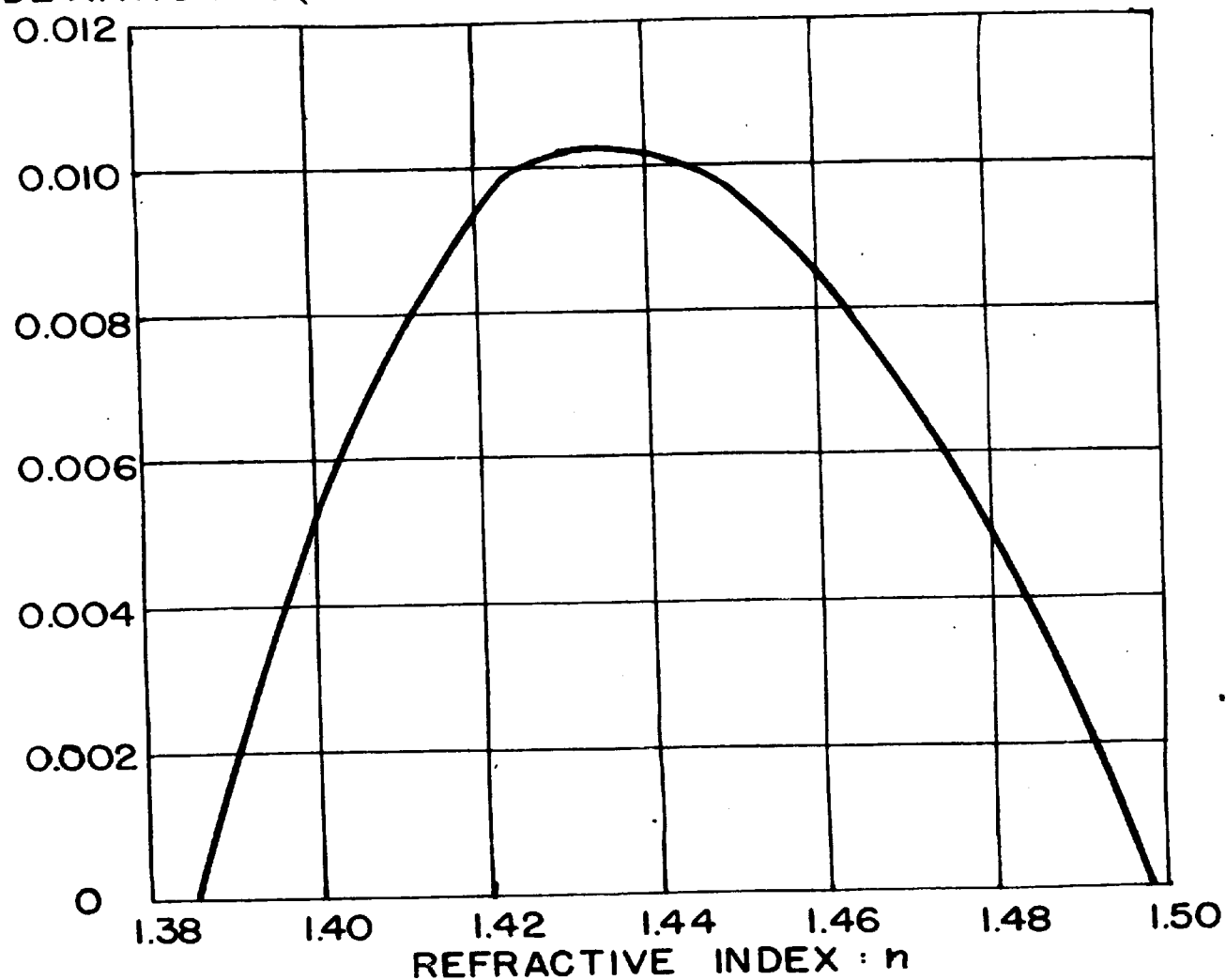


FIGURE XIX DENSITY OF N-HEPTANE AND BENZENE MIXTURES

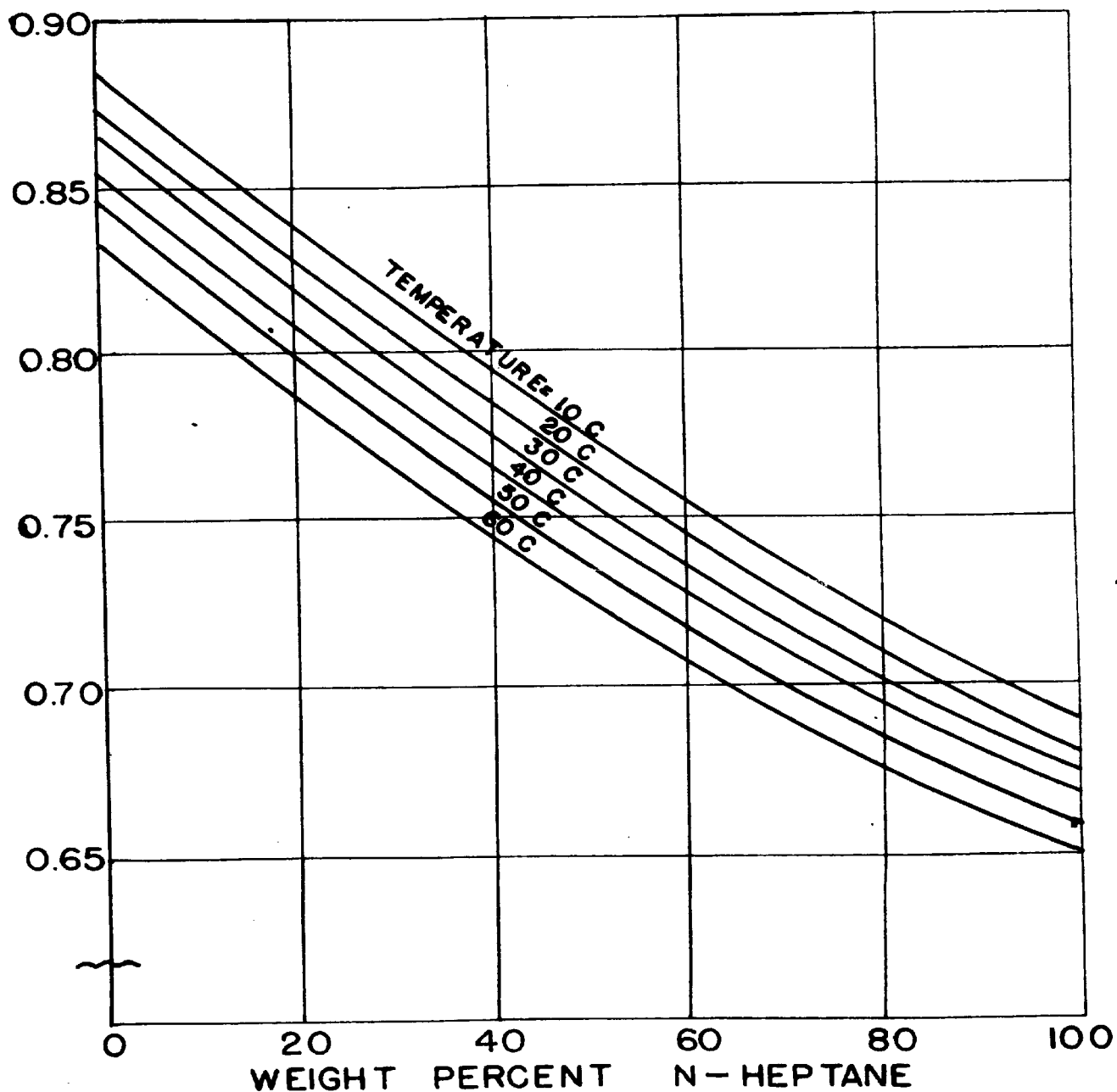
DENSITY - GM/CM³

FIGURE XX EXPANSION COEFFICIENT OF N-HEPTANE-BENZENE MIXTURES

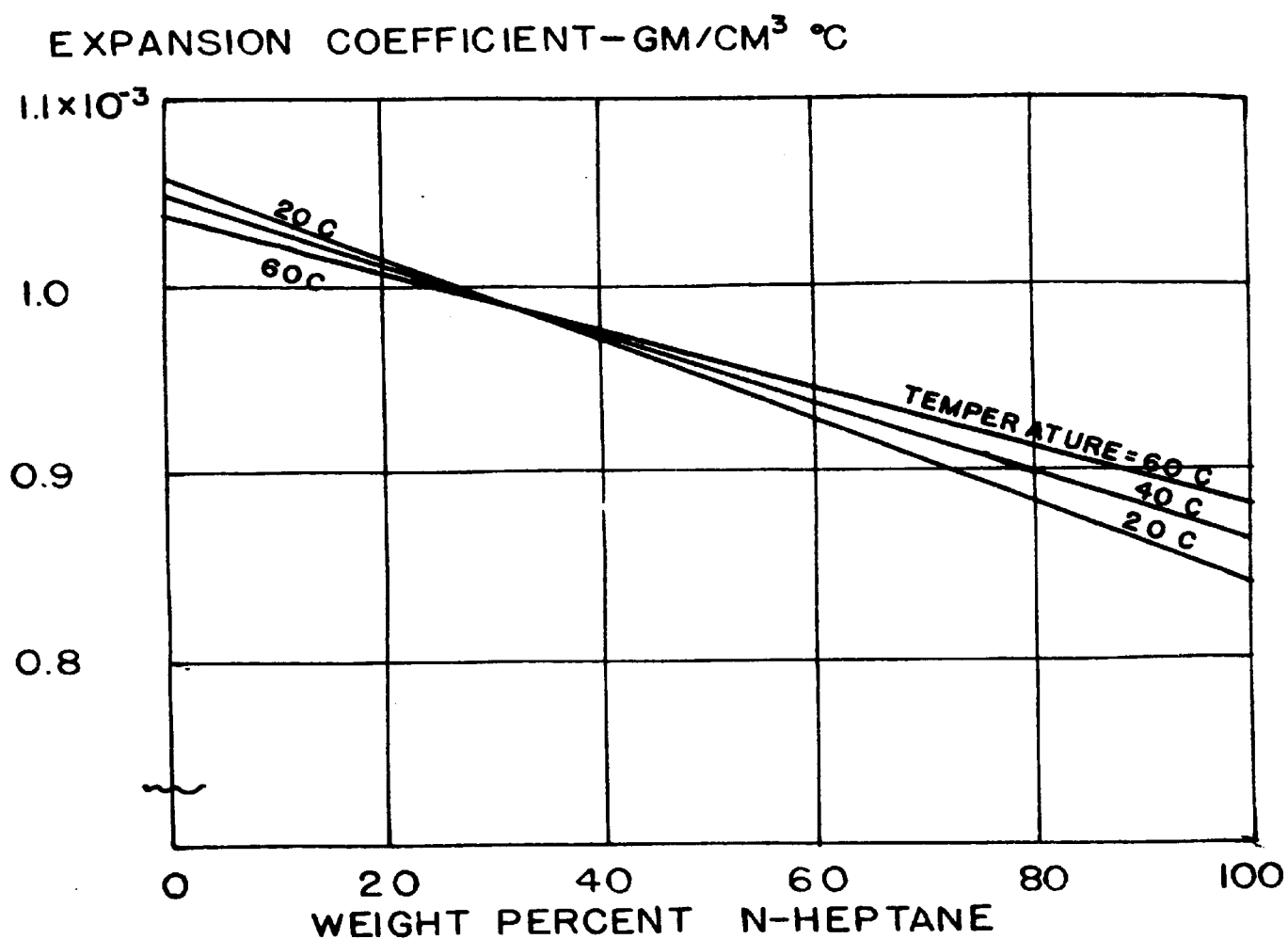


FIGURE XXI VISCOSITY OF N-HEPTANE AND BENZENE MIXTURES

VISCOSITY - CENTIPOISE

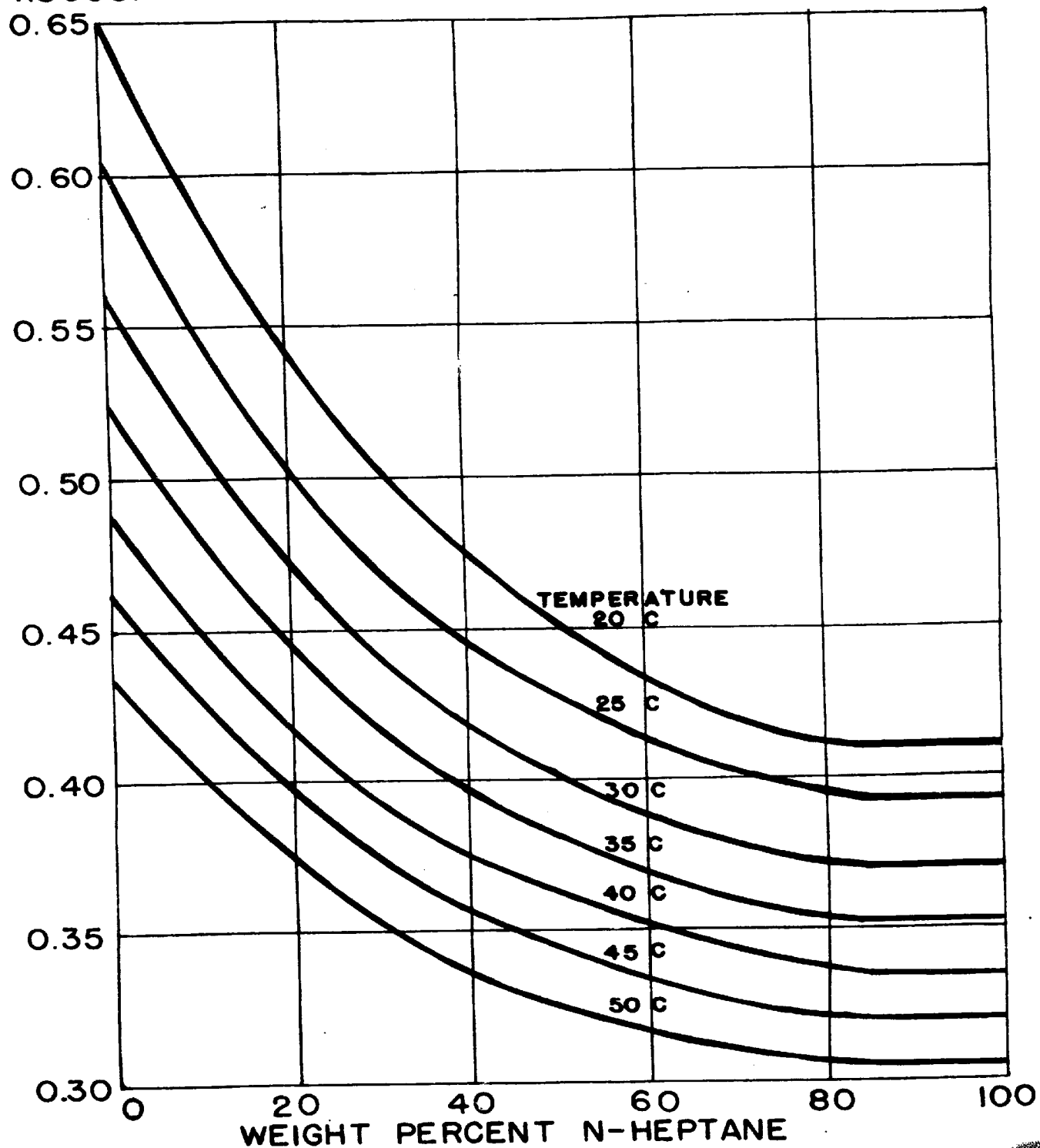


FIGURE XXII ACTIVITY COEFFICIENTS FOR N-HEPTANE-BENZENE MIXTURES

LOG ACTIVITY COEFFICIENT

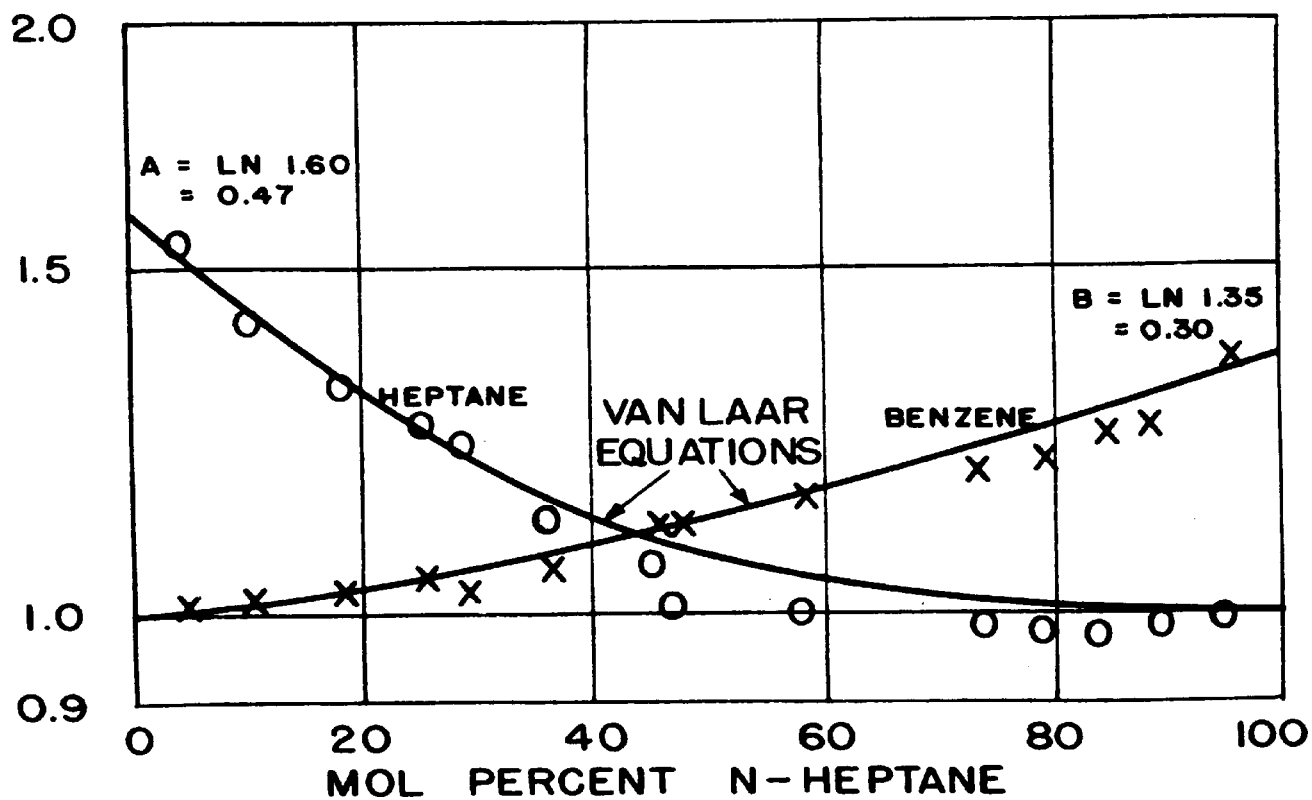
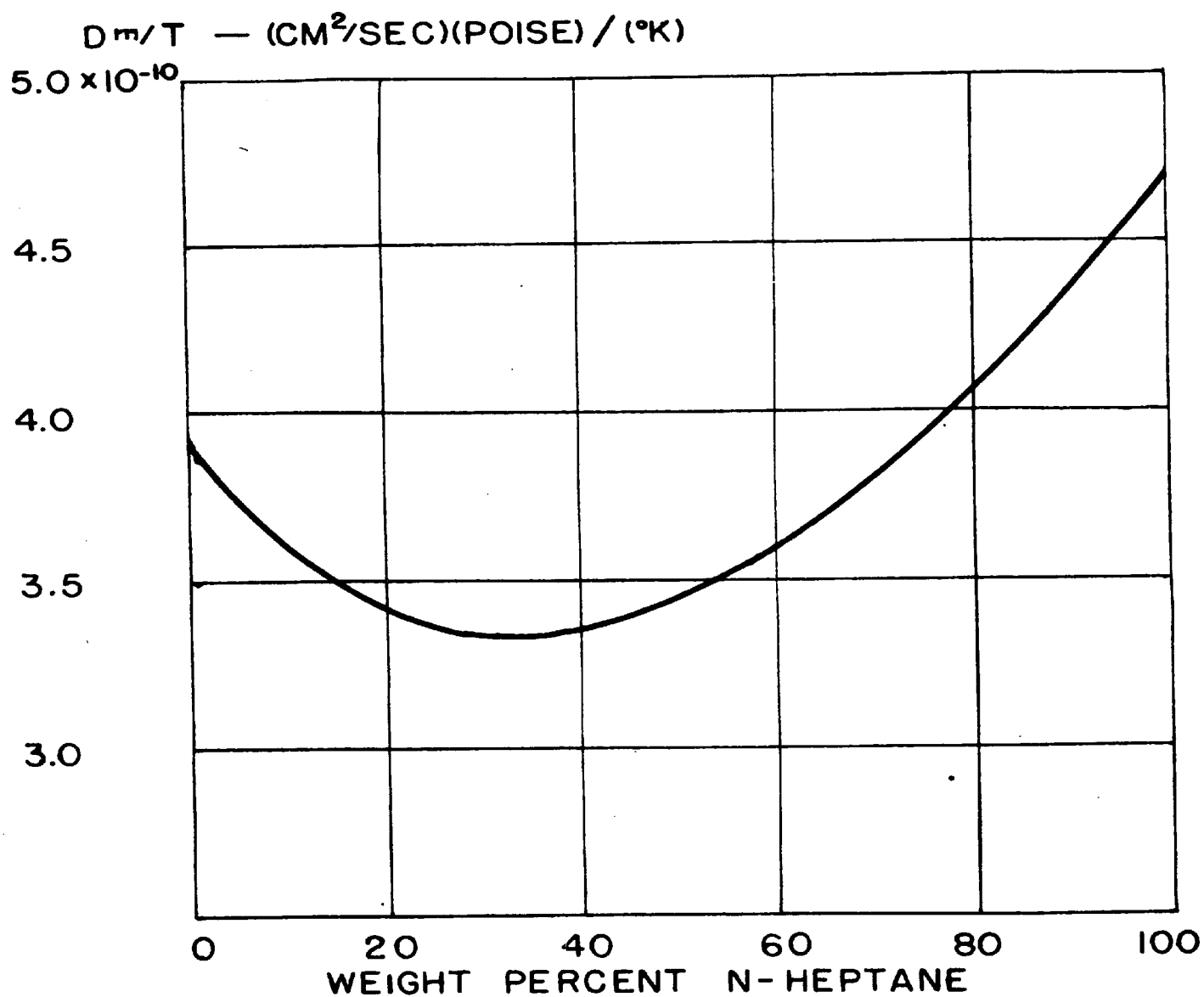


FIGURE XXIII
 D_m/T FOR N-HEPTANE
AND BENZENE MIXTURES



NOMENCLATURE

A	Coefficient of $(FL/4K)^{0.75}$
B	Bottom product rate - gm/sec
C	Mass fraction (of n-heptane in the n-heptane - benzene system)
D	Top product rate - gm/sec
D_L	Diffusivity - cm^2/sec
E	Circumference or width of column - cm
F	Feed rate - gm/sec
G	Function defined by equation 28
H	Transport coefficient - gm/sec
J	Diffusion flux vector - gm/sec cm^2
K	Transport coefficient - gm cm/sec
L	Height of column - cm
M	Molecular weight
N	Mol fraction
P	Pressure - dyne/ cm^2
Q	Heat flux - cal/sec cm^2
S	Separation - weight fraction
T	Temperature - $^{\circ}\text{K}$ or $^{\circ}\text{C}$
ΔT	Temperature difference - $^{\circ}\text{K}$ or $^{\circ}\text{C}$
V	Velocity vector - cm/sec
V	Molal volume - $\text{cm}^3/\text{gm mol}$
W	Transport up column - gm/sec
a	Spacing - cm
a'	Activity
f	Coefficient of α'

g	Acceleration of gravity - cm/sec^2
$\mathbf{i}, \mathbf{j}, \mathbf{k}$	Unit cartesian vectors
k	Thermal conductivity - $\text{cal/sec cm } ^\circ\text{C}$
m	Viscosity - gm/cm sec
n	Refractive index
p	Exponent of $FL/4K$
s	Density - gm/cm^3
q	Separation factor
t	Time - sec
u, v, w	Velocity components of $\vec{V}$ - cm/sec
x, y, z	Cartesian coordinates - cm
α	Thermal diffusion coefficient
α'	Relative thermal diffusion coefficient
β	Coefficient of expansion

Subscripts refer to the following:

B	Bottom product
C	Cold wall
D	Top product
F	Feed
H	Hot wall
b	Benzene
f	Float
h	Heptane
i	Ideal value

o Average value
r Reference value
' Total reflux
l,k Component l,k

REFERENCES

1. Arnold, J. "J. Am. Chem. Soc." 52 3937 (1930)
2. Carr, H. E. "J. Chem. Phys." 12 349 (1944)
3. Chapman, S. "Phil. Trans. Roy. Soc." A211 433 (1911)
4. Chapman, S. and Dootson, F. W. "Phil. Mag." 33 248 (1917)
5. Clark, A. M. "Trans. Faraday Soc." 41 718 (1945)
6. Clusius, K. and Dickel, G. "Naturwiss." 26 546 (1938)
7. Clusius, K. and Dickel, G. "Naturwiss." 27 148 (1939)
8. Debye, P. J. W. "U. S. Patent 2,567,765" (Sept. 1951)
9. Debye, P. J. W. and Beuche, A. M. "High Polymer Physics"
Chemical Rubber Publishing Co., Brooklyn, 1948
10. de Groot, S. R. "The Thermodynamics of Irreversible
Processes" Interscience, 1951
11. de Groot, S. R. "Physica" 9 699, 801, 923 (1943)
12. de Groot, S. R. "Physica" 13 555 (1947)
13. de Groot, S. R. "J. Phys. Radium" 8 129, 188 (1947)
14. Enskog, D. "Physik. Z." 12 56, 533 (1911)
15. Fournier, A. "J. Phys. Radium" 5 45 (1948)
16. Furry, W. H. and Jones, R. C. "Phys. Rev." 57 561 (1940)
17. Furry, W. H. and Jones, R. C. "Phys. Rev." 69 459 (1946)
18. Furry, W. H., Jones, R. C., and Onsager, L. "Phys. Rev."
55 1083 (1939)
19. "International Critical Tables" McGraw-Hill, New York,
1929
20. Jones, A. L. "Pet. Proc." 6 132 (Feb. 1951)
21. Jones, A. L. and Foreman, R. W. "Ind. Eng. Chem." 44
2249 (1952)
22. Jones, A. L. and Hughes, E. C. "U. S. Patents 2,541,069;
2,541,070; and 2,541,071 (Feb. 1951)
23. Jones, A. L. and Milberger, E. C. "Ind. Eng. Chem." 45
2689 (1953)

24. Jones, R. C. and Furry, W. H. "Rev. Modern Phys." 18
151 (1946)
25. Jost, W. "Diffusion in Gases, Liquids, and Solids"
Academic Press, New York, 1952
26. Korsching, H. "Naturwiss." 31 348 (1943)
27. Korsching, H. and Wirtz, K. "Naturwiss." 27 110, 367 (1939)
28. Ludwig, C. "Wien, Akad. Ber." 20 539 (1856)
29. MacAdams, W. H. "Heat Transmission, 2nd Ed." McGraw-Hill,
New York, 1942
30. Martin, J. J. "Chem. Eng. Progress" 45 338 - 342
(1949)
31. Prigogine, I., de Brouchère, L., and Amand, R. "Physica"
16 577, 851 (1950)
32. Soret, C. "Arch. de Genève" 3 48 (1879)
33. Soret, C. "Arch. de Genève" 4 209 (1880)
34. Soret, C. "Ann. Chim. Phys." 22 293 (1891)
35. Trevoy, D. J. and Drickamer, H. G. "J. Chem. Phys." 17
1117, 1120 (1949)
36. van Dranen, J. and Bergsma, F. "Physica" 13 558 (1947)
37. van Velden, P. F., van der Voort, H., and Gorter, G.
"Physica" 12 151 (1946)
38. Wilke, C. R. "Chem. Eng. Progress" 45 218 (1949)
39. Wirtz, K. "Naturwiss." 31 349, 416 (1943)