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BOYER, Lyndon Dean, 1930-
AN EXPERIMENTAL AND THEORETICAL
INVESTIGATION OF VERTICAL BARRIERS
IN LIQUID THERMAL DIFFUSION COLUMNS.

The University of Oklahoma, Ph.D., 1961
Engineering, chemical

University Microfilms, Inc., Ann Arbor, Michigan

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

AN EXPERIMENTAL AND THEORETICAL INVESTIGATION OF VERTICAL
BARRIERS IN LIQUID THERMAL DIFFUSION COLUMNS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

LYNDON DEAN BOYER

Norman, Oklahoma

1961

AN EXPERIMENTAL AND THEORETICAL INVESTIGATION OF VERTICAL
BARRIERS IN LIQUID THERMAL DIFFUSION COLUMNS

APPROVED BY











DISSERTATION COMMITTEE

ACKNOWLEDGMENT

The author wishes to thank the many people at the University of Oklahoma who helped with this investigation. Dr. J. E. Powers acted as research director throughout the project. The advice and suggestions offered by the staff of the Chemical Engineering Department are appreciated. The outspoken criticisms of all members of the chemical engineering graduate class resulted in some assistance and no little humor.

The author is particularly indebted to Mr. F. Maginnis of the Research Instrument Company. Mr. Maginnis did all the precision machine work required by the investigation and helped with some phases of the mechanical design.

Mr. C. Crownover helped in collecting some of the experimental data. A large part of the repetitive calculations were carried out on the IBM 650 computer of the University of Oklahoma by Mr. S. Dhillon. The figures were prepared by Messrs. B. Evans and F. Morris. The excellent job of typing by Mrs. Elaine McClure is appreciated.

The author wishes to thank the Ethyl Corporation and Monsanto Chemical Company for financial support. The major sponsor of this project has been the National Science Foundation.

Lyndon Dean Boyer

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AN EXPERIMENTAL AND THEORETICAL INVESTIGATION OF VERTICAL BARRIERS IN LIQUID THERMAL DIFFUSION COLUMNS

CHAPTER I

INTRODUCTION

Thermal diffusion arises when a temperature difference is impressed across a uniform mixture. A degree of separation occurs; one component tending to concentrate toward the hot side, the other component toward the cold side. The inverse effect is also known; that is, a temperature gradient as a result of a concentration gradient. Thermal diffusion was first observed over a century ago, however, the majority of the work in this field has been done since just before World War II.

Before 1938 investigations of thermal diffusion were made only in single-stage cells. The single-stage cell is usually subjected to a vertical temperature gradient, with the higher temperature at the top of the cell to minimize convective currents (Figure 1A). The separation attained in liquids used in such cells is very small for two reasons. Obviously, when thermal diffusion effects any separation, ordinary diffusion--mass transfer caused solely by a

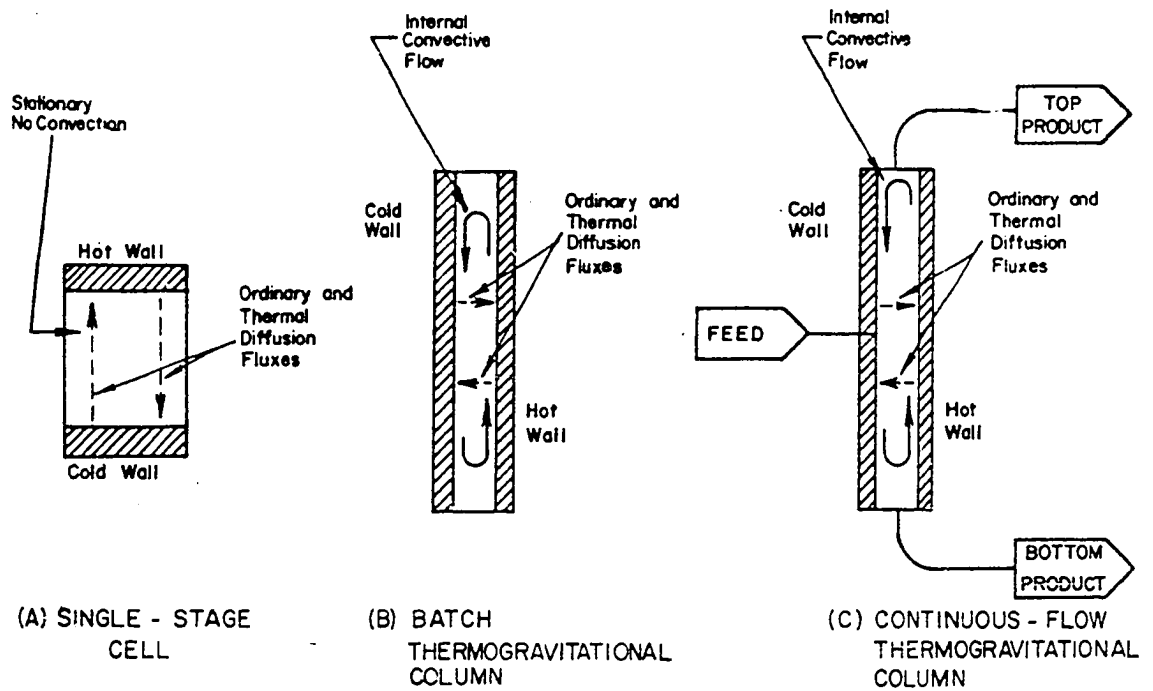


Figure 1 - Representation of Conventional Thermal Diffusion Equipment

concentration gradient--immediately tends to destroy the separation. The second reason is that the temperature difference across the cell is limited by the boiling and freezing points of the liquid. Because of these limitations, and because the time required to approach steady state is very long even for small cells, such cells received little attention as a possible means of carrying out commercial separations. In 1922, Mulliken (1) showed that thermal diffusion was inferior to other processes for separating mixtures of isotopes.

In 1938 Clusius and Dickel (2) discovered a method of greatly multiplying the thermal diffusion effect. Their approach consisted of applying the temperature gradient horizontally across a mixture, causing horizontal thermal diffusion and vertical convection. A device employing this method is called a thermogravitational column, or frequently a Clusius-Dickel column, after the inventors. These columns may be either batch or continuous, as shown schematically in Figures 1B and 1C. In a thermogravitational column, the component which tends toward the hot side is carried up by convection to concentrate at the top of the column. The other component is driven to the cold side and carried down to concentrate at the bottom of the column. Various theories have been proposed which explain, qualitatively at least, the behavior of thermogravitational columns.

Because all types of thermal diffusion are

thermodynamically irreversible processes, the energy requirements are very high. Therefore, thermogravitational thermal diffusion has never been used successfully as a large scale separation process. Its main utility has been as an analytical tool. Thermal diffusion can separate mixtures which are difficult to separate by ordinary means. Laboratory quantities of isotopes and complex organic mixtures have been separated by thermal diffusion. Benedict (3) and Powers (4) have shown that the thermogravitational column is uneconomic when used to separate ordinary materials. Before thermal diffusion is used as a separation method in commercial scale plants, except for special high-cost materials processing, means must be found to radically improve the separation efficiency.

Unusual effects have been reported when baffles or barriers have been introduced into thermogravitational thermal diffusion columns. In general, the effect of introducing barriers has been to increase the separation; sometimes in spectacular fashion. Practically no theoretical work has been done to explain these effects.

Objectives

This investigation is a start on a long-range theoretical and experimental research program directed toward the complete understanding of the function of barriers in thermogravitational thermal diffusion columns. Ultimately it is hoped that design procedures will result which can be

used to predict optimum barrier systems in thermogravitational columns.

The specific objective of the present work was to develop theoretical explanations of the effect of vertical barriers in liquid thermogravitational columns. These theories were then to be tested by a careful, systematic experimental program.

CHAPTER II

REVIEW OF PREVIOUS WORK

General Review

Early Work.--In the year 1856 Ludwig (5) noted that the concentration of solute in an aqueous solution of sodium sulfate varied with position when temperature gradients were present in the system. His announcement received little attention. Soret (6) rediscovered the thermal diffusion effect in 1879. The thermal diffusion effect in liquids is known as the Soret or Ludwig-Soret effect. Ludwig, Soret, and other early investigators (7-16) conducted experiments in aqueous solutions.

The inverse effect, a temperature gradient as a result of a concentration difference, was discovered in 1872 by Dufour (17,18), and bears his name. The presence of the thermal diffusion effect in gases was predicted theoretically by Enskog (19-21) and Chapman (22-24). These pioneers in the kinetic theory of gases derived their result independently. Chapman and Dootson (25) experimentally verified the thermal diffusion effect in gases in 1917. Wessels (26) in 1914 first noted the Soret effect in solids.

All of the early investigators used single-stage cells (sometimes called the static method) as discussed in Chapter I. This method is not a practical means of separating materials, as was pointed out by Mulliken (1).

Thermogravitational Column.--The announcement of the development of the thermogravitational thermal diffusion column in 1938 by Clusius and Dickel (2) served to stimulate interest in thermal diffusion. The thermal diffusion effect is multiplied many times by the thermogravitational method. The essentials of the operation of the thermogravitational column have been outlined in Chapter I. The first thermogravitational column of Clusius and Dickel was an externally cooled vertical tube with a hot wire in the center. They called this device "das trennrohr," or the separation tube. The use of the space between hot and cold vertical concentric cylinders for the thermogravitational method was suggested by Bramley and Brewer (27) and by Korsching and Wirtz (28). Vertical parallel hot and cold plates were first used as thermogravitational thermal diffusion columns by Clusius and Dickel (29) and Korsching and Wirtz (30,31).

Numerous theories (32-40) have been proposed to explain the operation of the thermogravitational column. The theoretical equations resulting have been shown to be in substantial agreement (41). The theoretical treatments differ primarily in the degree of approximations used, and the severity of the assumptions made. Apparently the general

theory gaining the widest acceptance has been the approach originally suggested by Furry, Jones, and Onsager (35).

Many reviews on thermal diffusion are available (37, 42-62). With regard to thermogravitational column theory, a number of reviews are outstanding. A very comprehensive study of the Soret effect in liquids and solids has been presented by de Groot (37). The review by Jones and Furry (54) contains an excellent treatment of thermogravitational column theory. Furry, Jones, and Onsager (35) originally extended their theoretical results on batch columns to cover continuous-flow equipment. Jones and Furry also treat columns with and without reservoirs, and multi-stage arrangements. The work of Von Halle (50) is noteworthy because of his extensive mathematical work on the "forgotten effect," an anomaly pointed out by de Groot (63). The "forgotten effect" will be explained in mathematical terms in a later chapter. Also included in the paper by Von Halle is a complete summary of Soret coefficients measured by all investigators up to about 1957. Measurements made in both single-stage cells and thermogravitational columns are summarized. In addition, Von Halle presents a very complete bibliography containing 676 references.

Thermal diffusion is an irreversible process, and as such requires a relatively high energy consumption to effect a given separation. The thermodynamic efficiency has been derived and discussed by Onsager (64), Prigogine (65), and

White (66). In a later paper, White (67) showed that thermogravitational thermal diffusion columns sometimes can approach the limiting thermodynamic efficiency.

Because of its low thermodynamic and actual efficiency, the main utility of the thermogravitational column has been as an analytical tool (68-78). Laboratory quantities of isotopes and complex organic mixtures have been separated by thermal diffusion. A comprehensive list of references relating to isotope separation by thermogravitational means is presented by Von Halle (50).

Multicomponent thermogravitational thermal diffusion has been attempted by numerous investigators (79-114); usually with isotopic mixtures or petroleum fractions. An interesting possibility is the addition of a third component to a binary mixture in a thermogravitational column to promote separation (84,85,109). This operation is quite analogous to azeotropic or extractive distillation in conventional vapor-liquid separations.

Evidence of some commercial interest in thermal diffusion is found in the profusion of patents (115-172) issued in the field. Most of these deal with mechanical details of thermogravitational column construction and with various modes of flow operation, frequently of a rather bizarre nature. A number of the more interesting patents will be discussed later in this chapter.

As pointed out in Chapter I, the thermogravitational

column can be operated in a batch or continuous manner. With batch operation, numerous investigators (32-34, 173-181) have studied the transient approach to steady state, and, in general, these workers found that the experimental data agreed well with theory. The approach to steady state of the batch column is an excellent means of studying thermogravitational column theory.

Several workers (182-184) have been able to predict continuous-flow thermogravitational separation from experimental results obtained by operating the same columns in a batch manner. A number of authors (58,67,185-189) have investigated flow rate as a variable in thermogravitational columns. Nearly all investigators have found some degree of agreement with theory at low flow rates. This is somewhat surprising in view of the rather arbitrary manner in which Furry, Jones, and Onsager (35) introduce flow rate into thermogravitational column theory. The work of Jones (187) and Jones and Foreman (188) was rather qualitative in nature, whereas Heines and co-workers (185) showed considerable scatter in their data. Correlations of dimensionless groups were proposed by Longmire (189). Powers (58) found the basic theory excellent at low flow rates, and developed corrections to the theory for higher flow rates.

The effect of temperature difference across thermogravitational thermal diffusion columns has been investigated by Powers (58), Trevoy and Drickamer (180), Heines and

co-workers (185), and Libby (190). These investigators claimed good agreement with theory with the exception of Becker (205) and Heines (185), who found rather good agreement in batch columns; but questionable theoretical agreement in continuous-flow thermogravitational columns. Actually, all these workers' data show some discrepancy.

Several workers have experimentally considered thermogravitational column length (58, 97, 106, 177). All but Lawrence (177) have found good agreement with theory.

The plate spacing (distance between hot and cold plates in a parallel plate thermogravitational column) appears in the fundamental column theory in such severe fashion (35), that experimental investigations of this theoretical effect could be expected to differ widely. Such is the case. Only Lawrence (177) and Drickamer and co-workers (206-212) show good experimental agreement with thermogravitational theory. Powers (58), Debye and Bueche (89), and Longmire (106) all show fair confirmation of theory. Rather poor agreement was found by Becker (205) and Heines and co-workers (185). All investigations at large plate spacings show poor agreement.

Thermogravitational Column Innovations

In an attempt to improve the separations achieved in thermogravitational thermal diffusion columns, a number of novel plans have been tried. These innovations will now be the subject of some discussion.

Pulsed Columns.--Because it has been shown that pressure pulses have a beneficial effect on liquid-liquid extraction columns (191), de Maria and Benenati (192,193) introduced pulses into a batch liquid thermogravitational column. Their results showed that without exception, pulsing hindered thermogravitational separations because pulses promote longitudinal mixing.

Packed Columns.--Packing in thermogravitational thermal diffusion columns has been used by Debye (89,122,194) and by Sullivan and co-workers (195,196). Debye (122) has patented the use of packing in thermogravitational columns. The most quantitative work has been carried out by Sullivan, Ruppel, and Willingham (196). With glass wool packing, they found that the batch thermogravitational separation was a direct function of packing density, all other parameters being equal. However, the increased separations required a much longer time to reach steady-state.

Changing Effective Gravitational Field and Rate of Shear.--It was pointed out by de Groot (37) that the effective gravitational field in a parallel plate thermogravitational column can be changed by changing the angle of the column from the vertical. This possibility has been investigated by Carr (173) and Powers (58). Both found substantial agreement with theory. The batch separation increased as predicted when the angle from the vertical was increased. In a continuous-flow column, the advantage of

inclining the column disappears at any appreciable flow rate.

Some investigators have increased the effective gravitational field by centrifugal force. Tilvis (179) and Farber and Libby (190) devised methods of rotating their columns to increase convective flow. Both the experimental procedures and the theoretical analysis (179) are more complicated in such apparatus. Hoen (197) maintained the inner part of a centrifugal separator at a high temperature and the outer part at a low temperature to increase separation. A novel separating device called the "separation disk" has been developed by Schultz-Grunow (198), according to Von Halle (50). Two disks, one hot and one cold, confine the mixture to be separated. One disk is rotated to cause radial circulating currents to flow outward near the spinning disk, and return near the stationary disk.

Sullivan, Ruppel, and Willingham (195) devised a concentric cylinder thermogravitational column in which one of the cylinders could be rotated. The peripheral shearing action markedly increased the separation attained in a given column, probably due to an increased effective length. This type of concentric spinning apparatus is described in the patent literature by Frazier (126) and Jansma (134,135).

Beams (117) obtained a patent on a device to promote longitudinal shear in thermal diffusion. While not precisely a thermogravitational device, its operation is quite similar. The working space is between two endless moving belts; one

heated and the other cooled. Equipment of this type has been analyzed theoretically by Niini (199) and Ramser (200).

Turbulence in Conventional Thermogravitational Columns.--Bramley and Brewer (201) first suggested that turbulence may be beneficial in thermogravitational columns, although theory predicts that turbulence should inhibit separation. A number of authors (181, 202-205) have presented views on the effect of turbulence. Becker (205) was able to approximate his experimental results by assuming that the effective plate spacing was reduced by turbulence.

Drickamer and his co-workers (206-212) have done extensive work with gases in thermogravitational columns operating in the laminar and turbulent regime. Drickamer, Mellow, and Tung (208) proposed semi-empirical correction factors to the theory. Becker (205) agreed with the use of these correction factors in the turbulent region, but did not believe they should apply when laminar flow prevails. Powers (58) supported the use of such correction factors, and presented a correlation of the factors based on dimensional analysis. Hirota and Koboyashi (213) have reported data which supposedly support the Drickamer modifications. However, both Powers (58) and Von Halle (50) have stated that the equations used by Hirota and Koboyashi are in error. It was also pointed out by Von Halle (50) that a paper by Bowring (214) reportedly agrees with the Drickamer modification, but actually uses the incorrect equations of

Hirota and Koboyashi (213).

Turbulence, Baffles, and Barriers.--As previously mentioned, Bramley and Brewer (201) suggested in 1939 that turbulence may serve to increase separation. In a later publication (215) and patent (118) they suggest the use of baffles to induce swirls in gaseous thermogravitational thermal diffusion columns. In some of their early work with a hot-wire column, Clusius and Dickel (216) found that spacers holding the wire in place seemed to enhance separations. Akhlayou, Murin, and Ratner (217) found in 1943 that baffles of cinematographic film magnified separations in batch thermogravitational columns, with only a small increase in the time required to achieve steady state.

Jones and Furry (54) disagreed with the hypothesis that separations were improved by swirls or turbulence. They contended that if separations increased with the introduction of baffles in thermogravitational columns, then the function of the baffles was to reduce turbulence previously existing in the column. The work of Donaldson and Watson (202) and Watson (218) in 1951 and 1952 tended to support the work of Bramley and Brewer (201, 215). Watson introduced small wire turbulence promoters along the column, and markedly improved the separations obtained. However, David (219) in 1954 reported reduced column effectiveness because of wire spacers. Also, in 1956, Corbett and Watson (220) found that spacers had no effect on the separations they obtained in a

gaseous thermogravitational thermal diffusion column. They explained this as a consequence of their carefully constructed column.

Treacy (221) and Treacy and Rich (222) installed various horizontal, vertical, and combinations of horizontal and vertical barriers in a gaseous thermogravitational column. In every case, they showed an increase in separation in continuous-flow experiments. In batch runs they showed an excellent increase in separation with barriers. However, in contrast to Alkhouy, Murin and Ratner (217), Treacy and Rich report a decrease in the time required to reach steady-state with barriers when compared to no barriers in their batch thermogravitational column. The work of Treacy and Rich will be discussed in more detail later in this chapter.

In a patent, Jones and Milberger (152) present considerable qualitative continuous-flow data obtained using a single vertical barrier in a liquid thermogravitational column. They showed an increase in separation with the use of vertical barriers with unusual and normal flow patterns. This work will be reviewed later in this chapter.

Also in the patent literature, Scovill (157) recommends the use of vertical barriers in an unusual arrangement of thermogravitational columns. No data are presented.

The apparatus of Von Halle (50) was not a thermogravitational column, but was a horizontal thermal diffusion apparatus with circulation provided by external pumps. The

passing streams were separated by a permeable cellophane barrier. Advantages claimed were: no appearance of the "forgotten effect," less parasitic remixing of passing streams, and optimum control of flow in the passing streams (rather than relying on convection as in the thermogravitational method). In the theoretical analysis presented, Von Halle chose to interpret the results in terms of stage length and separation factor, because the approach of Furry, Jones, and Onsager could not be used.

Discussion of Previous Vertical Barrier Work

In this discussion, the word barrier will always mean a device affecting the flow or diffusion pattern in a thermogravitational thermal diffusion column. These barriers should not be confused with the fritted glass (58, 223-225) or cellophane (226-228) diaphragms as used in single-stage thermal diffusion cells by the investigators cited above. Single-stage cells have been briefly described in Chapter I.

Treacy and Rich (221, 222).--The gas-phase thermogravitational column used was somewhat crudely constructed, but apparently operated satisfactorily. The apparatus was a concentric cylinder device. The outer cooled wall was made from 2-inch water pipe, and the inner heated cylinder from 1/4-inch water pipe. The column was 23 inches long, and closed with couplers and plugs. Sample cocks could be used for batch or continuous-flow operation. The system used in all runs was methane-nitrogen.

Horizontal barriers were metallic disks supported in the column with a small clearance at the hot and cold walls. Vertical barriers were made from perforated metallic conduit and supported in the column. Combinations of these types of barriers were also used.

In transient batch experiments, every type of barrier showed a separation enhancement over the separation attained in the column operated without barriers; sometimes by as much as a factor of six. The rate of separation was increased by as much as a factor of ten. The most effective barrier arrangement consisted of one vertical barrier, in combination with horizontal barriers spaced along the length of the column.

Under steady-state continuous-flow conditions, the separation achieved with all types of barriers was significantly better than obtained without barriers. Unusual maxima occurred in the separations at certain product flow rates.

The effect of the size of the perforations in the vertical barriers was investigated. No change in separation was detected when the perforation size was varied from $1/64$ to $9/64$ inches, keeping the percentage open area in the vertical barrier the same. A maximum separation was noted at about 20 per cent open area when the percentage open area in the vertical barrier was varied while keeping the same perforation size.

The spacing between horizontal barriers was varied. When separation as a function of horizontal barrier spacing

was plotted, a rather broad maximum was noted. This maximum occurred when the distance between horizontal barriers was roughly equal to the space between the hot and cold surfaces in the column. When asbestos horizontal barriers were tested, separation was not effected. This was attributed to the difference in thermal conductivity between asbestos and metallic barriers.

Treacy and Rich offer considerable conjecture and discussion about all of the above effects. However, almost no theoretical and mathematical work is presented.

Jones and Milberger (152).--Considerable qualitative data, obtained in parallel-plate liquid thermogravitational thermal diffusion columns, is presented in this patent. Vertical barriers were installed in the columns, similar to the arrangements sketched in Chapter III. Jones and Milberger recommend plate spacings of up to 0.15 inches. They state that there is no lower limit to the plate spacings that can be used, but feel that the mechanical problems encountered in installing vertical barriers at very low plate spacings (below 0.01 inches) are almost insurmountable. The writer is in wholehearted agreement on this point.

The vertical barriers used were permeable membranes including bond paper of various grades, duplicator paper, tracing paper, porous stainless steel, clay impregnated fiber-glass, and films of bentonite clay. These investigators suggest that the pores in the preferred membranes should be

large enough to allow free molecular transfer (diffusion), but sufficiently small to allow a minimum of gross transport (bulk flow).

The columns of Jones and Milberger were operated under continuous-flow steady-state conditions. The liquid feed used in all cases was an equal molar mixture of cetane and methylnaphthalene. Separations obtained were expressed as a difference in refractive index measured at 20°C. A variety of flow patterns were used, and, in general, separations obtained using a vertical barrier were significantly greater than the separations attained in the same column without a barrier. In some cases, using unusual flow patterns, the separations exhibited a maximum at certain flow rates. Such maxima were also observed by Treacy and Rich (222).

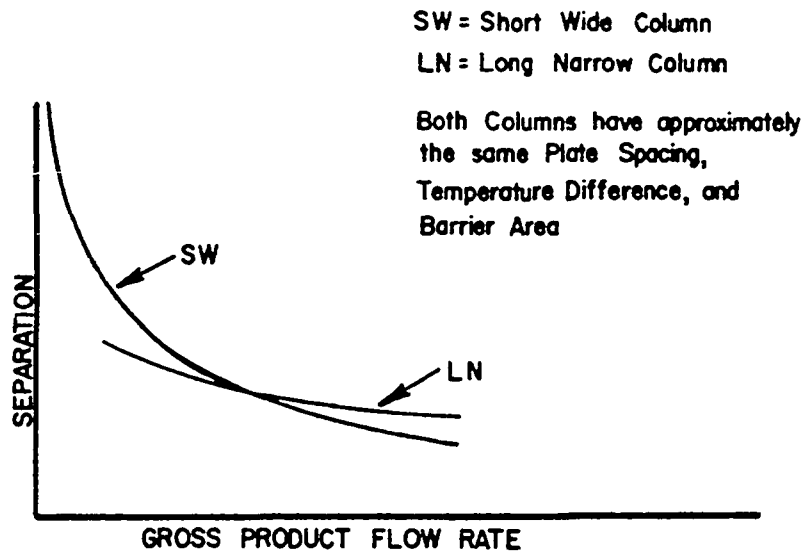
While the data of Jones and Milberger seem reasonable, some of their conclusions appear to be in error. These errors were probably induced by a faulty type of graphical presentation. They state that in a thermogravitational column, the separation is proportional to length. This is true only for the batch case. In fact at appreciable product flow rates the theoretical separation (54) becomes independent of length; a view substantiated by Powers (58) and Longmire (106). In studying the effect of column length using vertical barriers, Jones and Milberger used two columns. Both columns had about the same plate spacing, temperature difference, and

barrier area. However, one column was long and narrow and the other short and wide; the length varying by a factor of four. A qualitative sketch of the type of separation-flow data obtained with the two vertical barrier thermogravitational columns as reported by Jones and Milberger is shown in Figure 2A. From this type of plot they draw the conclusion that the separation is not any function of length; but is only proportional to the barrier area, all other things being equal. However, if such data are replotted in terms of flow per unit width, as in Figure 2B, the longer column shows, qualitatively at least, the advantage expected from theory. Jones and Milberger present no other explanations of the operation of thermogravitational columns with vertical barriers.

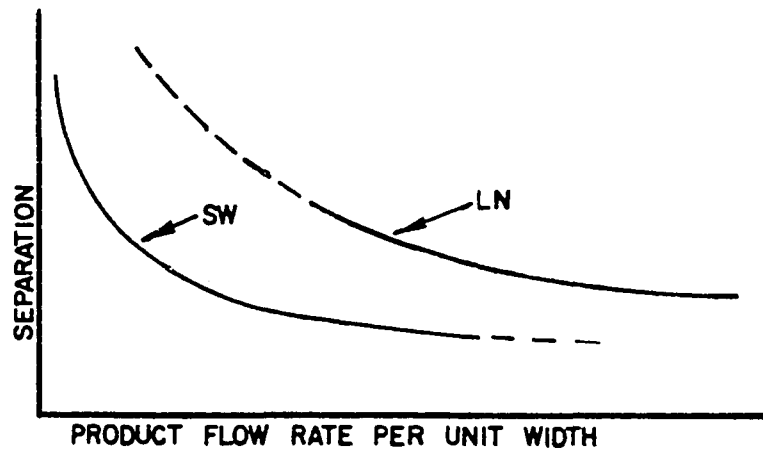
Conclusion

On the basis of the literature reviewed in this chapter, the following conclusions are drawn:

- a) The thermogravitational thermal diffusion column theory is qualitatively correct, and can be used to predict the effect of changes in column operation if the fluid is in laminar flow.
- b) Turbulence and numerous mechanical devices have been tried in attempts to increase separations obtained in thermogravitational columns with some success, but little agreement between various workers.
- c) Almost no theoretical work has been directed toward an



(A) Data as plotted by Jones and Milberger



(B) Data replotted on basis of Flow Rate per Unit Width

Figure 2 - Qualitative Representation of Vertical Barrier Data of Jones and Milberger

explanation of the function of barriers in thermogravitational columns, and such theory is needed to design optimum barrier systems.

CHAPTER III

EXPERIMENTAL INVESTIGATION

Continuous-Flow Thermogravitational Column

The basic thermogravitational thermal diffusion column without barriers and its auxiliary equipment will be described first. Following this, the vertical barriers inserted in the column and related apparatus will be discussed.

Equipment Without Barriers.--The vertical thermogravitational column used in this investigation was a parallel flat plate device. The working dimensions of the plates measured about 4 by 58 inches. Because the product and sample ports were not quite at the end of the working space, the effective length was nearer 57 inches. The distance between the plates could be varied by using different thicknesses of gasket between the plates. The gasket material used was Garlock No. 7021.

The working space between the plates is illustrated in Figure 3. The plates were made from 304 stainless steel and the working faces were ground and hand polished to a mirror finish. The overall dimensions of each plate were 3/8

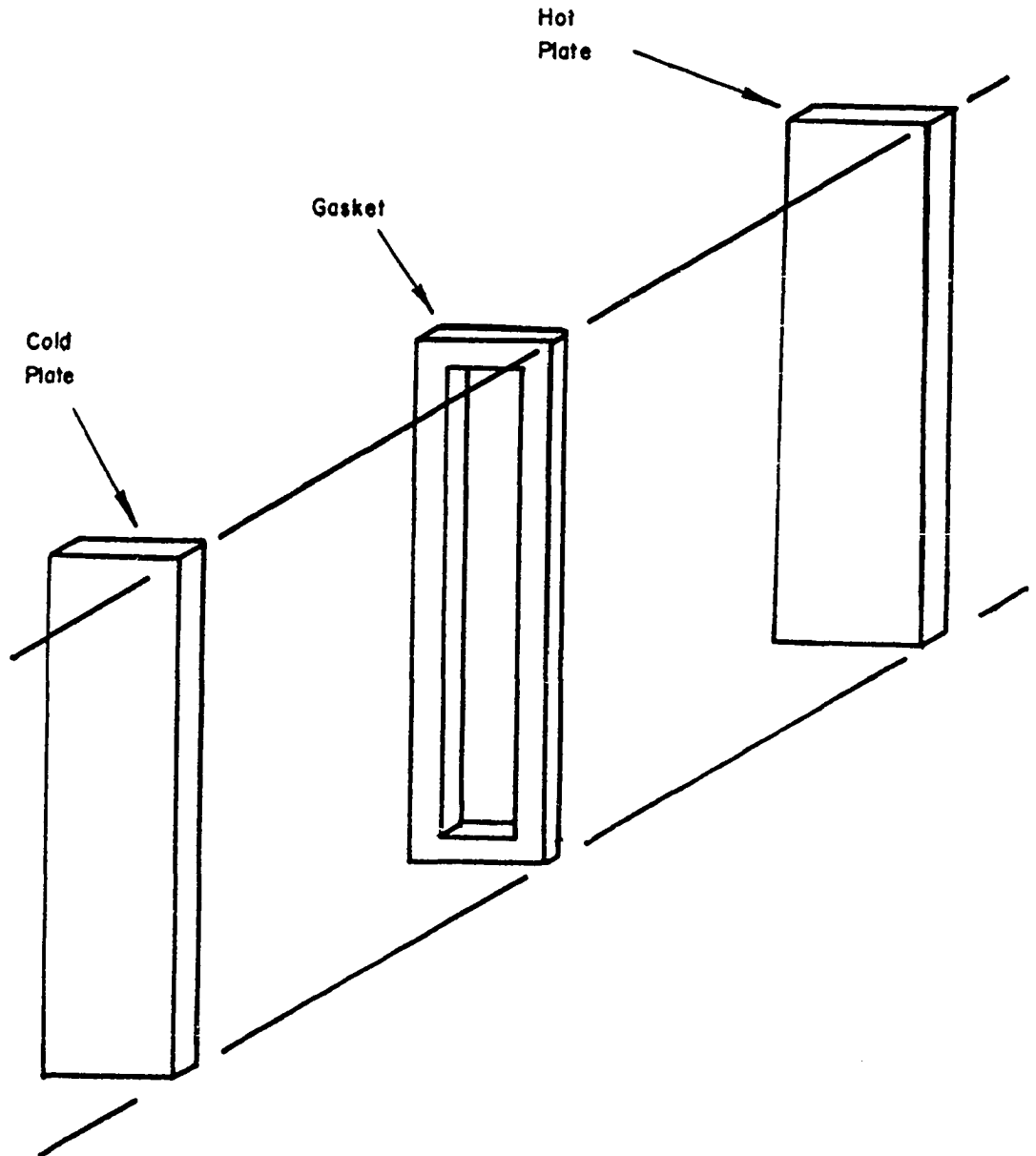


Figure 3 - Exploded View of Working Space Between Hot and Cold Plates with No Barrier in Place (All water jackets, bolts, thermocouples, and feed and product ports omitted for clarity. Vertical scale greatly foreshortened.)

by 6 by 60 inches. Two iron-constantan thermocouples were imbedded in the working face of each plate. The installation of these thermocouples was quite similar to that detailed by Powers (58). Temperatures were obtained by a Leeds and Northrup 8662 precision potentiometer.

A temperature difference across the working space was maintained by hot and cold water jackets bolted on the backs of the plates. The components of the column are shown in Figure 4. The entire assembly was held together with bolts around the periphery of the column, spaced every three inches. The bolts were of 3/8-inch diameter by 5 inches long, with National Fine Threads. These bolts have been omitted for clarity in Figures 3, 4, and 5, but are clearly visible in Figure 6. In addition to the bolts holding the entire column together, a few bolts extended only half way through the column. These few "holding" bolts were never removed, thus enabled the working space to be opened by removing the peripheral bolts without disassembling the water jackets.

A cross-section of the assembled thermal diffusion column is illustrated by Figure 5. The column was supported from the bottom by a metal stand, and was braced to the wall in a vertical position. A view of the vertical continuous-flow thermogravitational thermal diffusion column is shown in Figure 6. A vertical barrier can be seen protruding from the column in Figure 6. Barriers and barrier holding equipment will be described in detail later in this chapter.

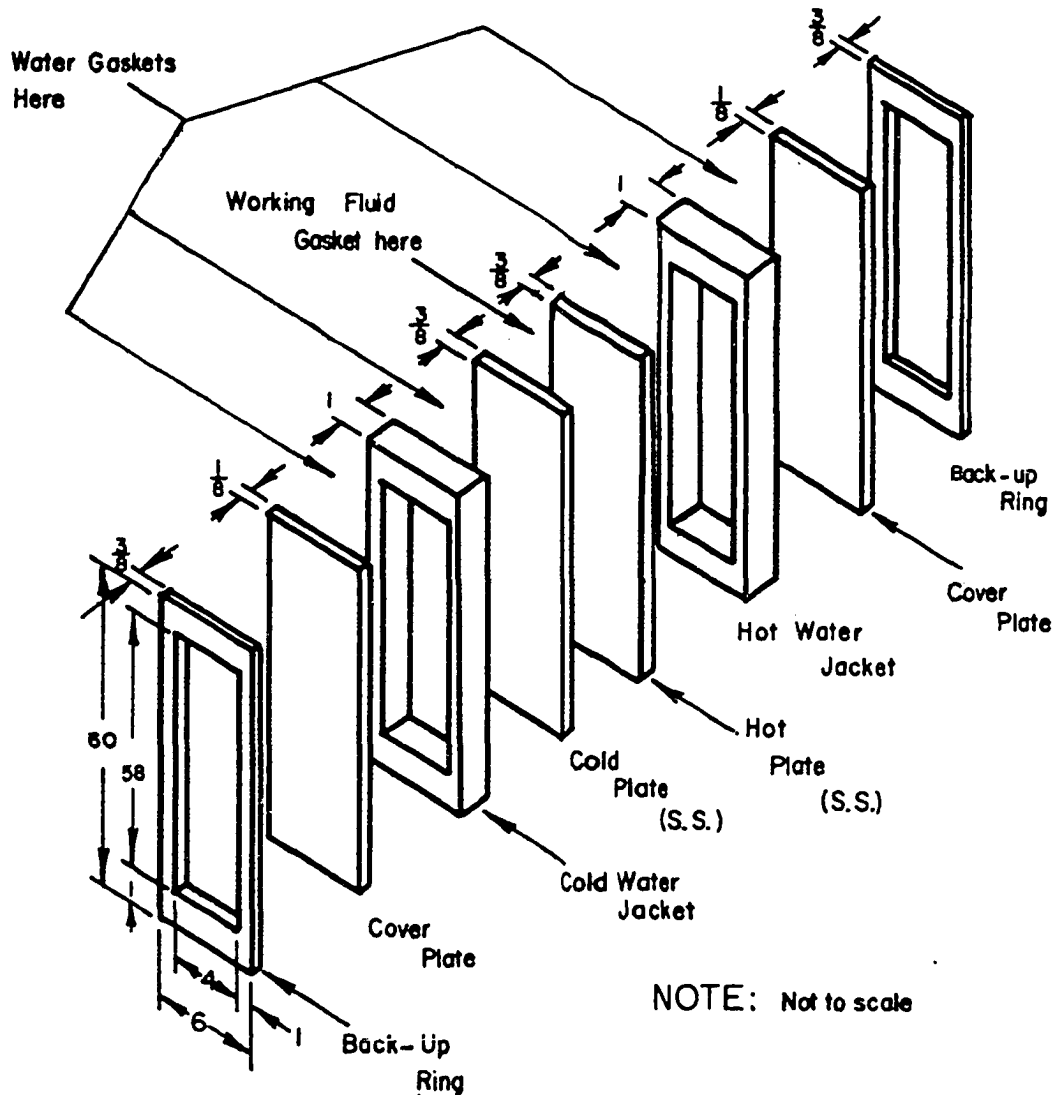


Figure 4 - Exploded Sketch of Components of Thermo-gravitational Thermal Diffusion Column
(All bolts, bolt holes, gaskets, thermocouples, hot and cold water ports, and feed and product ports have been omitted for clarity.)

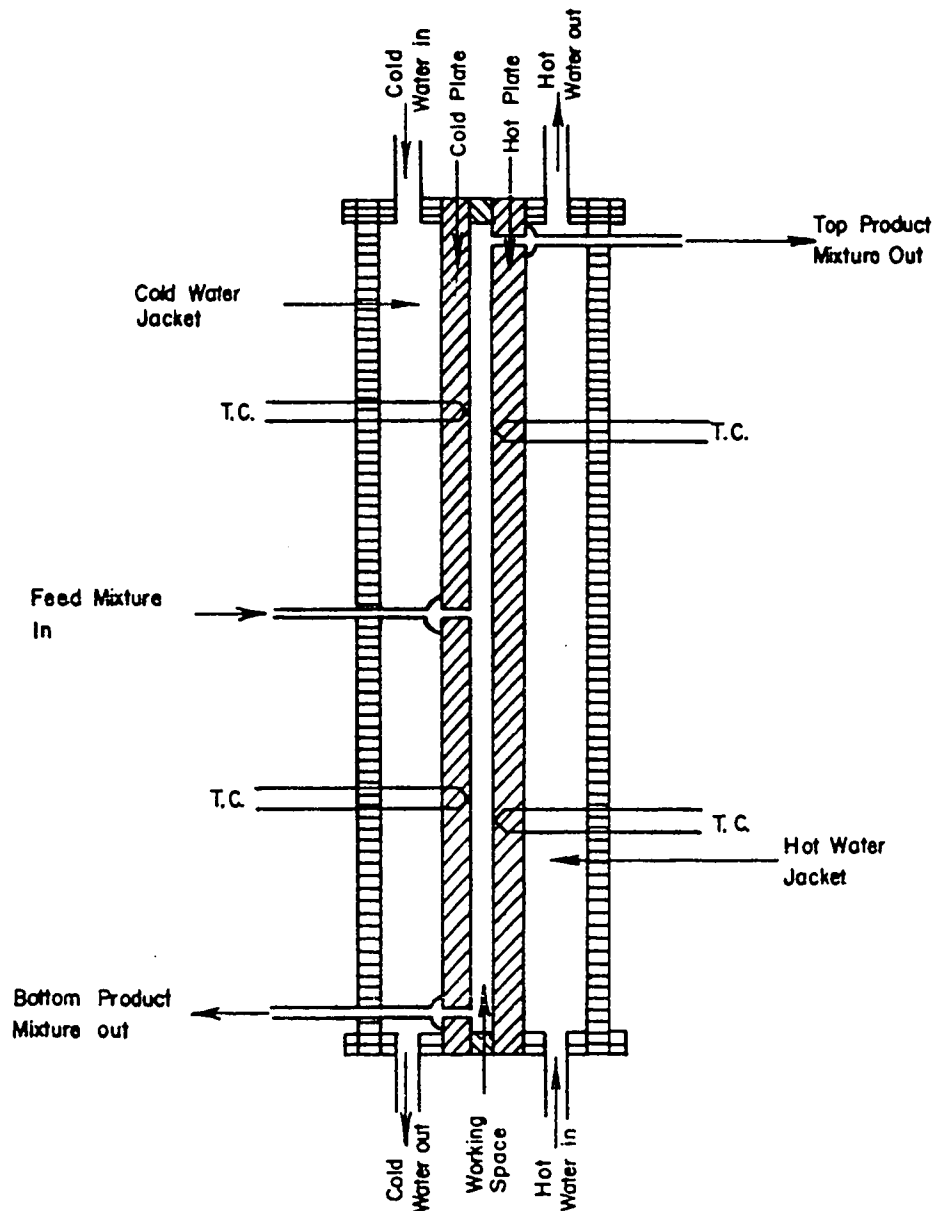


Figure 5 - Cross Section of Continuous Thermogravimetric Thermal Diffusion Column Without Barriers (Vertical scale greatly foreshortened. Bolts and bolt holes omitted for clarity.)



Figure 6 - View of Thermogravitational Thermal Diffusion
Column (Tracing Paper Barrier in Place)

The essentials of the gravity-flow feed and product draw-off system are presented in Figure 7. All material contacted by the working fluid was either aluminum, copper, brass, Teflon, stainless steel, or glass.

The feed was stored in a 15-gallon aluminum vessel about 13 feet above floor level. A sight glass was provided to observe the liquid level in the feed tank. Feed solution was periodically added to the feed tank through a line not shown in Figure 7. Air pressure was used to rapidly elevate 5-gallon batches of feed as required. A number of runs could be made without refilling the gravity feed tank.

Any dissolved gases in the liquid feed were driven off by an electric heater surrounding the feed line below the feed tank. A thermocouple soldered to the feed line downstream of the heater measured the degassing temperature. A Powerstat in the heater circuit regulated the degassing temperature to a level always higher than the temperatures encountered in the column. Any feed liquid vaporized in the degassing operation was returned to the system by a condenser on the vent line. The feed was cooled to room temperature with tap water before entering the column.

Each feed entry or product draw-off in the column consisted of 40 holes, each 1/32-inch in diameter, drilled horizontally through the plates. A header soldered over the holes on the back of the plate distributed the feed or gathered the product to or from the holes. The products from

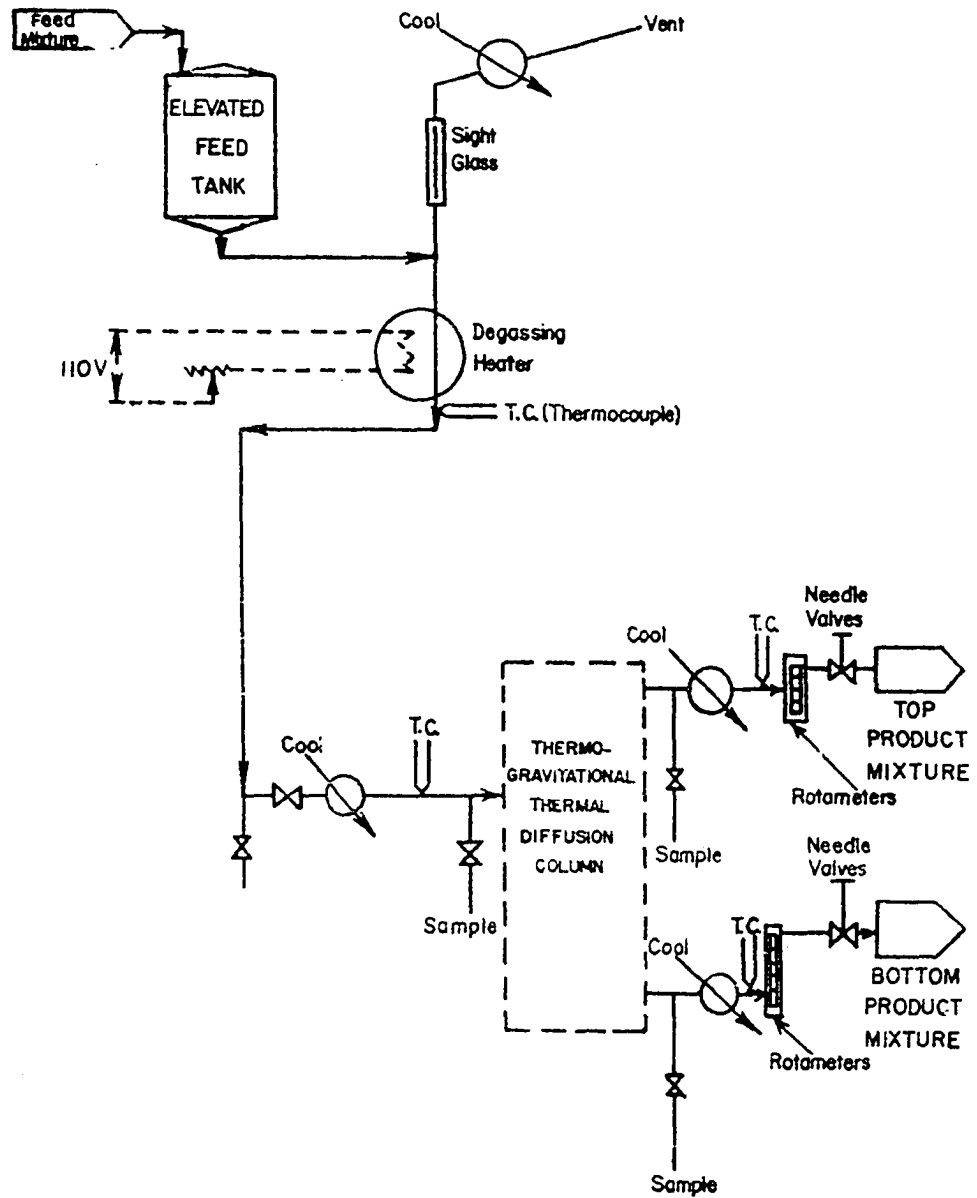


Figure 7 - Feed and Product Mixture Flow Diagram

the column were cooled with tap water. Sample taps were long hypodermic needles which were installed in the feed or product lines as shown in Figure 8. The needles extended all the way into the column to eliminate any sampling lag. This also allowed transient batch (no flow) studies.

The product flow rates were indicated on two banks of Fischer and Porter Flowrater rotameters. The range covered by these rotameters was about 0.02 to 200 grams per minute. The product flow rates were controlled at high rates (greater than one gram per minute) by 1/4 and 1/8-inch needle valves (AVECO Series 1050). At low flow rates (less than one gram per minute), the needle valves were unreliable. Various lengths of 26-gauge stainless steel tubing were placed in series with the product lines to obtain steady flow at low rates.

The flow diagram for the hot and cold circulating water systems which maintained a temperature difference across the thermogravitational thermal diffusion column is depicted in Figure 9. A hot and cold water flow rate of 25 gallons per minute was maintained on all runs. This flow rate limited the vertical temperature change of either the hot or cold water through the water jackets to less than 0.6°C.

Elevated hot and cold water surge tanks were made from 55-gallon drums. These surge tanks were insulated with two layers of hair-felt building insulation and two layers

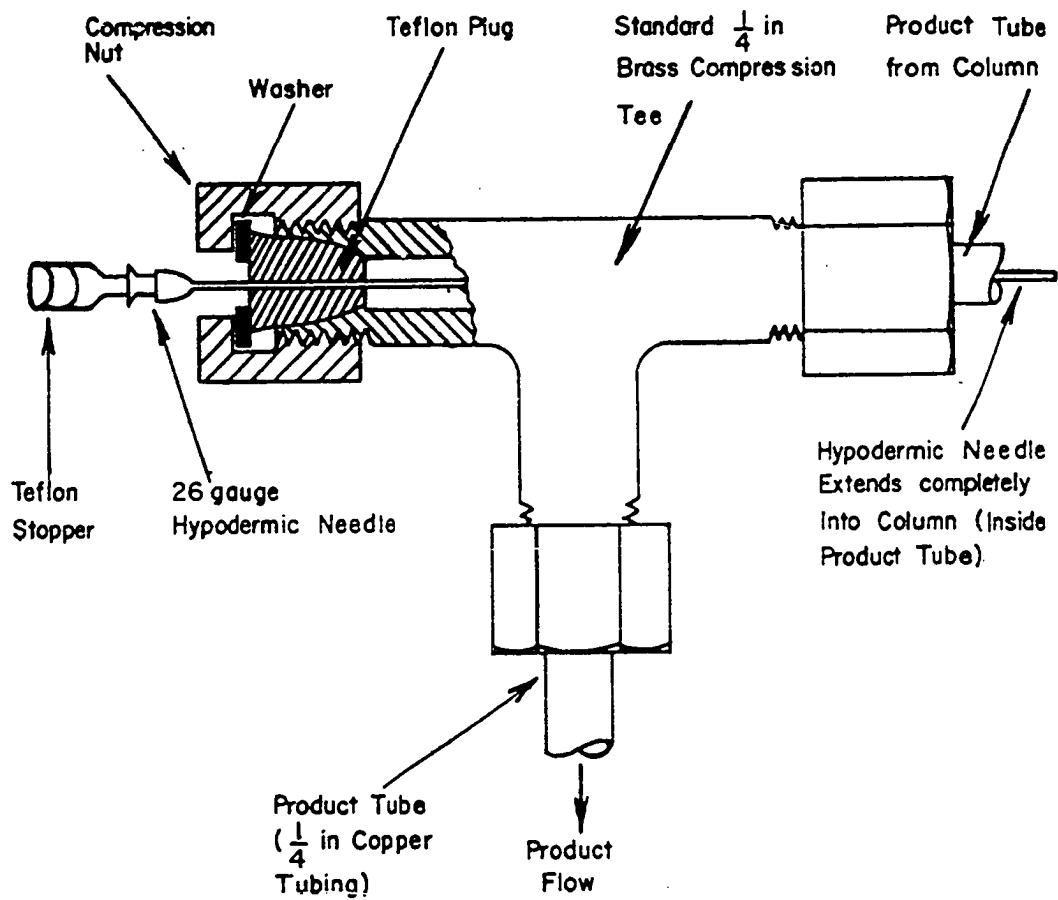


Figure 8 - Detail of Sample Tap

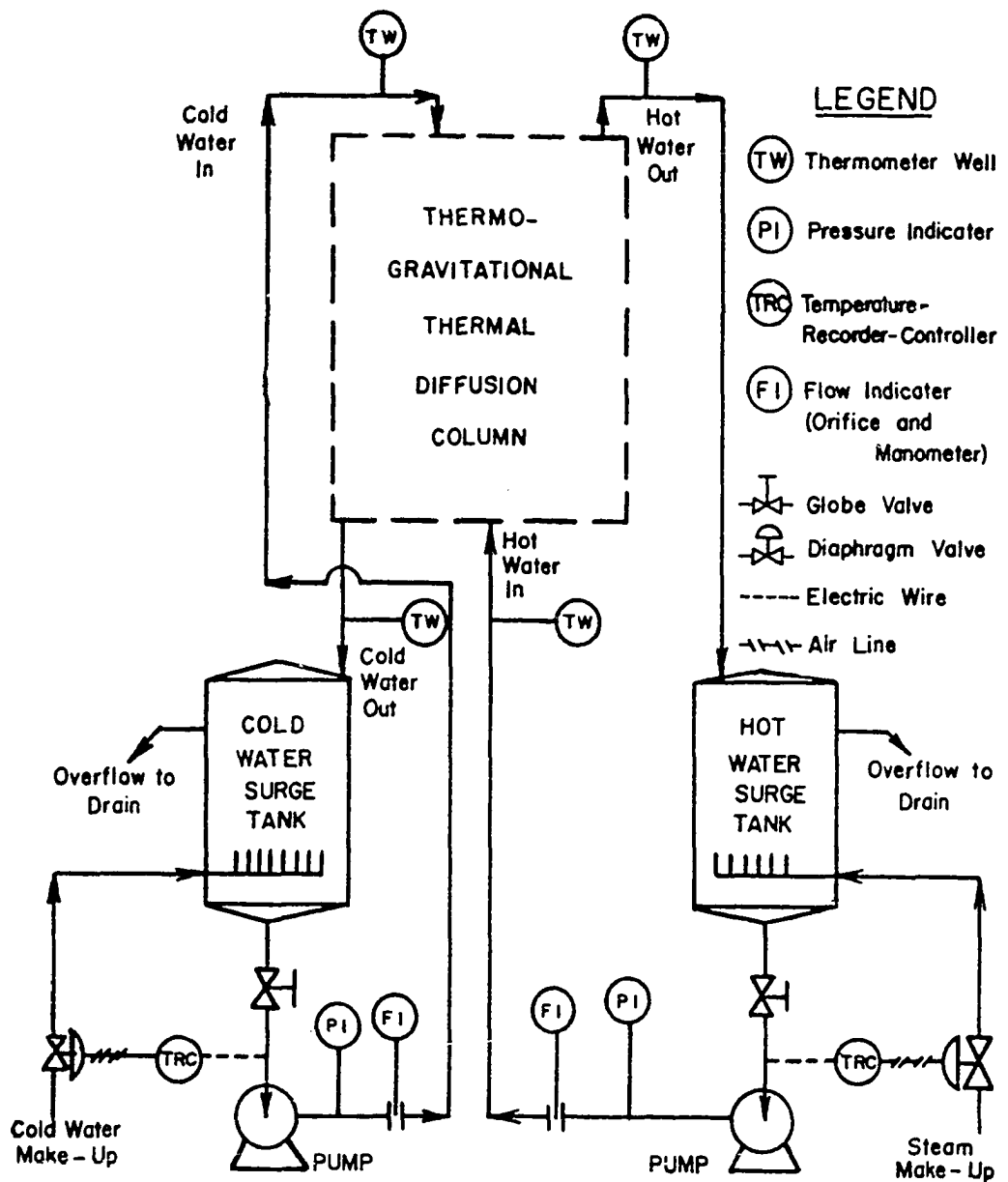


Figure 9 - Hot and Cold Circulating Water Flow Diagram

of tar paper. Cold tap water was added to the cold water tank, and 85 psig saturated steam added to the hot water tank through spargers near the bottom of the tanks. Overflow lines were provided near the top of the tanks. Liquid level could be observed in sight glasses. A view of these hot and cold circulating water surge tanks is shown in Figure 10. The hot and cold water was circulated by 1/2-horsepower pumps (Worthington, Model 1DN-2). A view of these pumps is shown in Figure 11.

The amount of cold tap water and steam added to the circulating systems was regulated by Honeywell air operated diaphragm valves. These valves were actuated by Brown circular-chart Electronik temperature-recorder-controllers. Thermocouples (Brown Type T, copper-constantan) located in the pump suctions supplied the input signals to the controllers. Temperature variations were generally less than 0.1°C.

The amount of water circulated was regulated by globe valves. The water flow rates were indicated by mercury manometers. The manometers were used in conjunction with sharp-edged orifices in the water circulating lines. The manometers were calibrated in place, and the calibration data are presented in Appendix N.

All the main lines in the water systems were of nominal 1½-inch diameter, schedule 40 pipe. The lines were covered with Air-O-Cell insulation. The piping was connected to the column by rubber hoses as seen in Figure 6.

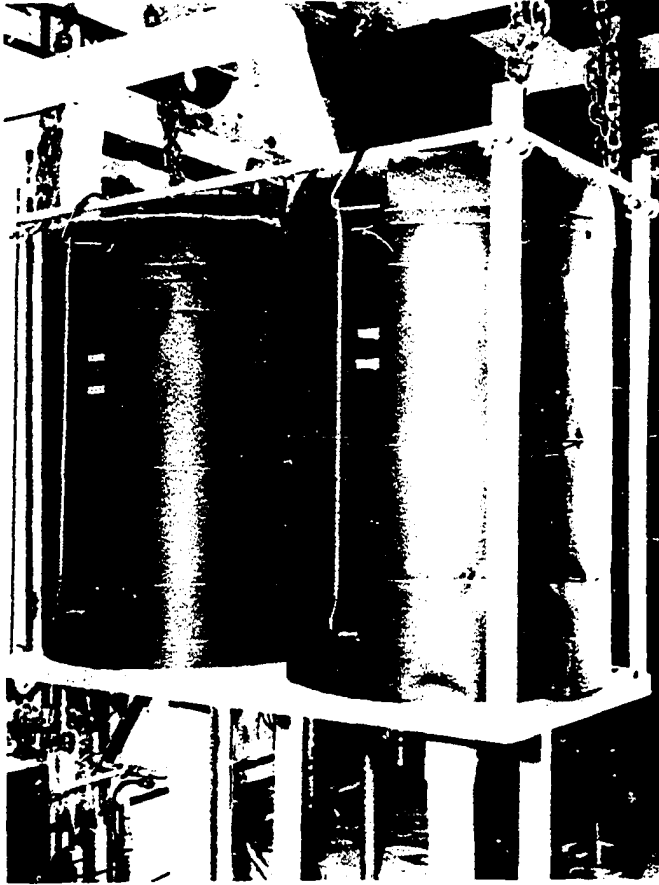


Figure 10 - Elevated Hot and Cold water Surge Tanks

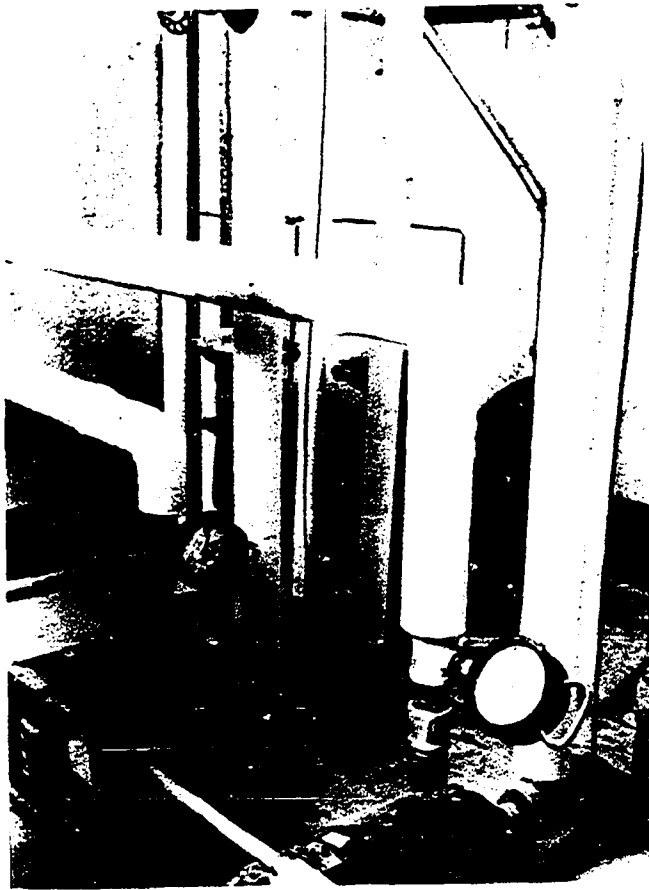


Figure 11 - Hot and Cold Water Pumps

Thermometers installed in all water lines entering and leaving the column served as checks on the temperature-recorder-controllers.

Where possible, instruments were centralized on a control panel. A view of the control panel is shown in Figure 12.

Barriers and Barrier Auxiliaries.---Several types of single vertical barriers were tested during this investigation; perforated aluminum foil, perforated Mylar, and tracing paper. Detailed specifications of all barriers are presented in Appendix D.

The location of the vertical barrier in the working space of the column is illustrated by Figure 13. A cross-section of the column with a vertical barrier in place is shown in Figure 14. Notice that the column was modified to have feed and product ports on both the hot and cold plates during most runs with barriers. The flow patterns used on all experimental sets of data are given in Appendix E. Individual flow rate control was exercised on all product flows.

In order to center the barrier between the plates and prevent sagging, the barrier was tightly stretched horizontally. Barriers were always cut large enough to extend beyond the sides of the column. The edges of the barrier were clamped between metal strips which could be pulled away from the column with thumbscrews. A sketch of the arrangement



Figure 12 - Central Control Panel

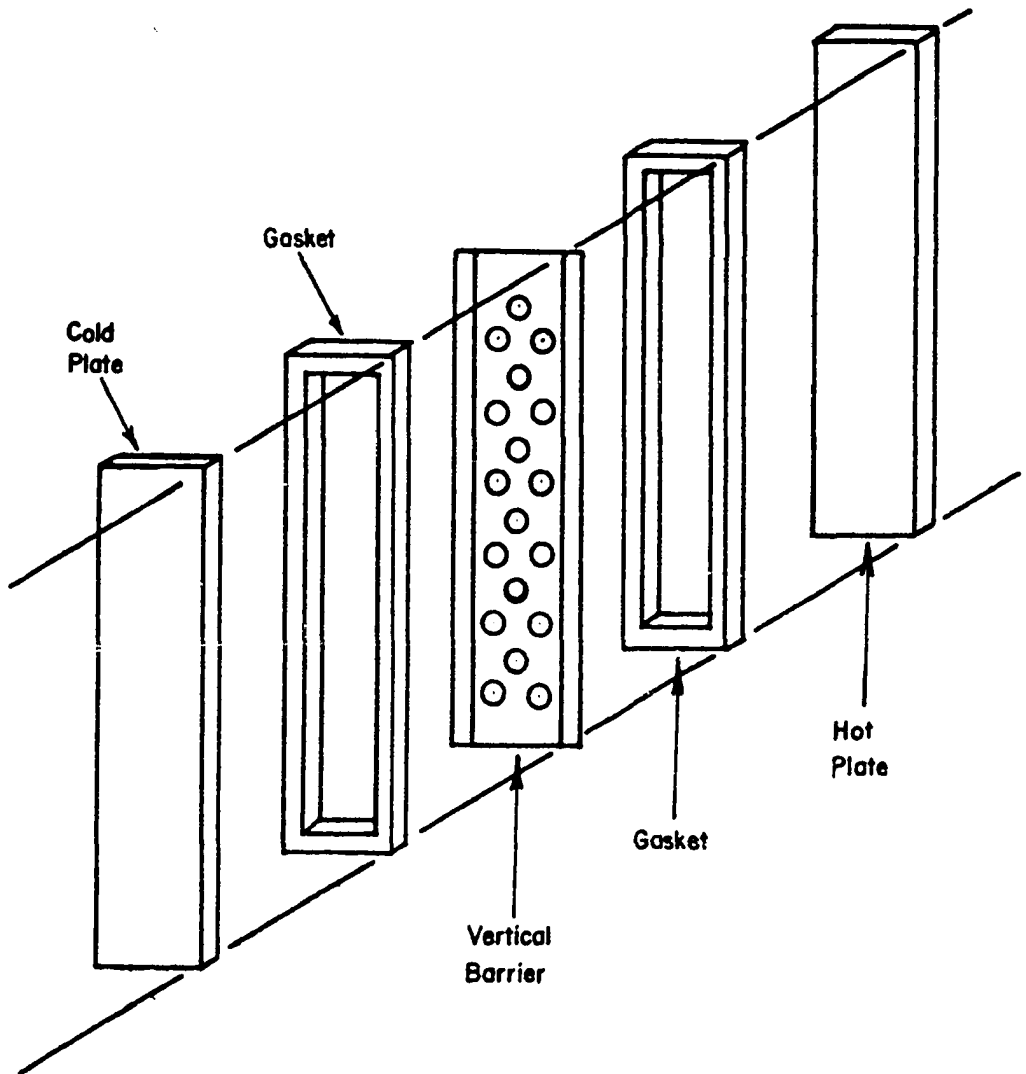


Figure 13 - Exploded View of Working Space Between Hot and Cold Plates with a Single Vertical Barrier in Place (All water jackets, bolts, thermocouples, and feed and product ports omitted for clarity. Vertical scale greatly foreshortened and size of barrier perforations greatly exaggerated.)

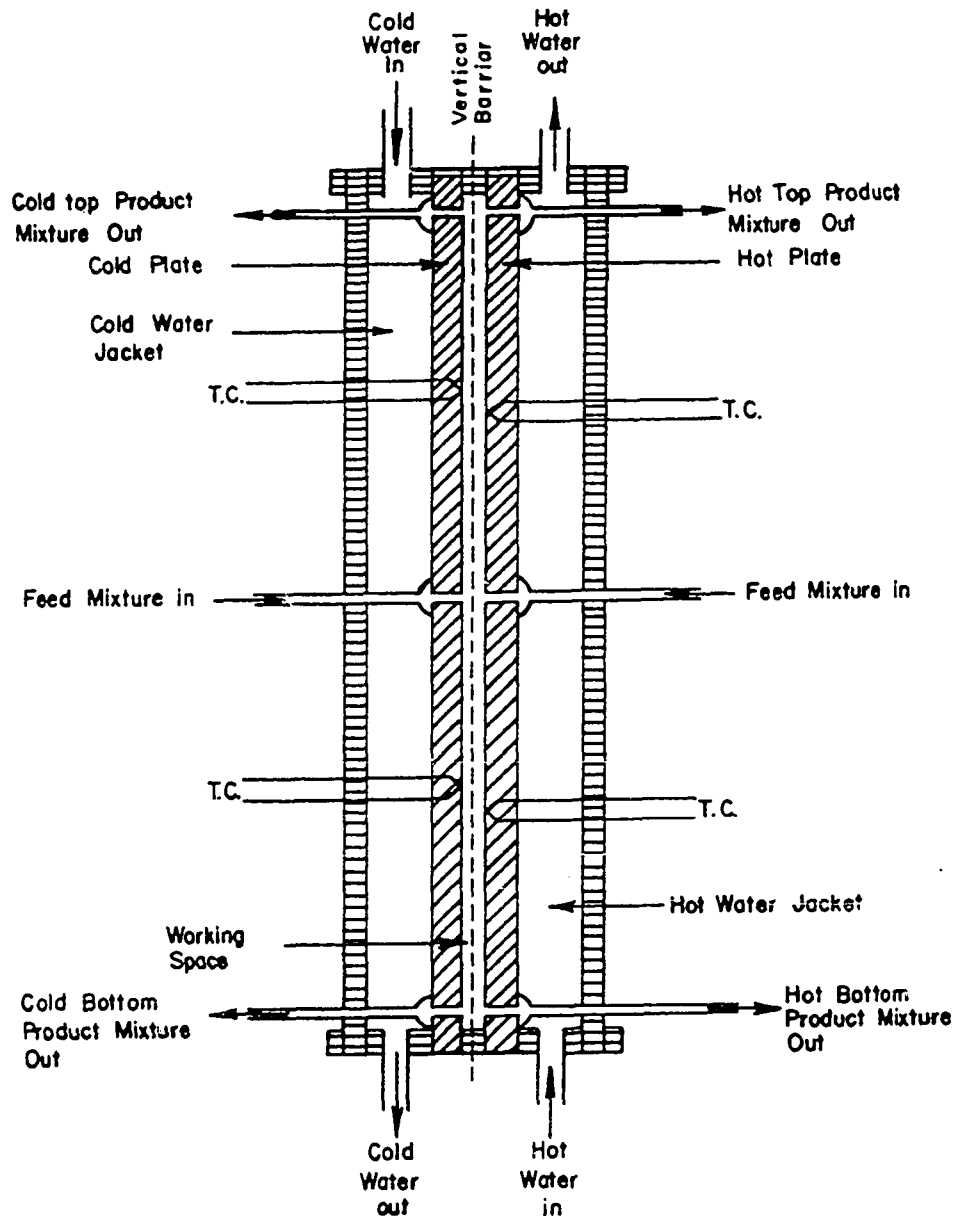


Figure 14 - Cross Section of Continuous Thermogravitational Thermal Diffusion Column with Vertical Barrier (Vertical scale greatly foreshortened. Bolts and bolt holes omitted for clarity.)

of the clamping strips and stretching screws is shown in Figure 15. A close-up view of the stretching device used is presented in Figure 16. The clamping strips extended over the vertical length of the column. Four stretching screws as shown in Figures 15 and 16 were spaced along the clamping strips. The clamping strips holding a barrier on one side of the column are visible in Figure 6.

The barrier stretching apparatus described above worked very well for Mylar barriers. The apparatus was also satisfactory for tracing paper barriers, with one qualification. The paper used sagged when initially wetted with the process solution. Therefore, when tracing paper barriers were installed, they were subjected to alternate soaking and stretching operation to attain a tightly stretched barrier. The stretching apparatus was completely unsatisfactory for aluminum foil barriers. Aluminum foil could not be uniformly stretched, and wrinkles in the barrier could not be eliminated.

Procedures.--In experimental runs with the continuous-flow thermogravitational thermal diffusion column, the steady-state separation was obtained as a function of flow rate. The temperature difference and plate spacing were treated as parameters. A set of runs consisted of a series of separation-flow rate determinations for a fixed temperature difference and plate spacing. The type of barrier is also obviously a parameter in data taken with barriers installed in the column.

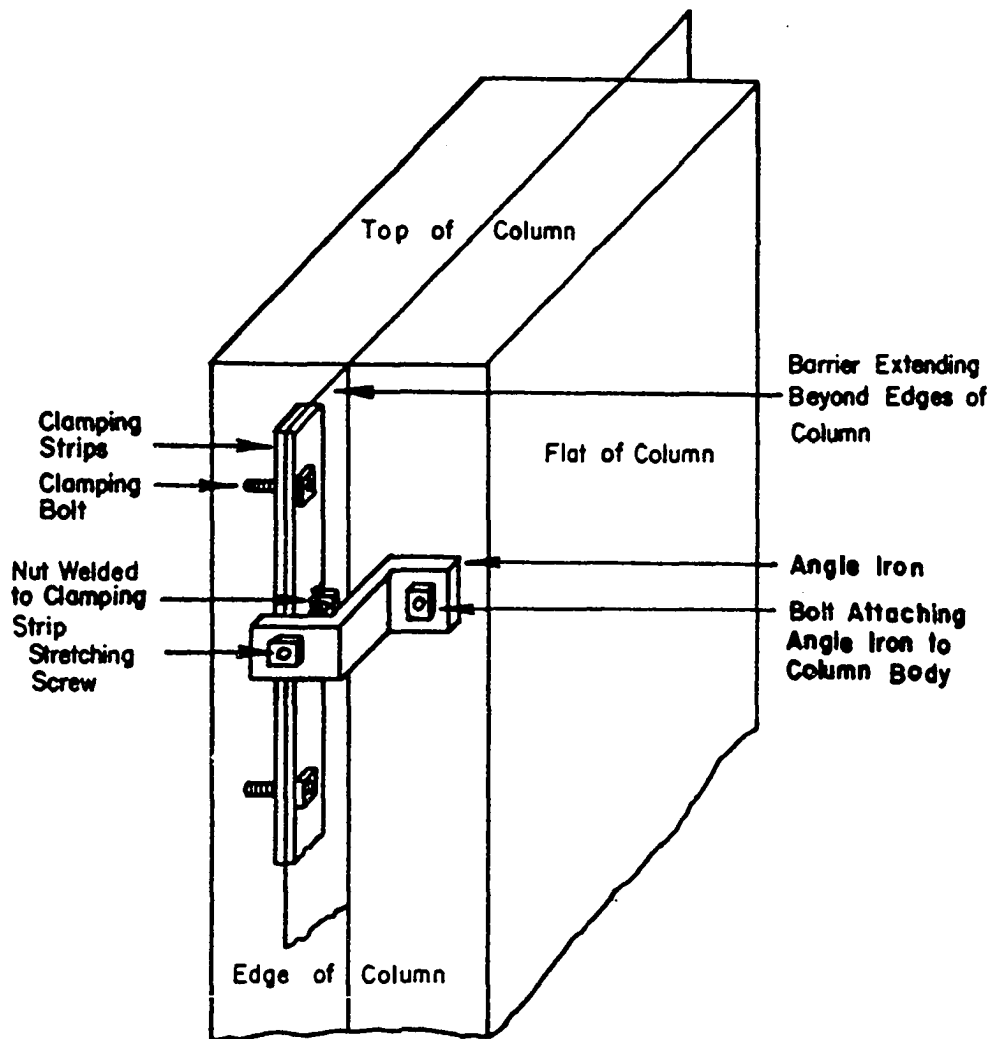


Figure 15 - Sketch Showing Clamps and Stretchers for
Barriers



Figure 16 - Close-up View of One Barrier Stretcher

A new barrier was installed each time the column was taken apart.--

Because the plate spacing appears in the theory in such a severe fashion, a special technique was developed to accurately determine this quantity. Pairs of hardened steel balls were attached adjacent to each other on the edges of the hot and cold plates. The column was bolted together with no gasket in place. The distance between a pair of balls was determined by a micrometer (modified Lufkin, Model 1945 V) reading to one ten-thousandth of an inch. This distance is indicated as δ_1 in Figure 17A. The column was then taken apart and reassembled with a gasket (or gaskets and barrier) in place, and another reading taken between the same pair of balls. This reading is shown as δ_2 in Figure 17B. The plate spacing at that point is then the difference between the readings δ_2 and δ_1 . Eight pairs of balls were spaced around the edges of the column, and the average of all measured points was reported as the plate spacing for a run. This method of plate spacing determination was checked with the volumetric method described by Powers (58), and found to be in good agreement.

Prior to taking a set of data, the column was assembled with whatever barrier and gasket thickness (approximate plate spacing) was to be investigated. The column was carefully assembled with alignment pins and a torque wrench. The gaskets used exhibited some elastic creep, and no

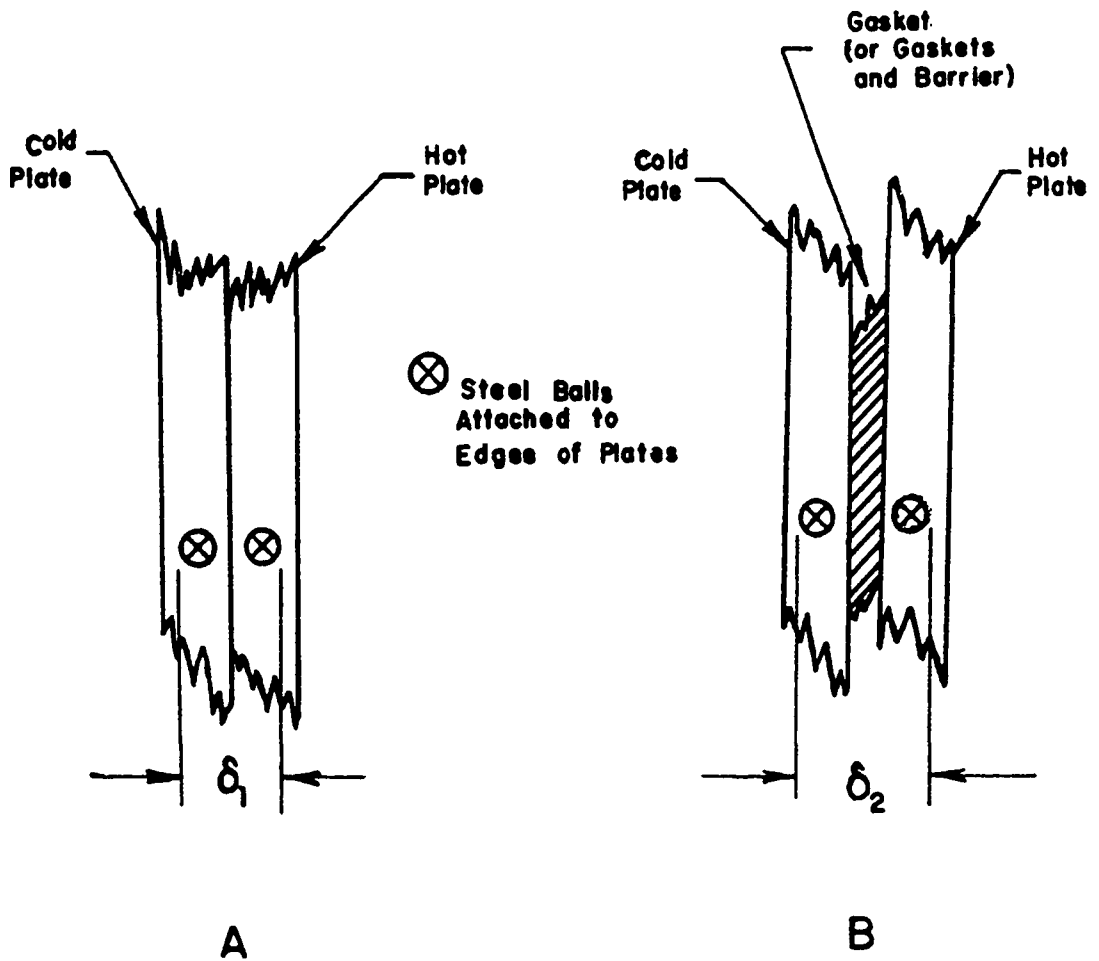


Figure 17 - Illustrating Method of Determining Plate Spacing

experimental data were taken until plate spacing measurements were stable over a period of several days. About a week was required for the greater part of the gasket creep to occur.

When the plate spacing measurements stabilized, the hot and cold circulating water systems were started up and lined out at the selected temperatures. The mean column temperature level was taken as the arithmetic average of the values indicated by the hot and cold water temperature-recorder-controllers. The mean thermogravitational column temperature, on this basis, was held at 48.9°C. (120°F.) during all experimental runs.

The feed lines were purged and product flow rates set at the desired values, as indicated by rotameters. Actual reported flow rates were calculated from weighed samples taken over a measured time interval. Flow rate sample bottles were immersed in ice water during collection of the samples to reduce evaporation losses in low flow rate samples. Product composition samples were taken from the column with hypodermic syringes, and analyzed with a calibrated refractometer. Product composition samples were repeated until steady-state was indicated.

When steady-state was achieved, three readings of all values were taken and averaged for a reported run. Sufficient time was allowed between samples for sampling disturbances to be eliminated. Sample data sheets are presented in Appendix L.

Results.---Primary data resulting were separation and flow rate for a given set of parameters. These data are summarized in Appendix B. Column and system parameters for the various sets of runs are presented in Appendix C. The type of barrier and flow pattern used are detailed in Appendices D and E. An estimate of the reliability of the various sets of data is presented in Appendix G.

Reagents and Analysis

The system ethyl alcohol-water was used throughout this investigation. A feed composition of about 40 weight percent ethyl alcohol was maintained. Mixtures were prepared from U.S.I. azeotropic (about 95 weight percent) alcohol and distilled water.

Density and viscosity data for this system were taken from the International Critical Tables (229). The International Critical Table density data were extended to higher temperatures by Powers (58) using the data of Rakshit (230). Values of the temperature coefficient of expansion were calculated by Powers (58) by determining the slopes of the above temperature-density data. Values of the diffusion coefficient were obtained from data reported by Smith and Starrow (231), Lemonde (232), and Franke (233). Values of physical properties used in the calculations are presented in Appendix K.

The ethyl alcohol-water solutions were analyzed with a Bausch and Lomb Precision Refractometer (Model No.

33-45-01). The instrument was calibrated at 25.0°C, and all determinations were made at that temperature. The calibration procedures and data are given in Appendix N. A view of the analytical laboratory is shown in Figure 18.

Barrier Bulk Flow Tests

As developed in Chapter IV on theoretical analysis, one critical characteristic of vertical barriers in thermal diffusion columns is the amount of bulk flow through the barrier. Tests were made to evaluate the flow through the tracing paper used as a barrier material.

Equipment.--The apparatus used in making these bulk flow tests is shown schematically in Figure 19. A view of the equipment is shown in Figure 20.

The apparatus consisted of two chambers formed by two open vessels clamped together with the barrier sealed between them as shown in Figures 19 and 20. The area of the barrier was measured before assembly. Both chambers were fitted with air purge nozzles to insure a liquid-full system. One chamber was equipped with an overflow device. The other chamber had a receiving cup mounted above it. A burette was placed immediately above the receiving cup.

Procedure.--The vessels were filled with 40 weight percent ethyl alcohol-water solution, and the air carefully purged. The solution was allowed to stand for at least a day to make sure the barrier was completely wetted. Then a constant head was established across the barrier and maintained

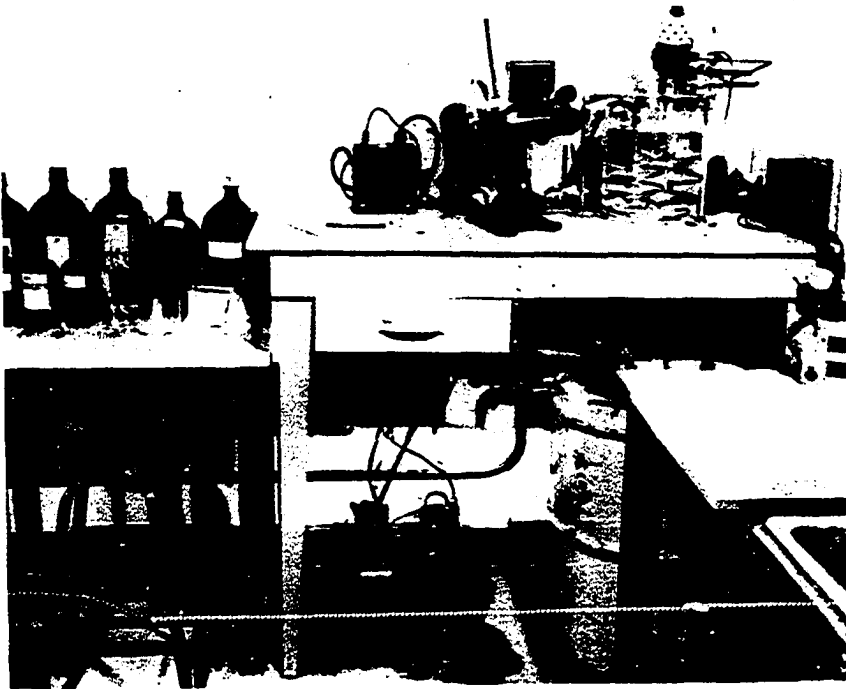


Figure 18 - Analytical Laboratory

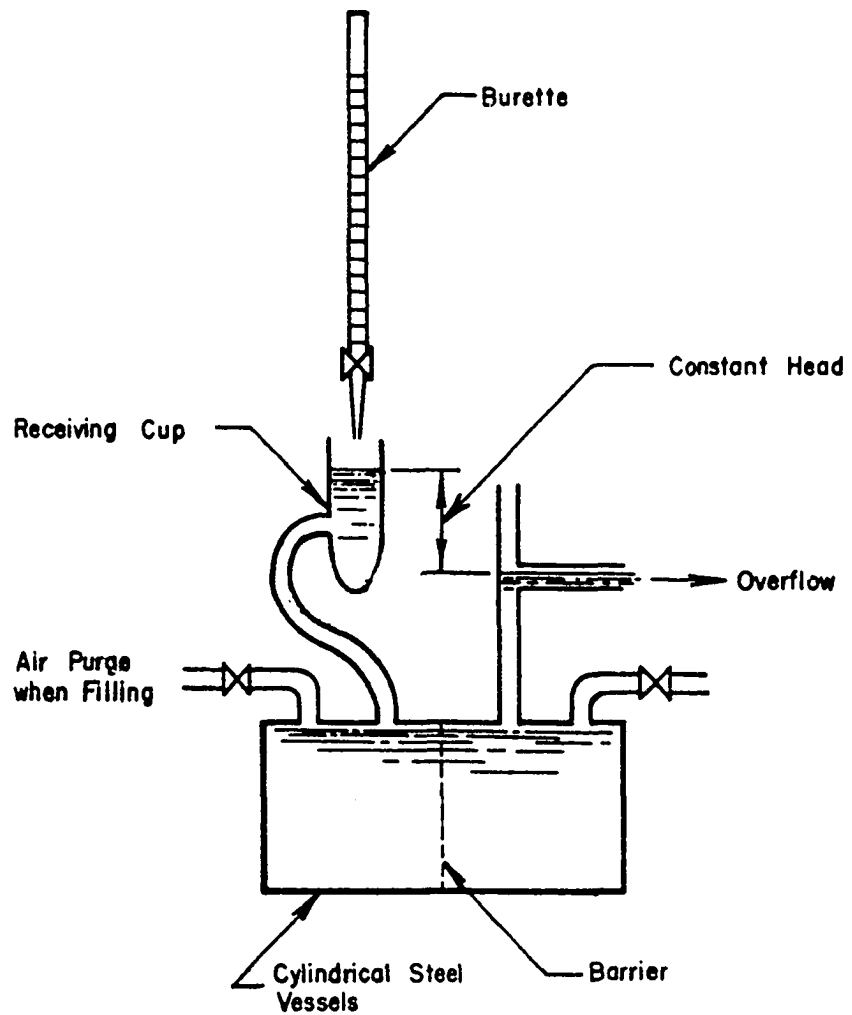


Figure 19 - Schematic Diagram of Apparatus for
Measuring Bulk Flow Through Barriers

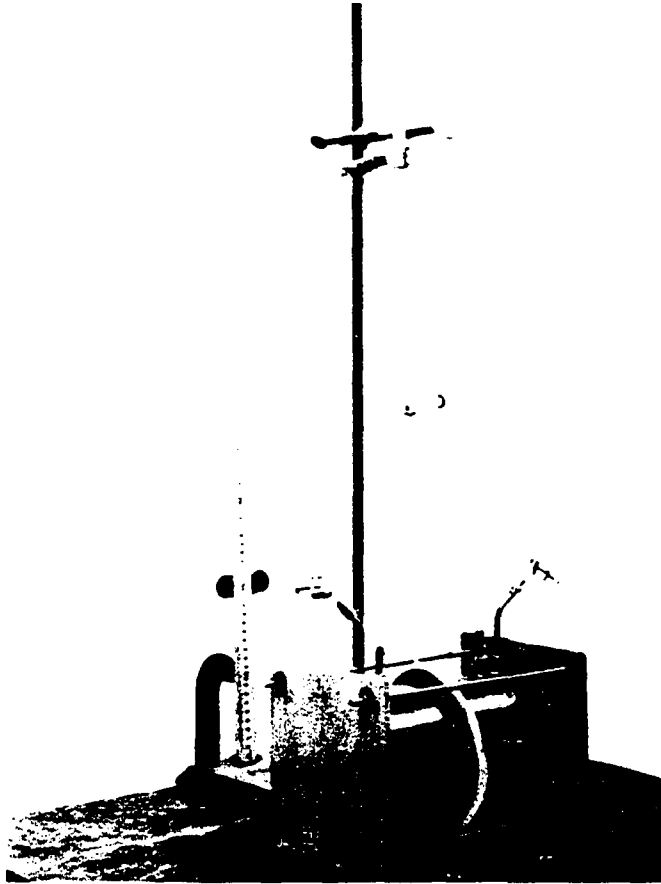


Figure 20 - View of Apparatus for Measuring Bulk Flow
Through Barriers

for several hours to allow any stretching of the barrier that might take place to occur.

After these preliminaries, the burette reading was taken and the time noted. The head was then maintained at the selected height by additions from the burette. The head was measured with a ruler, and the room temperature was noted. After a few hours (during which periodic additions were made from the burette), time and burette readings were taken again.

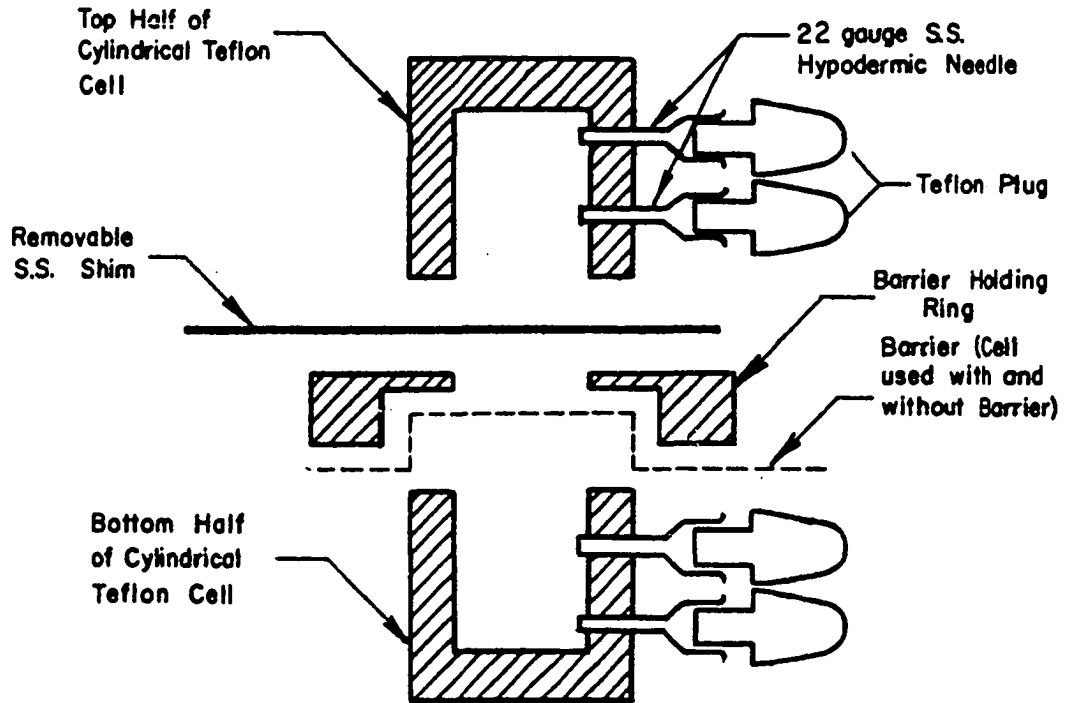
Results.--The data obtained from these tests are presented in Appendix H. Sample calculations on these data are shown in Appendix M, and the results discussed in Chapter V.

Barrier Diffusion Impedence Tests

Another important characteristic of vertical barriers developed in Chapter IV is the diffusion impedence offered by the barrier. Ordinary diffusion tests were made in a diffusion cell with and without a tracing paper barrier to evaluate the diffusion impedence for this type of barrier material.

Equipment.--The apparatus used in the diffusion impedence tests is schematically depicted in Figure 21. A view of the assembled cell is shown in Figure 22.

The diffusion cell was a Teflon cylinder, divided in the center by a removable stainless steel shim. A Teflon ring held the barrier in place during runs made with a barrier. Two hypodermic needles were imbedded in each half



NOTE: When cell is used, the assembly is clamped tightly together to prevent leakage.

Figure 21 - Exploded Schematic Diagram of Apparatus
Used for Measuring Diffusion Impedence
of Barriers

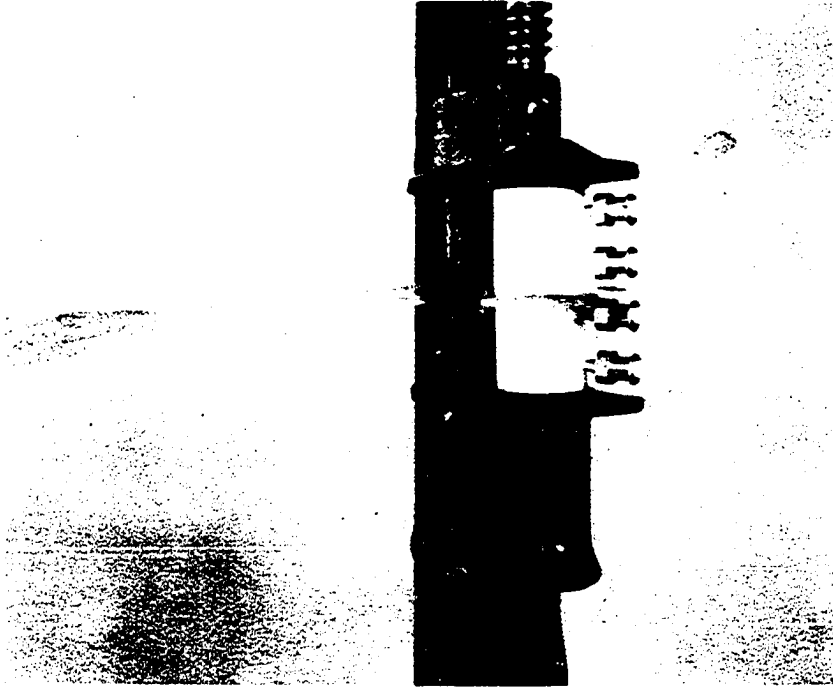


Figure 22 - View of Apparatus Used for Measuring Diffusion
Impedence of Barriers

of the cell for filling and sampling.

Procedure.--The solutions to be tested for diffusion were analyzed with the calibrated Bausch and Lomb Precision refractometer. The lower half of the cell was filled with the water-rich (more dense) of the two ethyl alcohol-water solutions to be diffused. The barrier, presoaked in 40 weight percent ethyl alcohol-water solution, was installed. This step was omitted in runs made without a barrier. The cell was then clamped together with the shim in place. The upper half of the cell was filled with the alcohol-rich (less dense) of the two ethyl alcohol-water solutions to be diffused.

The time was noted and the shim gently removed. Liquid loss when the shim was removed was insignificant. The room temperature was recorded. At the completion of the run, the time was again noted and the shim carefully replaced. With the shim in place, the cell was subjected to periodic shaking for one day to attain a uniform composition in each half. Samples were removed from each half of the cell with hypodermic syringes and analyzed.

Results.--The data from these tests and cell dimensions are shown in Appendix I. The results are discussed in Chapter V.

CHAPTER IV

THEORETICAL ANALYSIS

The mathematical analysis originally proposed by Furry, Jones, and Onsager (35) and extended by Jones and Furry (54) has been shown to be rather successful in predicting the behavior of thermogravitational thermal diffusion columns (58, 206-212). Certain parts of the developments of Furry, Jones, and Onsager should be applicable to thermal diffusion columns with barriers. Therefore, a brief presentation of the conventional theory without barriers will be given before proceeding to the more difficult problem of columns with barriers.

Conventional Theory

A straightforward approach to the theory of Furry, Jones, and Onsager will be outlined. The development will be based first on batch thermogravitational columns, and then will be extended to cover continuous-flow operation. In general the notation of Jones and Furry will be used. The symbols used will be explained as they occur, and a table of symbols is presented in Appendix A.

Mathematical Formulation of the Problem With and

Without Barriers.--As discussed in Chapter I, thermal and ordinary diffusive fluxes plus convective flow result when a temperature gradient is applied across a parallel plate thermogravitational thermal diffusion column. An attempt will now be made to obtain a mathematical description of these processes. The coordinate system used in this chapter is shown by Figure 23.

In an ideal column, a temperature gradient exists only in the direction normal to the plates. We will assume

ΔT^* - temperature gradients only in the x direction.

The flux of component one due to thermal diffusion, J_{x-TD} is given by (54)

$$J_{x-TD} = + \frac{\alpha D}{T} C_1 C_2 \frac{dT}{dx}, \quad \text{IV-1}$$

where

α is the thermal diffusion "constant,"

D , the ordinary diffusion coefficient,

T , the absolute temperature,

C_1 , C_2 , the fraction of components 1, 2 in a binary solution, and

x , the direction normal to the plates.

Equation IV-1 was developed for isotopic gas mixtures, which are certainly quite different from liquids. However, we shall use Equation IV-1 as the defining equation for α , the

*All assumptions made in this chapter will be listed as needed in the mathematical developments. Assumptions will be numbered consecutively and designated with a capital A.

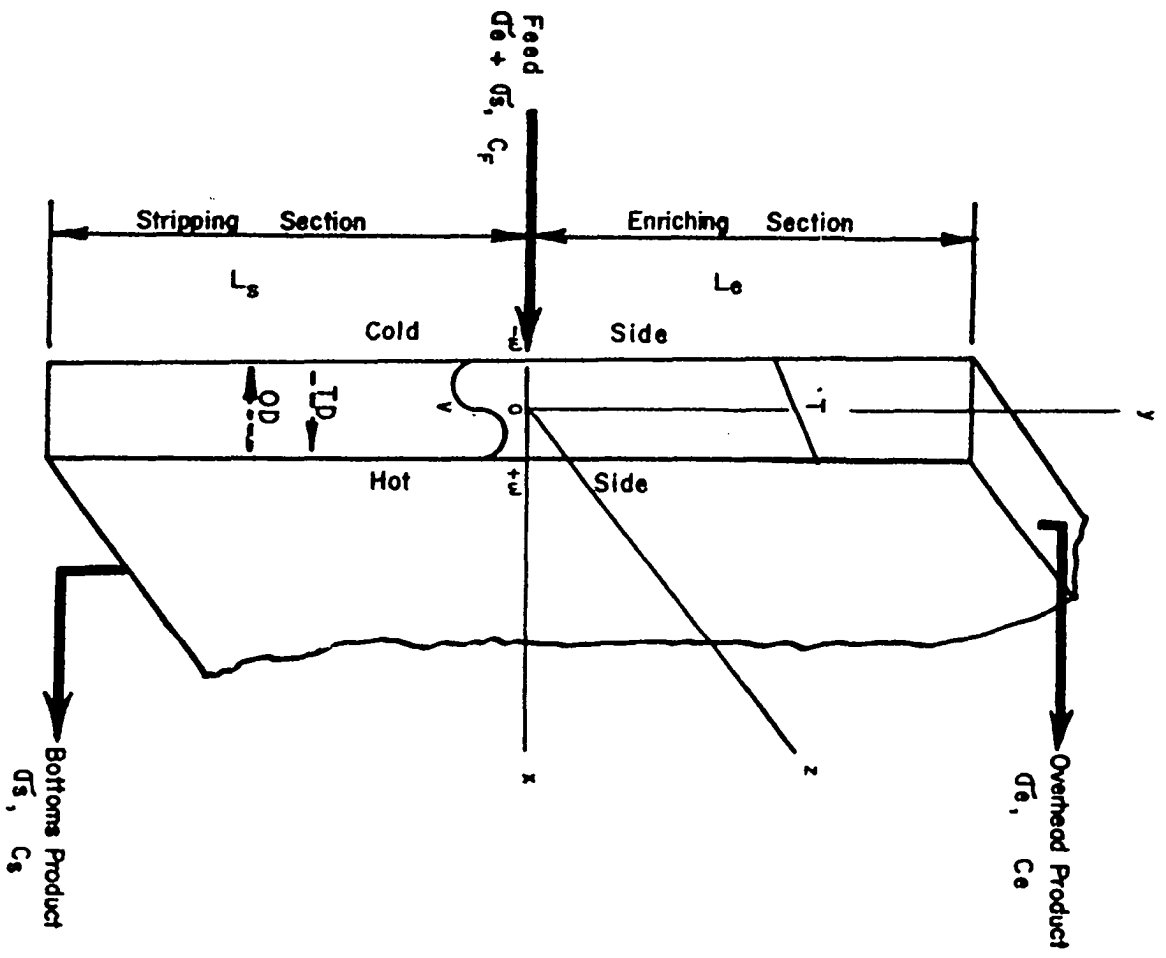


Figure 23 - Coordinate System

thermal diffusion "constant" for liquids.

The concentration gradients set up due to thermal diffusion and convection cause ordinary diffusion to occur. Now it will be assumed that there are

A2 - no gradients in the Z direction.

Then ordinary diffusion will occur only in the x and y directions as given by

$$J_{x-OD} = - D \frac{\partial C_1}{\partial x} \quad \text{IV-2}$$

and

$$J_{y-OD} = - D \frac{\partial C_1}{\partial y} , \quad \text{IV-3}$$

where J_{x-OD} and J_{y-OD} represent the fluxes due to ordinary diffusion in the x and y directions, respectively. Ordinary and thermal diffusion fluxes are indicated schematically in Figures 1 and 23.

The following assumptions will now be made:

A3 - the convective velocity is not a function of y,
and end effects can be neglected,

A4 - a mean temperature level, $\bar{T}$, can be used,

A5 - α is a constant, and

A6 - the ordinary diffusivity, D, is constant.

The first three assumptions should be reasonable for a carefully constructed column with a width (in the z direction) much greater than the plate spacing (in the x direction).

The third, fourth, and fifth assumptions seem justified if separations and temperature differences are not large. Emery (234) has shown that for the range of temperature differences

usually encountered in liquid thermal diffusion columns, assumption A6 is very good.

With these assumptions and the previously defined fluxes, a material balance around an incremental element over a time increment yields (in the limit) the general partial differential equation

$$\frac{\partial C_1}{\partial t} = D \left[\frac{\partial^2 C_1}{\partial x^2} + \frac{\partial^2 C_1}{\partial y^2} \right] - \frac{\alpha D}{T} \frac{dT}{dx} \frac{\partial (C_1 C_2)}{\partial x} - v(x) \frac{\partial C_1}{\partial y} \quad \text{IV-4}$$

The net transfer of material due to ordinary and thermal diffusion must be zero at the walls. Therefore, any solution to Equation IV-4 must be subject to the boundary condition that

$$- D \frac{\partial C_1}{\partial x} + \frac{\alpha D}{T} C_1 C_2 \frac{dT}{dx} = 0 \quad \text{at} \quad x = \pm \omega \quad \text{IV-5}$$

A solution to Equation IV-4 must also be subject to a material balance around any part of the column. Such a material balance is represented by

$$\tau = B \int_{-\omega}^{\omega} \rho C_1 v(x) dx - B \int_{-\omega}^{\omega} D \frac{\partial C_1}{\partial y} dx, \quad \text{IV-6}$$

where

B is the column width,

ρ is the density, and

τ is the net transport of component 1 up the column.

The net transport, τ , is obviously the difference between the vertical convection and vertical ordinary diffusion.

Let us assume

A7 - a mean density can be used to convert volumetric to mass flow rates.

Included in Equation IV-6 is the assumption that

A8 - the column has a constant width, B , in the z direction.

Equations IV-4, 5 and 6 represent a mathematical description of the processes taking place within the usual thermogravitational thermal diffusion column. Notice that it has not been necessary to mention whether or not a vertical barrier is present in the column.

Because Equation IV-4 is a non-linear second order partial differential equation, a rigorous general solution would be extremely difficult to obtain. Furry, Jones, and Onsager have shown how Equations IV-4, 5 and 6 can be reduced to an ordinary differential equation of first order in y , with constant coefficients, which they call the transport equation. The procedure appears reasonable because the concentration change in the x direction is small compared with the total concentration difference in the y direction. Their basic development is for a batch column, but can be extended to continuous-flow operation.

Derivation of the Transport Equation for Batch and Continuous-Flow Thermal Diffusion Columns.--The following development will be made without regard to whether or not a barrier is present in the column. The form of Equation IV-4 can be simplified somewhat by

A9 - neglecting vertical diffusion with respect to convection

$$\left(D \frac{\partial^2 C_1}{\partial y^2} \ll v(x) \frac{\partial C_1}{\partial y} \right),$$

A10 - considering only the steady-state solution

$$\left(\frac{\partial C_1}{\partial t} = 0 \right), \text{ and}$$

A11 - assuming laminar convective flow so that dT/dx can be replaced by $\Delta T/2\omega$.

Applying these assumptions to Equation IV-4 yields

$$D \frac{\partial^2 C_1}{\partial x^2} - \frac{\alpha D}{\bar{T}} \frac{\Delta T}{2\omega} \frac{\partial(C_1 C_2)}{\partial x} - v(x) \frac{\partial C_1}{\partial y} = 0. \quad \text{IV-7}$$

The boundary conditions of Equation IV-4 are also modified to give

$$D \frac{\partial C_1}{\partial x} - \frac{\alpha D}{\bar{T}} \frac{\Delta T}{2\omega} C_1 C_2 = 0 \text{ at } x = \pm \omega. \quad \text{IV-8}$$

Notice that Furry, Jones, and Onsager elected to retain the vertical diffusion term in the material balance boundary condition, Equation IV-6, but discard it in partial differential Equation IV-4.

At this point, Furry, Jones, and Onsager boldly suggest that the first term on the right of Equation IV-6 be integrated by parts. Such an operation yields

$$\tau = B\rho \left[C_1 \int_{-\omega}^x v(x) dx \right]_{-\omega}^{\omega} - B\rho \int_{-\omega}^{\omega} \frac{\partial C_1}{\partial x} \left[\int_{-\omega}^x v(x) dx \right] dx - B \int_{-\omega}^{\omega} \rho D \frac{\partial C_1}{\partial y} dx. \quad \text{IV-9}$$

The first term on the right of the above equation vanishes at both limits for the batch case, so Equation IV-9 can be

rewritten as

$$\gamma = -B\rho \int_{-\omega}^{\omega} \frac{\partial C_1}{\partial x} \left[\int_{-\omega}^x v(x) dx \right] dx - B \int_{-\omega}^{\omega} \rho D \frac{\partial C_1}{\partial y} dx. \quad \text{IV-10}$$

A partial integration of Equation IV-7 with respect to x gives

$$D \frac{\partial C_1}{\partial x} - \frac{\alpha D}{T} \frac{\Delta T}{2\omega} C_1 C_2 - \int_{-\omega}^x v(x) \frac{\partial C_1}{\partial y} dx = f(y); \quad \text{IV-11}$$

but from the boundary condition at $x = -\omega$, Equation IV-8, the constant of integration $f(y)$ is zero, so that

$$D \frac{\partial C_1}{\partial x} - \frac{\alpha D}{T} \frac{\Delta T}{2\omega} C_1 C_2 - \int_{-\omega}^x v(x) \frac{\partial C_1}{\partial y} dx = 0. \quad \text{IV-12}$$

If Equation IV-12 is solved for $\frac{\partial C_1}{\partial x}$ and inserted in Equation IV-10, the result is

$$\begin{aligned} \gamma = & -B\rho \int_{-\omega}^{\omega} \left[\frac{\alpha}{T} \frac{\Delta T}{2\omega} C_1 C_2 + \frac{1}{D} \int_{-\omega}^x v(x) \frac{\partial C_1}{\partial y} dx \right] \left[\int_{-\omega}^x v(x) dx \right] dx \\ & - B\rho D \int_{-\omega}^{\omega} \frac{\partial C_1}{\partial y} dx. \end{aligned} \quad \text{IV-13}$$

Furry, Jones, and Onsager now choose to

A12 - assume $C_1 C_2$ is not a function of x ,

A13 - assume $\frac{\partial C_1}{\partial y}$ is not a function of x , with all necessary x dependence retained within the integrals,
and

A14 - say that the mean concentrations at $x = 0$ will be satisfactory in defining a y dependence of composition.

Applying these restrictions and rearranging a bit gives

$$\begin{aligned} \gamma = \overline{C_1 C_2} \left[\left\{ - \frac{\alpha \rho B \Delta T}{T 2 \omega} \int_{-\omega}^{\omega} \int_{-\omega}^x v(x) dx dx \right\} \right] \\ - \frac{d\overline{C_1}}{dy} \left[\left\{ \frac{B \rho}{D} \int_{-\omega}^{\omega} \left[\int_{-\omega}^x v(x) dx \right]^2 dx \right\} + \left\{ B \rho D \int_{-\omega}^{\omega} dx \right\} \right] \end{aligned} \quad \text{IV-14}$$

where the superbars on concentration refer to mean compositions with respect to x , evaluated at $x = 0$.

Inspection of Equation IV-14 reveals that all groupings within curly brackets contain definite integrals. Thus, given a velocity distribution $v(x)$, all expressions could be integrated to yield simply constants. These groups will now be defined as

$$H \equiv - \frac{\alpha \rho B \Delta T}{T 2 \omega} \int_{-\omega}^{\omega} \int_{-\omega}^x v(x) dx dx, \quad \text{IV-15}$$

$$K_C \equiv \frac{B \rho}{D} \int_{-\omega}^{\omega} \left[\int_{-\omega}^x v(x) dx \right]^2 dx, \quad \text{IV-16}$$

and

$$K_d \equiv B \rho D \int_{-\omega}^{\omega} dx. \quad \text{IV-17}$$

Further, these K definitions can be combined into

$$K \equiv K_C + K_d + K_p \quad \text{IV-18}$$

where K_p is an empirical factor, appended to the theory by Furry, Jones, and Onsager to account for the effects of parasitic remixing. Velocity profiles and integrations of these defining equations will be discussed later.

With the above definitions, Equation IV-14 can be rewritten as

$$\tau = \overline{C_1 C_2} H - K \frac{d\overline{C_1}}{dy} . \quad \text{IV-19}$$

This is the transport equation as evolved by Furry, Jones, and Onsager for a batch thermogravitational thermal diffusion column. Obviously at steady state, the batch transport τ is zero.

At this point, Furry, Jones, and Onsager suggest, because of the linearity in the y direction of the velocity distribution (due to assumption A11), that

A15 - an additional linear transport may be impressed in the y direction.

For instance, in the enriching section

$$\tau' = \overline{C_1 C_2} H_e - K_e \frac{d\overline{C_1}}{dy} + \sigma_e \overline{C_1} \quad \text{IV-20}$$

where σ_e is the impressed mass flow rate per unit time and

τ' is the new net transport up the column.

As a result, a net draw-off from the enriching section results. The new draw-off must be the total net transport, τ' so that Equation IV-20 can be modified to

$$\sigma_e C_e = \tau' = \overline{C_1 C_2} H_e - K_e \frac{d\overline{C_1}}{dy} + \sigma_e \overline{C_1} \quad \text{IV-21}$$

where C_e is the concentration of component 1 leaving the enriching section.

Rearranging Equation IV-21 for the enriching section yields

$$\sigma_e(C_e - \bar{C}_1) = \bar{C}_1 \bar{C}_2 H_e - K_e \frac{d\bar{C}_1}{dy} . \quad \text{IV-22}$$

Similar reasoning applied to the stripping section gives

$$\sigma_s(\bar{C}_1 - C_s) = \bar{C}_1 \bar{C}_2 H_s - K_s \frac{d\bar{C}_1}{dy} , \quad \text{IV-23}$$

where C_s is the concentration of component 1 leaving the stripping section.

Equations IV-22 and IV-23 are the final forms of the transport equation for the continuous-flow columns. Values for H and K as defined by Equations IV-15, 16, 17 and 18 may be evaluated from batch velocity profiles if the net draw-off is small compared to the internal convective flow. That is, for small product flow rates.

Powers (58) derived identical transport equations on a continuous-flow basis without the severe assumption, A15, of superimposing a continuous-flow transport of material on the transport equation for a batch column. The definitions of H and K used by Powers were different because $\frac{\partial C_1}{\partial y}$ was assumed as a linear function of x --not independent of x as Furry, Jones, and Onsager had done.

Again it should be emphasized that it has not been necessary to mention whether or not vertical barriers are present in the column in the development of the transport equations.

Derivation of Velocity Profile.--The usual type of velocity profile will be developed for a batch column without barriers. As previously mentioned, batch velocity profiles are satisfactory for evaluating H and K for

continuous columns, if the internal circulation is large compared to the net product draw-off.

The velocity distribution may be obtained by solving the Navier-Stokes equation with suitable boundary conditions. With the simplification of no gradients in the z direction, assumption A2, this takes the form of

$$\frac{dP}{dy} + g\rho = \eta \frac{d^2v(x)}{dx^2} \quad \text{IV-24}$$

where P is the pressure,

g the acceleration of gravity, and

η the coefficient of viscosity.

Since it is already assumed in Equation IV-24 that

A16 - viscosity is a constant,

Equation IV-14 may be differentiated with respect to x to give

$$g \frac{\partial \rho}{\partial x} = \eta \frac{d^3v(x)}{dx^3} \quad \text{IV-25}$$

Emery (234) and others have shown that assumption A16 is satisfactory for temperature differences normally encountered in liquid thermogravitational columns. If the term $\frac{\partial \rho}{\partial x}$ can be replaced by a constant,

$$\text{A17 - } \beta^* = - \frac{\partial \rho}{\partial x},$$

a triple integration of Equation IV-25 yields

$$v(x) = - \frac{g\beta^*x^3}{6\eta} + \frac{I_1}{2}x^2 + I_2x + I_3 \quad \text{IV-26}$$

where I_1 , I_2 and I_3 represent integration constants to be evaluated.

The boundary conditions for a batch thermogravitational column without barriers are

$$v(x) = 0 \quad \text{at} \quad x = \pm \omega \quad \text{IV-27}$$

and

$$\int_{-\omega}^{\omega} v(x) dx = 0. \quad \text{IV-28}$$

If the constants in Equation IV-26 are evaluated using Equations IV-27 and IV-28, the following form evolves

$$v(x) = \frac{g\beta^*}{6\eta} (\omega^2 x - x^3). \quad \text{IV-29}$$

The term $\beta^* = - \frac{\partial \rho}{\partial x}$ is composed of two terms

$$\frac{\partial \rho}{\partial x} = \frac{\partial \rho}{\partial T} \frac{dT}{dx} + \frac{\partial \rho}{\partial C_1} \frac{\partial C_1}{\partial x}. \quad \text{IV-30}$$

Frequently the second term on the right-hand side of Equation IV-30 is neglected, which is equivalent to saying

A18 - density is a function of temperature only.

This is not always a good assumption, and it is this simplification that deGroot, Hoogenstraaten, and Gorter (63) have named the "forgotten effect." In the present case this assumption will be made, and when combined with assumption A11, results in

$$\beta^* = \beta_T \frac{\Delta T}{2\omega} \quad \text{IV-31}$$

where β_T is $-\frac{\partial \rho}{\partial T}$. This definition should not be confused with the usual definition of β as the temperature coefficient of cubical expansion, $-\frac{1}{\rho} \frac{\partial \rho}{\partial T}$.

The velocity profile thus described is

$$v(x) = \frac{\beta_T g \Delta T}{12 \omega \eta} (\omega^2 x - x^3) \quad \text{IV-32}$$

which holds for $-\omega \leq x \leq \omega$. Such a velocity profile is sketched in Figure 23, shown previously. This equation holds strictly only for a batch column without barriers, but may be used with little error to evaluate H and K values for a continuous-flow column without barriers at low flow rates.

Theoretical Evaluation of Constants H and K.--The constants H and K will now be evaluated for a column without barriers to show the usual form of the equations evolved.

If the velocity profile of Equation IV-32 is inserted in the defining integrals for H and K, Equations IV-15, 16 and 17, and the integrations carried out, the resulting formulas are:

$$H = \frac{\alpha \beta_T \rho g B (\Delta T)^2 (2\omega)^3}{6 \cdot \bar{T} \eta} \quad \text{IV-33}$$

$$K_c = \frac{\beta_T^2 \rho g^2 B (\Delta T)^2 (2\omega)^7}{9 \cdot D \eta^2} \quad \text{IV-34}$$

$$K_d = 2\omega D B \rho \quad \text{IV-35}$$

Powers (58) designated such H and K values as $H^{(0)}$ and $K^{(0)}$ when developed from batch velocity profiles.

However, in this work, the superscripts will be omitted because H and K will always be evaluated from batch velocity profiles.

Solutions of the Transport Equations.---In this section, some solutions of the transport equations will be presented. The solutions will be general and should be applicable to a column with or without vertical barriers, if the effect of the barriers can be accounted for in the H and K values.

Repeated below is the transport equation for the enriching section,

$$\sigma_e(C_e - \bar{C}_1) = \bar{C}_1 \bar{C}_2 H - K \frac{d\bar{C}_1}{dy}, \quad \text{IV-22}$$

Attention will be restricted to concentrated binary mixtures with concentrations of $0.3 < C_1 < 0.7$ weight fraction. Over this range, the excellent assumption can be made that

A19 - $\bar{C}_1 \bar{C}_2$ is about equal to 1/4.

With this assumption, Equation IV-22 reduces to

$$\sigma_e(C_e - \bar{C}_1) = \frac{H}{4} - K \frac{d\bar{C}_1}{dy} \quad \text{IV-36}$$

in which the variables are easily separable. The limits for integration over the enriching section are obvious upon inspection of the coordinate system, Figure 23. Thus the integrals are

$$\int_0^{L_e} dy = - \int_{C_F}^{C_e} \frac{K d\bar{C}_1}{\sigma_e(C_e - \bar{C}_1) - H/4} \quad \text{IV-37}$$

where C_F is the concentration of component 1 in the feed.

Carrying out the integrations and rearranging yields

$$C_e - C_F = \frac{H}{4\sigma_e} \left(1 - e^{-\frac{\sigma_e L_e}{K}} \right) \quad \text{IV-38}$$

giving the separation obtained in the enriching section. If a similar integration is carried out over the stripping section, the result is

$$C_F - C_s = \frac{H}{4\sigma_s} \left(1 - e^{-\frac{\sigma_s L_s}{K}} \right). \quad \text{IV-39}$$

Defining the total separation as Δ , the difference between the top (enriching), and the bottom (stripping) compositions; combining Equations IV-38 and IV-39 gives

$$\Delta \equiv C_e - C_s = \frac{H}{4\sigma_e} \left(1 - e^{-\frac{\sigma_e L_e}{K}} \right) + \frac{H}{4\sigma_s} \left(1 - e^{-\frac{\sigma_s L_s}{K}} \right). \quad \text{IV-40}$$

If additional assumptions are made with regard to the symmetry of the column,

A20 - $\sigma_e = \sigma_s = \sigma$, equal product flows, and

$L_e = L_s = L/2$, center-fed column,

Equation IV-40 may be simplified to

$$\Delta = \frac{H}{2\sigma} \left(1 - e^{-\frac{\sigma L}{2K}} \right). \quad \text{IV-41}$$

For the limiting batch case, $\sigma \rightarrow 0$, Equation IV-41 reduces to

$$\Delta_0 = \frac{HL}{4K}, \quad \text{IV-42}$$

where Δ_0 refers to the batch steady-state separation. This batch result may also be readily obtained by integrating Equation IV-19 with zero transport and $\overline{C_1 C_2} = 1/4$ (assumption A19).

Equation IV-41 is the most useful form for describing steady-state separations in symmetrical, center-fed, continuous-flow thermogravitational thermal diffusion columns at low flow rates. This equation is applicable only to concentrated solutions, $0.3 < C_1 < 0.7$ weight fraction (assumption A19). Equation IV-41 is also applicable to columns with barriers, if the effect of the barriers can be described by modifying the H and K values used. This is not to say the theory is restricted in any way. Any solution to the transport equation (see for instance the many forms set forth by Jones and Furry) should be applicable to columns with vertical barriers, if the barrier or barriers can be accounted for in the H and K values.

Concept of the Ideal Barrier and Theory Modifications

Definition as a Mathematical Limit.--The theoretical aspects of vertical barriers will now be investigated by defining what might be described as an "ideal" barrier. The ideal vertical barrier is a mathematical limit. The ideal barrier has the following properties:

A21 - the ideal barrier is infinitely thin (dimensional ideality),

A22 - the ideal barrier offers no resistance to either molecular thermal or molecular ordinary diffusion (diffusive ideality), and

A23 - the ideal barrier allows no macroscopic bulk flow of material through it (hydrodynamic ideality).

This model was chosen because the theory of Furry, Jones, and Onsager can be reasonably modified using such a system.

Obviously any real barrier can never attain these idealized properties, because any barrier which allows no bulk flow will inhibit diffusion. And, of course, a real barrier has finite thickness. However, certain permeable membranes do show a degree of ideality within these terms of reference. Therefore, theoretical work using the ideal barrier concept should be useful in evaluating and comparing the performance of actual barriers.

Consider again the conventional column theory developed in the previous sections, and recall that the defining integrals for H and K (Equations IV-15, 16, 17 and 18) and the simplified forms of the solutions to the transport equations (Equations IV-41 and 42) were developed without regard to whether or not barriers were present in the column. Therefore, these equations should still apply if an ideal barrier is present in the column. After re-determining H and K , taking into account the effect of the ideal barrier on the velocity profile, the conventional solutions to the transport equations will still be applicable.

Derivation of Velocity Profile for One Ideal

Barrier.--Consider now a thermogravitational thermal diffusion column with a single vertical ideal barrier centered in it. The ideal barrier has the properties defined previously (infinitely thin, free diffusion, no bulk flow). A piece-wise representation of the velocity profile with a single vertical ideal barrier will now be developed. Again the derivation will be for a batch column. The type of batch velocity profile to be developed is illustrated in Figure 24B. For comparison, a sketch of the usual type of batch velocity profile without a barrier is shown in Figure 24A.

The starting point will be the same as that used for the case without a barrier; namely, the simplified Navier-Stokes law (Equation IV-24). The same ruse of an additional differentiation before integration will be employed. However, the presence of the ideal barrier requires that new fluid flow boundary conditions be used.

The velocity distribution will be developed separately on each side of the barrier. The boundary conditions for the left half of the column ($-\omega \leq x \leq 0$) are

$$v_L(x) = 0 \quad \text{at} \quad x = -\omega, \quad x = 0, \quad \text{IV-43}$$

and

$$\int_{-\omega}^0 v_L(x) dx = 0 \quad \text{IV-44}$$

where $v_L(x)$ is the velocity distribution on the left half of the column (left side of the barrier).

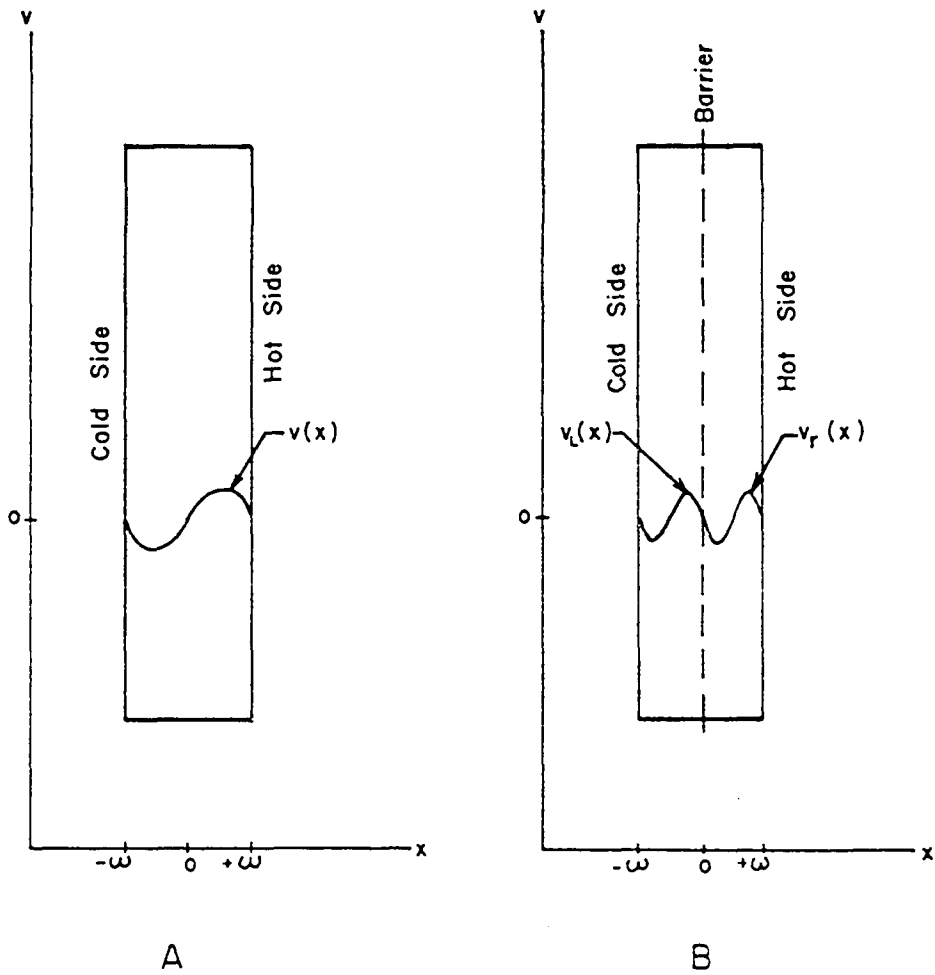


Figure 24 - Sketch of Batch Velocity Profiles in Identical Thermal Diffusion Columns Without and With Single Vertical Ideal Barrier (Vertical scale greatly fore-shortened.)

For the right half of the column, the boundary conditions are

$$v_R(x) = 0 \quad \text{at} \quad x = 0, x = \omega, \quad \text{IV-45}$$

and

$$\int_0^{\omega} v_R(x) dx = 0 \quad \text{IV-46}$$

where $v_R(x)$ is the velocity distribution on the right half of the column.

Equations IV-44 and 46 are a result of the ideal barrier property of no bulk flow. Applying these boundary conditions, we easily arrive at a piecewise representation of the velocity profile in a batch thermogravitational column with one ideal vertical barrier as

$$v_L(x) = \frac{-g\beta_T\Delta T}{24 \omega \eta} (2x^3 + 3\omega x^2 + \omega^2 x) \quad \text{for } -\omega \leq x \leq 0, \quad \text{IV-47}$$

and

$$v_R(x) = \frac{-g\beta_T\Delta T}{24 \omega \eta} (2x^3 - 3\omega x^2 + \omega^2 x) \quad \text{for } 0 \leq x \leq \omega. \quad \text{IV-48}$$

The above equations are understandably quite similar to the expression developed for the batch velocity profile for a column without a barrier, Equation IV-32.

Evaluation of Constants H and K for a Single Vertical Ideal Barrier.--Because the batch velocity profiles developed for a column with a single vertical ideal barrier are

piecewise in nature, the integrations to determine the values of H and K must be carried out in a piecewise fashion. (The parameter K_d does not contain the velocity distribution, and hence will be identical in columns with or without an ideal barrier.)

For illustration the defining integral for H will now be repeated.

$$H \equiv - \frac{\alpha \rho B \Delta T}{\bar{T} 2 \omega} \int_{-\omega}^{\omega} \int_{-\omega}^x v(x) dx dx \quad \text{IV-15}$$

To carry out the integration using piecewise velocity profiles, we break up the integration as follows

$$\begin{aligned} H_{IB}^1 = & - \frac{\alpha \rho B \Delta T}{\bar{T} 2 \omega} \int_{-\omega}^0 \int_{-\omega}^x v_L(x) dx dx \\ & - \frac{\alpha \rho B \Delta T}{\bar{T} 2 \omega} \int_0^{\omega} \int_0^x v_R(x) dx dx, \end{aligned} \quad \text{IV-49}$$

where the superscript on H refers to the number of ideal barriers, and the subscript IB refers to ideal barriers. Likewise, the defining integral for K_c (Equation IV-16) may be separated into

$$\begin{aligned} K_{cIB}^1 = & \frac{B \rho}{D} \int_{-\omega}^0 \left[\int_{-\omega}^x v_L(x) dx \right]^2 dx \\ & + \frac{B \rho}{D} \int_0^{\omega} \left[\int_0^x v_R(x) dx \right]^2 dx. \end{aligned} \quad \text{IV-50}$$

The use of zero as a lower limit on the inner integrals of the right hand terms of Equations IV-49 and 50 is permissible because the value of the inner integrals is always zero when x is zero.

If the piecewise velocity profiles for the single ideal barrier case (Equations IV-47 and 48) are inserted in these new defining integrals for H and K_C (Equations IV-49 and 50) and the integrations carried out, the new forms of H and K_C are now given by

$$H_{IB}^1 = \frac{\alpha \beta_T \rho g B (\Delta T)^2 (2\omega)^3}{6! \bar{T} \eta (2)^4} \quad \text{IV-51}$$

and

$$K_{CIB}^1 = \frac{\beta_T^2 \rho g^2 B (\Delta T)^2 (2\omega)^7}{9! D \eta^2 (2)^8} \quad \text{IV-52}$$

For comparison, the results of the integrations of the conventional case with no barriers are repeated below.

$$H = \frac{\alpha \beta_T \rho g B (\Delta T)^2 (2\omega)^3}{6! \bar{T} \eta} \quad \text{IV-33}$$

$$K_C = \frac{\beta_T^2 \rho g^2 B (\Delta T)^2 (2\omega)^7}{9! D \eta^2} \quad \text{IV-34}$$

Inspection of the results of these two cases (with and without a single vertical ideal barrier) shows that they differ only by numerical factors of $(2)^4$ for H and $(2)^8$ for K_C .

Thus for two thermogravitational thermal diffusion columns, identical in all respects except that one contains a single

vertical barrier, we are led to the relationships

$$H_{IB}^1 = \frac{H}{(2)^4} \quad \text{IV-53}$$

and

$$K_{CIB}^1 = \frac{K_C}{(2)^8} . \quad \text{IV-54}$$

Such H and K values can be used in any of the solutions to the transport equation.

Discussion of Theoretical Effect of a Single Vertical Ideal Barrier.--In nearly all cases in liquid thermogravitational columns, the value of K_d is negligibly small compared to K_C . (In this work K_d never exceeded 0.1 per cent of K_C in the most extreme case.) If the parasitic remixing term K_p is also neglected, then

$$A_{24} - K \approx K_C.$$

With this in mind and the equation for batch separation

$$\Delta_0 = \frac{HL}{4K} , \quad \text{IV-42}$$

together with the previously developed expressions for H_{IB}^1 and K_{CIB}^1 (Equations IV-53 and 54), sufficient information is available for comparing a column with and without a vertical barrier. It is readily developed that insertion of a single ideal barrier into a batch thermogravitational thermal diffusion column results in a ratio of batch separations of

$$\frac{\Delta_{OIB}^1}{\Delta_0} = (2)^4 , \quad \text{IV-55}$$

where the superscript refers to the number of vertical ideal barriers and the subscript IB refers to ideal barriers. Thus the steady-state batch theoretical separation in a column should improve by a factor of 16 when a single vertical ideal barrier is inserted.

For appreciable separations without a barrier ($\Delta_0 > 6.26$ weight percent), an improvement factor of 16 as given by Equation IV-55 yields the impossible result that the separation Δ_{OIB}^1 should be more than 100 percent. This is because the concentration range ($0.3 < C_1 < 0.7$ weight fraction) for which the equations were developed is exceeded, and in no way invalidates the explanation of separation improvement with barriers offered by the ideal barrier theory developed.

To demonstrate the implications of the ideal barrier theory in continuous-flow columns, some example theoretical separation verses flow rate curves have been calculated using Equation IV-41. The values of H or H_{IB}^1 and K_c or K_{cIB}^1 were computed using Equations IV-33, 34, 51 and 52. Dimensions and system properties used approximate those used experimentally. Column dimensions and parameters are summarized as Table 1. Physical properties used in all calculations are presented in Appendix K. The calculated theoretical separation verses flow rate curves are shown as Figure 25.

The hypothetical thermal diffusion columns of Curves A and B are identical except that the column for Curve B contains a single ideal vertical barrier, while the column

TABLE 1
VALUES USED IN CALCULATING EXAMPLE THEORETICAL SEPARATION
VERSUS FLOW RATE CURVES

Property or Dimension	Curve A No Barrier	Curve B One Ideal Barrier	Curve C Two Columns in Parallel, No Barrier
B (cm)	10.16	10.16	10.16 (each)
L (cm)	145	145	145 (each)
2ω (cm)	0.15	0.15	0.075 (each)
α	0.48	0.48	0.48
ΔT (°C)	32	32	16 (each)
H or H_{IB}^1 (gm/min)	0.278	0.0174	.00868(each)
K_C or K_{CIB}^1 (gm-cm/min)	1268	4.95	2.48 (each)

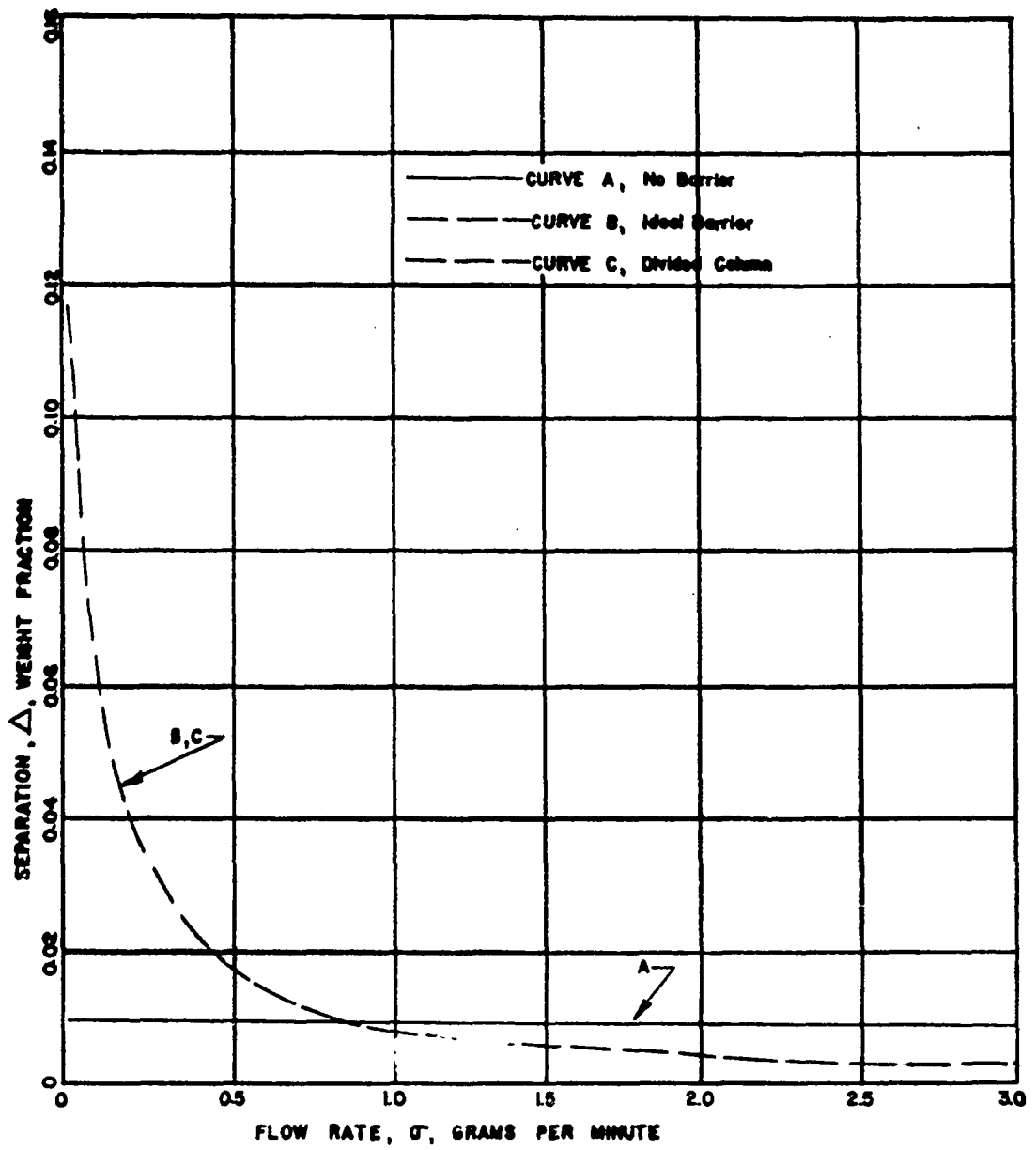


Figure 25 - Theoretical Effect of an Ideal Barrier and of Dividing the Column

of Curve A has no barrier. Curve C is of another type. It is calculated for two hypothetical columns operating in parallel; each with one-half the temperature difference and one-half the plate spacing of the columns of Curves A and B, with no barriers. That is, for Curve C, the column of Curve A is simply "cut in half" with the flow split between the two halves.

Inspection of Figure 25 shows that the installation of a single ideal vertical barrier in a column increases the batch separation by a factor of 16 (Curves A and B) as developed by ideal barrier theory. However, the ideal barrier separation advantage falls off rapidly with increasing flow rate until the separation is lower than that for a column without a barrier.

Curve C (simply cutting the column of Curve A in two) is identical with Curve B. From the theory developed, it is easy to show that the batch separations of B and C are exactly the same. However, for the flow case, due consideration must be given to splitting the flow between the "half-columns" before a mathematical identity can be proven.

The following major conclusions can be drawn from the theoretical curves of Figure 25:

- a) A single ideal vertical barrier inserted in a column shows striking increases in batch separation over the same column without a barrier.
- b) A single ideal vertical barrier is advantageous

only at low flow rates.

- c) Assuming an ideal barrier could be found, the advantage in separation if a barrier were installed in a column, would be no greater than simply "cutting the column in two."

Generalization to Any Number of Ideal Vertical Barriers.--The H and K_C expressions for a thermogravitational thermal diffusion column with more than one ideal vertical barrier can be derived by a simple extension of the technique used for developing the theory for one vertical barrier. If two ideal vertical barriers are equally spaced in a column of the usual 2ω width, barriers will be located at x equals plus or minus $\omega/3$. Thus the column is divided into three equal parts of width $2\omega/3$. Batch velocity profiles are easily established in these three regions, and the integrations for H and K_C performed in three parts in a manner completely analogous to the two-part integrations previously outlined for a column with a single vertical barrier.

Such mathematical operations to determine H and K_C have been carried out for two and three ideal vertical barriers in a thermogravitational column. The values of H and K_C for columns with a single ideal vertical barrier and no barriers have been developed previously in this chapter. All these H and K_C results are summarized in Table 2 as ratios of H or K_C values without barriers referred to an identical column with barriers. The general terms are

TABLE 2

THEORETICAL RATIOS OF H AND K_c VALUES--COLUMNS WITHOUT
 BARRIERS REFERRED TO COLUMNS WITH EQUALLY SPACED
 MULTIPLE IDEAL VERTICAL BARRIERS
 (Identical Thermogravitational Columns Under
 Identical Conditions)

Number of Barriers	H No Barrier	K_c No Barrier
	$\frac{H}{H}$ Ideal Barrier (s)	$\frac{K_c}{K_c}$ Ideal Barrier (s)
0	1	1
1	$16 = (2)^4$	$256 = (2)^8$
2	$81 = (3)^4$	$6,561 = (3)^8$
3	$256 = (4)^4$	$65,536 = (4)^8$
.	.	.
.	.	.
.	.	.
n	$(n + 1)^4$	$(n + 1)^8$

written immediately by inspection. For the general case, the relationships are

$$H_{IB}^n = \frac{H}{(n+1)^4} = \frac{\alpha \beta_T \rho g B (\Delta T)^2 (2\omega)^3}{6! \bar{T} \eta (n+1)^4} \quad \text{IV-56}$$

and

$$K_{CIB}^n = \frac{K_C}{(n+1)^8} = \frac{\beta_T^2 \rho g^2 B (\Delta T)^2 (2\omega)^7}{9! D \eta^2 (n+1)^8} \quad \text{IV-57}$$

where

$$n = 0, 1, 2, 3, \dots \quad \text{IV-58}$$

ideal vertical barriers. These theoretical H_{IB}^n and K_{CIB}^n values can be used directly in any of the solutions to the transport equations, including our rather restricted solutions, Equation IV-41 and 42.

Some interesting features of the generalized ideal barrier theory might be pointed out. Notice that when n is zero (no barriers), Equations IV-56 and 57 degenerate into the conventional theory of Furry, Jones, and Onsager for columns without barriers. The term $(n+1)$ has physical significance in that it represents the number of vertical compartments into which the column is divided by n ideal vertical barriers. All the conclusions drawn from Figure 25 for a single vertical ideal barrier generalize to multiple vertical ideal barriers.

With a factor such as $(n+1)^8$ in the denominator, K_{CIB}^n becomes small very rapidly as n is increased. Therefore, the assumption that K_d is negligibly small compared to K_C

(assumption A24) should be used with caution when applying ideal vertical barrier theory for many barriers.

Real Barrier Theory Modifications

As suggested when the ideal barrier concept was introduced, any real barrier can never completely possess the defining properties of the mathematical "ideal" barrier.

Discussion of Real Barrier Nonidealities.--There will always be some degree of dimensional nonideality (barrier not infinitely thin). In a column with a single vertical barrier, dimensional ideality can be approached by making the plate spacing large compared to the barrier thickness. Likewise, the free diffusion with no bulk flow criteria can sometimes be approached, but never completely achieved. If free diffusion were not allowed (diffusive nonideality), some modification of the boundary conditions of the fundamental partial differential equation would be required, making it improbable that the theory of Furry, Jones, and Onsager could be modified for this condition. Von Halle (50) attempted to treat diffusive impedance by using a multiplicative factor on area to arrive at an effective open area for diffusion through a membrane. As previously pointed out in Chapter II, Von Halle used a horizontal thermal diffusion apparatus in which the approach of Furry, Jones, and Onsager could not be applied. In the next chapter certain diffusion impedance tests will be discussed which show that within experimental error, certain types of membrane barriers apparently do not

inhibit diffusion. The theoretical effect of diffusive non-ideality will not be treated further in this work.

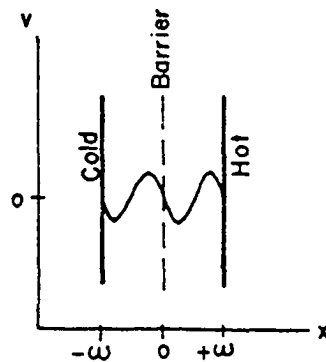
If a vertical barrier allows some degree of macroscopic bulk flow of material (hydrodynamic nonideality), some approximation to the resulting velocity profile can be made. The corrected velocity distribution can then be inserted in Equations IV-15 and 16 to obtain H and K_c results modified for a real barrier with hydrodynamic nonideality. The next few sections will be devoted to developing such corrections to the theory for a single vertical real barrier in a thermogravitational column.

Development of Batch Velocity Profile for a Single Vertical Real Barrier.---If a single vertical real barrier allowing some bulk flow of material (hydrodynamic nonideality) is centered in a thermal diffusion column, assumptions must be made about how much and where the bulk flow occurs. In order to use the approach of Furry, Jones, and Onsager, some velocity distribution must be developed which is independent of y ; that is, v is a function of x only.

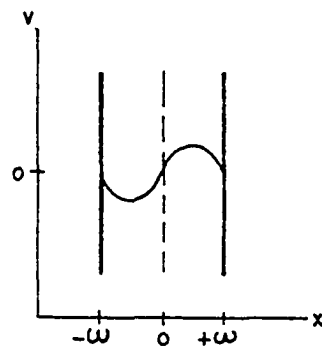
If hydrodynamic nonidealities are disregarded for the moment, the batch velocity profile would be of the ideal barrier type as resketched in Figure 26A. Now if different constant densities are assumed on the cold and hot halves of the column,

$$\bar{\rho}_C = \text{constant density from } -\omega < x < 0 \text{ and}$$

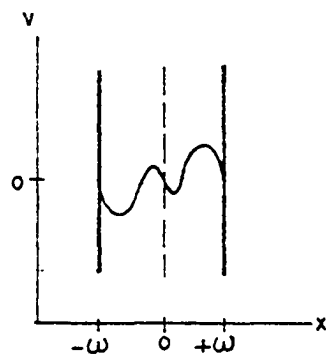
$$\bar{\rho}_H = \text{constant density from } 0 < x < \omega,$$



(A) Batch Velocity Profile
for Ideal Barrier



(B) Batch Parabolic Contribution
to Velocity Profile Due to
Hydrodynamic Nonideality



(C) Batch Total Velocity Profile
for Real Barrier With Hydro-
dynamic Nonideality (Sum
of Profiles in Figures 26A
and 26B)

Figure 26 - Batch Velocity Profile Sketches Showing
Components and Total Velocity Profiles
for Single Vertical Real Barrier with
Hydrodynamic Nonideality

and if it is further assumed that all bulk flow occurs at the top and bottom of the barrier,

A25 - all bulk flow occurs at $y = \pm L/2$, some type of batch parabolic contribution to the velocity profile (of the conventional type encountered in laminar flow between parallel surfaces) will arise of the type sketched in Figure 26B. Assuming individual treatment of these two velocity profile components is permissible,

A26 - ideal and parabolic profiles can be calculated separately, the resultant batch velocity distribution for a single vertical barrier with hydrodynamic nonideality is of the type sketched in Figure 26C.

An expression will now be developed for the parabolic contribution to the velocity distribution. Such a parabola will be governed by the following factors:

- a) the driving force for gross circulation, some function of the densities $\bar{\rho}_C$ and $\bar{\rho}_H$ and height,
- b) the frictional resistance to longitudinal (parabolic) flow in the y direction, and
- c) the frictional resistance to horizontal flow in the x direction through the barrier.

Stating this in terms of lost work due to friction or head loss,

$$(\overline{lw}_f)_y + (\overline{lw}_f)_x = \text{Driving Force} \quad \text{IV-59}$$

or

$$h_y + h_x = \frac{\bar{\rho}_C - \bar{\rho}_H}{\rho} L \frac{g}{g_C} \quad \text{IV-60}$$

where h_y is longitudinal head or friction loss in the y direction,

h_x is barrier friction loss or head loss in the x direction,

ρ is the mean density at the center of the column ($x = 0$),

g is the acceleration of gravity,

g_C is the gravitational constant, and

L is the total column length.

If $\bar{\rho}_C$ and $\bar{\rho}_H$ are evaluated at $x = -\omega/2$ and $x = +\omega/2$, an expression for the density difference can be written as

$$\bar{\rho}_C - \bar{\rho}_H = \frac{\beta_T \Delta T}{2}, \quad \text{IV-61}$$

and Equation IV-60 can be rewritten as

$$h_y + h_x = \frac{\beta_T \Delta T L g}{2 \rho g_C}. \quad \text{IV-62}$$

Turning now to the friction loss across the barrier,

A27 - a linear flow law will be assumed of the form

$$Q = Fh, \quad \text{IV-63}$$

where Q is the flow rate through the barrier in volume/time-unit area,

h is the head loss across the barrier in force-length/mass, and

F is a coefficient of flow in volume-mass/time-unit area - force - length.

The coefficient of flow, F , would be evaluated experimentally for any given barrier material at the conditions of interest.

In order to evaluate the magnitude of the bulk flow through the barrier, it is necessary to disregard for the moment assumption A25 which states that all flow through the barrier occurs at the very ends of the barrier. To more nearly evaluate the flow through the barrier,

A28 - a linear driving force will be assumed for bulk flow through the barrier, varying from zero at $y = 0$ and increasing linearly (but with opposite sign) towards the ends of the column.

Such a driving force is indicated diagrammatically by Figure 27A. The magnitude and direction of the resulting bulk flow through the barrier is then schematically illustrated in Figure 27B. The longitudinal parabolic (y direction) flow then will be zero at $y = \pm L/2$, increasing to a maximum at $y = 0$. The direction of the longitudinal parabolic (y direction) flow will be in the plus y direction on the right side of the barrier, and in the minus y direction on the left side of the vertical barrier. In fact, the magnitude of the parabolic flow on either side of the barrier is itself parabolic in y (as a consequence of assumption A28).

The total volumetric flow rate on one side of the barrier will now be defined as $\dot{M}(y)$. That is, if an xz -

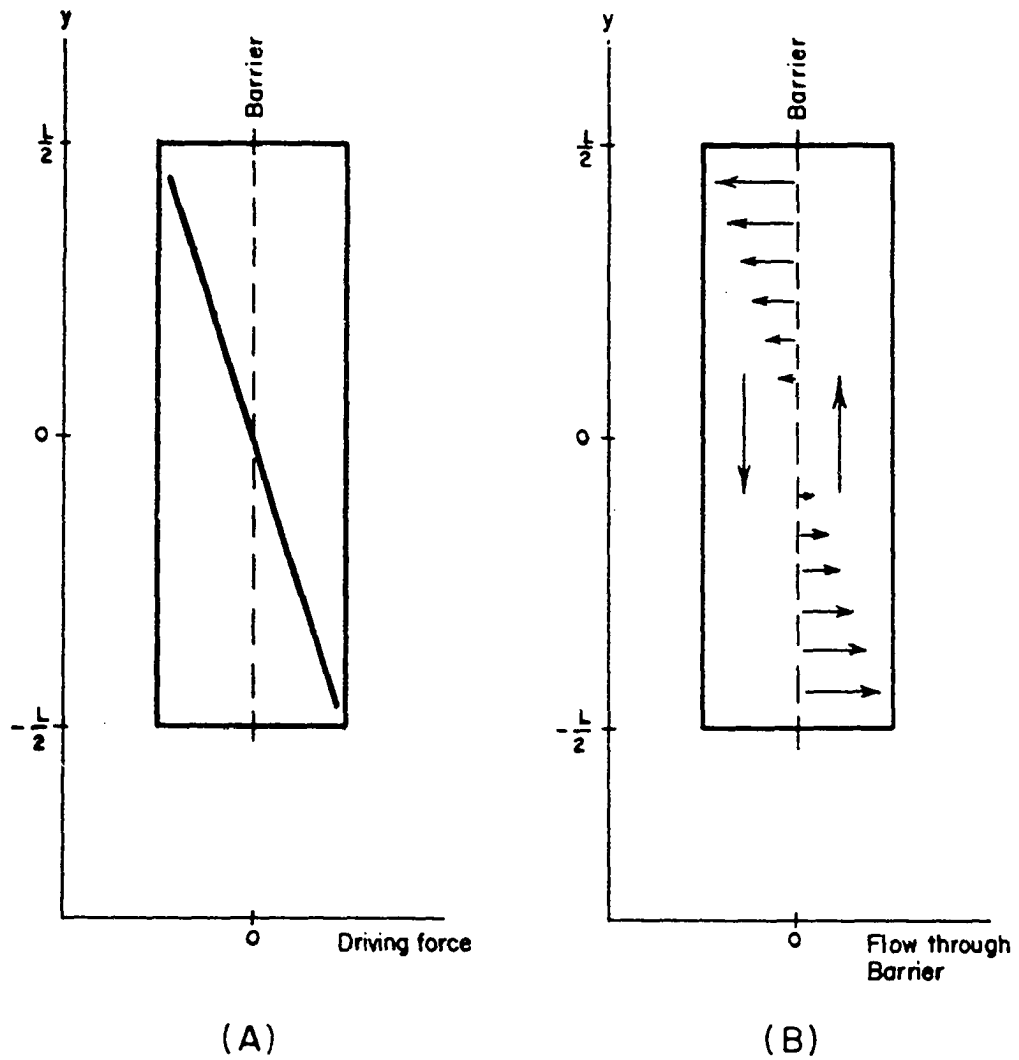


Figure 27 - Schematic Representation of Driving Force and Flow Through Real Vertical Barrier Causing Parabolic Contribution to Velocity Profile

plane is passed through the column at any y , $\dot{M}(y)$ is the volumetric flow rate passing through an area of the plane of dimensions B by ω . In order to develop a parabolic contribution to the velocity profile which is independent of y , it will be assumed that

A29 - an integrated average, $\bar{M}$, with respect to y can be applied for all y .

Because $\dot{M}(y)$ is in itself parabolic in y , it can be shown that

$$\bar{M} = 2/3 \dot{M}_{\max}, \quad \text{IV-64}$$

where $\bar{M}$ is the (constant) integrated average longitudinal (y direction) volumetric flow rate on one side of the barrier, and

$\dot{M}_{\max}$ is the maximum value of such a volumetric flow rate.

The $\dot{M}_{\max}$ value will occur at y equals zero. Recalling that h_y is the total longitudinal (y direction) head loss, the loss on one side of the barrier will be $h_y/2$. Bearing in mind assumptions A2 and A11, no gradients in the z direction and laminar flow, an expression for the laminar pressure drop between infinite planes can be derived or obtained from any standard work (235) and written for the longitudinal (y direction) flow on one side of the barrier as

$$\frac{h_y}{2} = \frac{12 \mu \bar{V} L}{\omega^2 g_C \rho} \quad \text{IV-65}$$

or

$$\bar{V} = \frac{\omega^2 g_C \rho}{24 \eta L} (h_y) , \quad \text{IV-66}$$

where $\bar{V}$ is the average linear velocity on one side of the barrier.

The total volumetric flow rate in the x direction through one-half the barrier area will now be defined as $\dot{B}$. Now consider a yz-plane at x equals zero (the vertical barrier). An elementary consideration of the circulation down the left side of the column (y minus direction), through the lower half of the barrier (plus x direction) up the right side of the column (plus y direction), and back through the upper half of the barrier (minus x direction) shows that

$$\dot{B} = \dot{M}_{\max} . \quad \text{IV-67}$$

Considering $\dot{B}$, the volumetric flow rate in the x direction through one-half the barrier of area $L/2$ times B , the average driving force for this flow will be one-half the maximum x direction driving force (due to assumption A28). If the total head loss due to flow through the barrier is h_x , the head loss through one-half the barrier will be $h_x/2$. The average driving force through one-half the barrier area will be $h_x/4$. Based on these driving forces, together with the area of $L/2$ times B , and the linear flow law (Equation IV-63), an expression can be written for $\dot{B}$ as

$$\dot{B} = \frac{FLB}{8} (h_x) . \quad \text{IV-68}$$

The quantities $\bar{M}$ and $\bar{V}$ are related through the cross-sectional area for longitudinal flow (y direction), of area B times ω , by

$$\bar{M} = \bar{V} \omega B . \quad \text{IV-69}$$

A relation between $v(x)$ and $\bar{V}$ may be readily derived or found in any fluid mechanics text (236) as

$$v_R(x)_{\text{par}} = \frac{6\bar{V}}{\omega^2} (\omega x - x^2) , \quad \text{IV-70}$$

where Equation IV-70 is written to represent the parabolic contribution to the velocity profile on the right side of the barrier ($0 \leq x \leq \omega$).

An analytic expression can now be found for the batch parabolic contribution to the velocity profile as a function of x and independent of y as desired. Equations IV-62, 64, 66-69 contain the unknowns h_x , h_y , $\bar{M}$, $\dot{M}_{\text{max}}$, $\dot{B}$, and $\bar{V}$. These six equations can be readily solved for $\bar{V}$. When this value is substituted into Equation IV-70, the result is an expression for the batch parabolic contribution to the velocity profile on the right side of a thermogravitational column with a hydrodynamically nonideal vertical barrier,

$$v_R(x)_{\text{par}} = \frac{2 \beta_T \Delta T g F L^2}{\rho g_C (2\omega)^3 + 16 \eta F L^2} (\omega x - x^2)$$

$$\text{for } 0 \leq x \leq \omega . \quad \text{IV-71}$$

In completely analogous fashion, the parabolic contribution to the velocity profile on the left side of the barrier is

written as

$$v_L(x)_{\text{par}} = \frac{2 \beta_T \Delta T g F L^2}{\rho g_C (2\omega)^3 + 16 \eta F L^2} (\omega x + x^2)$$

$$\text{for } -\omega \leq x \leq 0 . \quad \text{IV-72}$$

Notice that the coefficient of bulk flow through the barrier, F , appears prominently in these equations.

Previously developed as Equations IV-47 and 48 are the batch ideal barrier velocity profile contributions. The resultant batch velocity profile for a single vertical barrier with some degree of hydrodynamic nonideality is determined by adding Equations IV-47, 48 to IV-71, 72 which may be written symbolically for the right half of the column as

$$v_R(x)_{AB} = v_R(x)_{IB} + v_R(x)_{\text{par}} , \quad \text{IV-73}$$

where the subscripts AB, IB, and par refer to actual barrier, ideal barrier, and parabolic contribution. Writing out the expressions completely for both sides of the barrier yields

$$v_L(x)_{AB} = \frac{-g \beta_T \Delta T}{24 \omega \eta} (2x^3 + 3\omega x^2 + \omega^2 x) + \frac{2 \beta_T \Delta T g F L^2}{\rho g_C (2\omega)^3 + 16 \eta F L^2} (\omega x + x^2)$$

$$\text{for } -\omega \leq x \leq 0 , \quad \text{IV-74}$$

and

$$v_R(x)_{AB} = \frac{-g\beta_T \Delta T}{24 \omega \eta} (2x^3 - 3\omega x^2 + \omega^2 x) + \frac{2 \beta_T \Delta T g F L^2}{\rho g_C (2\omega)^3 + 16 \eta F L^2} (\omega x - x^2)$$

for $0 \leq x \leq \omega$.

IV-75

With reference again to Figure 26; the type of ideal barrier batch velocity profile contribution of Figure 26A is represented by Equations IV-47 and 48. The type of hydrodynamically nonideal parabolic contribution to the batch velocity profile of Figure 26B is given by Equations IV-71 and 72, and the resultant batch velocity distribution for an actual barrier with hydrodynamic nonideality sketched in Figure 26C is represented by Equations IV-74 and 75.

Evaluation of H_{AB}^1 and K_{CAB}^1 for a Single Real Vertical Barrier.--Solutions for the defining integrals for H and K_C (Equations IV-15 and 16) will now be presented using the batch velocity profiles developed for a single vertical real barrier with some degree of hydrodynamic nonideality (Equations IV-74 and 75). The integrations were carried out piecewise employing the same technique used in developing H_{IB}^1 and K_{CIB}^1 for a single ideal barrier. However, care must be exercised in defining the lower limits of the inner integrals of Equations IV-49 and 50 because the value of the inner integrals is not zero at x equals zero.

Because of the algebraically complex nature of the integrations, the work can be simplified by carrying out the integration from $-\omega$ to zero and multiplying by two to arrive

at H_{AB}^1 and K_{CAB}^1 . This method is admissible because a velocity profile of the type of Figure 26C is an odd function. This method of integration can also be applied in the case of purely ideal barriers if desired.

When the batch velocity profiles for a single vertical barrier with hydrodynamic nonideality (Equations IV-74 and 75) are substituted in the defining integrals for H and K_c and the integrals evaluated by either of the above procedures, the results are given by

$$H_{AB}^1 = \frac{\alpha \beta_T \rho g B (\Delta T)^2 (2\omega)^3}{6! \bar{T} \eta (2)^4} + \frac{15 \alpha \beta_T \rho g B (\Delta T)^2 (2\omega)^3 FL^2}{6! \bar{T} [\rho g_C (2\omega)^3 + 16 \eta FL^2]} \quad \text{IV-76}$$

and

$$K_{CAB}^1 = \frac{\beta_T^2 g^2 \rho B (\Delta T)^2 (2\omega)^7}{9! D \eta^2 (2)^8} + \frac{26 \beta_T^2 g^2 \rho B (\Delta T)^2 (2\omega)^7 F^2 L^4}{8! D [\rho g_C (2\omega)^3 + 16 \eta FL^2]^2} + \frac{\beta_T^2 g^2 \rho B (\Delta T)^2 (2\omega)^7 FL^2}{(384) 6! D \eta [\rho g_C (2\omega)^3 + 16 \eta FL^2]} \quad \text{IV-77}$$

Again it should be emphasized that such H and K values can be used in any of the solutions to the transport equation.

It is seen that the H_{AB}^1 and K_{CAB}^1 values are made up of an ideal barrier term plus an additive factor accounting

for hydrodynamic nonideality. As such they may be rewritten as

$$H_{AB}^1 = H_{IB}^1 + h_{AB} \quad \text{IV-78}$$

and

$$K_{CAB}^1 = K_{CIB}^1 + k_{AB}, \quad \text{IV-79}$$

where H_{IB}^1 and K_{CIB}^1 have been previously developed (Equations IV-51 and 52) and h_{AB} and k_{AB} are now defined as

$$h_{AB} = \frac{15 \alpha \rho_T^2 g_B (\Delta T)^2 (2\omega)^3 F L^2}{6! T [\rho g_C (2\omega)^3 + 16 \eta F L^2]} \quad \text{IV-80}$$

and

$$k_{AB} = \frac{26 \beta_T^2 \rho_B (\Delta T)^2 (2\omega)^7 F^2 L^4}{8! D [\rho g_C (2\omega)^3 + 16 \eta F L^2]^2} + \frac{\beta_T^2 \rho_B (\Delta T)^2 (2\omega)^7 F L^2}{(384) 6! D \eta [\rho g_C (2\omega)^3 + 16 \eta F L^2]}. \quad \text{IV-81}$$

One criterion for H_{AB}^1 and K_{CAB}^1 values should be that they resolve to ideal barrier theory as the hydrodynamic ideality goes to zero. Inspection of Equations IV-76 to 81 shows this to be the case. That is, as the coefficient of bulk flow through the barrier, F , goes to zero; the nonideal contributions vanish.

An additional criterion of H_{AB}^1 and K_{CAB}^1 is that as F becomes very large, the H and K_C values should approach the H and K_C values for a column without a barrier. Taking the limit as F goes to infinity of the hydrodynamically nonideal

contributions to H and K_C values as expressed by Equations IV-80 and 81 results in

$$\lim_{F \rightarrow \infty} h_{AB} = \frac{15 \alpha \beta_T \rho g B (\Delta T)^2 (2\omega)^3}{(2)^4 6! T \eta} = 15 H_{IB}^1 \quad \text{IV-82}$$

and

$$\lim_{F \rightarrow \infty} k_{AB} = \frac{255 \beta_T^2 g^2 \rho B (\Delta T)^2 (2\omega)^7}{(2)^8 9! D \eta^2} = 255 K_{CIB}^1. \quad \text{IV-83}$$

Combining these results with the ideal contributions according to Equations IV-78 and 79 yields

$$\lim_{F \rightarrow \infty} H_{AB}^1 = 16 H_{IB}^1 \quad \text{IV-84}$$

and

$$\lim_{F \rightarrow \infty} K_{CAB}^1 = 256 K_{CIB}^1. \quad \text{IV-85}$$

From these relationships previously developed between a column with and without a single ideal vertical barrier (Equations IV-53 and 54), it is readily seen that a column with a totally hydrodynamically nonideal barrier (F approaching infinity) is indeed identical to a column with no barrier.

Theoretical Effect of F on Separations.--The importance of the degree of hydrodynamic ideality on steady-state separations attained in continuous-flow thermogravitational columns will be demonstrated by calculating some theoretical separation versus flow-rate curves with parameters of F .

These calculations were carried out using Equation IV-41 with H_{AB}^1 and K_{CAB}^1 computed from Equation IV-76 and 77. Column dimensions and systems properties are the same as listed in Table 1 and Appendix K. The results of these calculations are presented as Figure 28. Parameters of F are listed on the curves. It will be recalled that the units on F are

$$\frac{\text{vol} - \text{mass}}{\text{area} - \text{time} - \text{force} - \text{length}}$$

or in this case F is in

$$\frac{\text{cm}^3}{\text{cm}^2} \frac{\text{gm-m}}{\text{sec gm-f cm}}$$

Figure 28 shows that as F increases (decreasing hydrodynamic ideality), the batch separations are drastically reduced. However, at appreciable flow rates, the more ideal barriers (lower F) lose their advantage and in fact show lower separations than less ideal barriers. Notice that when the barrier is completely hydrodynamically ideal (F equals zero), the calculated curve of Figure 28 is identical to the ideal barrier Curve B of Figure 25 which was calculated for the same physical system. Also the curve for total hydrodynamic nonideality (F equals infinity) of Figure 28 is the same as the no barrier Curve A of Figure 25.

Conclusion

The fundamental thermogravitational thermal diffusion column theory of Furry, Jones, and Onsager has been reviewed.

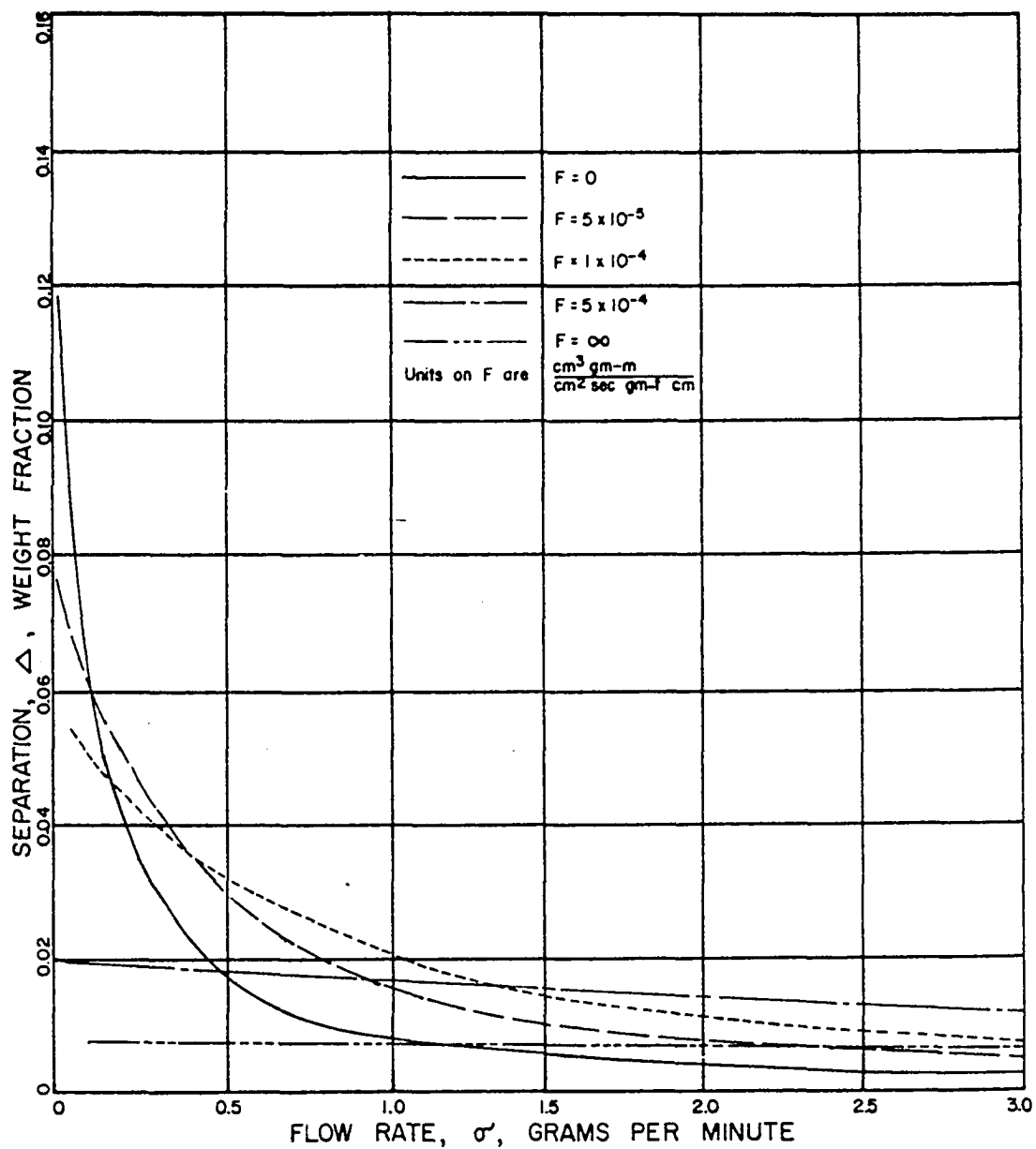


Figure 28 - Theoretical Effect of Hydrodynamic Non-idealities for a Vertical Barrier

The concept of "ideal" vertical barriers has been proposed. The mathematical ideal vertical barrier has the following properties:

- a) is infinitely thin (dimensional ideality),
- b) allows free molecular diffusion (diffusive ideality), and
- c) allows no macroscopic bulk flow (hydrodynamic ideality).

This model was chosen because the theory of Furry, Jones, and Onsager can be reasonably modified using such a system. With these definitions, the theory of Furry, Jones, and Onsager has been modified to account for any number of equally spaced ideal vertical barriers. The ideal barrier theory developed was extended to include hydrodynamic non-idealities encountered in real barriers. The ideal and real barrier theory developed affects only H and K values and can be used with any conventional solution to the transport equation.

The theory developed predicts striking increases in separation with an ideal vertical barrier in a thermogravitational column at low product flow rates. At increasing flow rates the theoretical barrier advantage decreases; and in fact, barriers are not advantageous at high throughputs. Also, the theory predicts that the advantage of ideal barriers is identical to that obtained by operating multiple columns in parallel with proportionally reduced temperature

differences, plate spacings, and flow rates.

All theory was developed using batch velocity profiles, and as such can only be applied to continuous-flow thermogravitational columns at low flow rates. Other major assumptions are listed in the developments.

The following is a summary of the major equations developed in this chapter.

Solution to the transport equation for a center-fed symmetrical steady-state continuous-flow thermogravitational column

$$\Delta = \frac{H}{2\sigma} (1 - e^{-\frac{\sigma L}{2K}}). \quad \text{IV-41}$$

Solution to the transport equation for a steady-state batch thermogravitational column

$$\Delta_0 = \frac{HL}{4K}. \quad \text{IV-42}$$

These are very restricted solutions to the transport equation which apply to later experimental work, and are no reflection on the generality of the ideal or real vertical barrier theory evolved in this work.

Furry, Jones, and Onsager conventional equations for parameters H and K in solutions to the transport equations

$$H = \frac{\alpha \beta_T \rho g B (\Delta T)^2 (2.7)^3}{6! \bar{T} \tau} \quad \text{IV-33}$$

$$K = K_c + K_d + K_p \quad \text{IV-18}$$

(In this work K_p and K_d can be neglected with respect to K_c such that $K \approx K_c$)

$$K_c = \frac{\beta_T^2 \rho g^2 B (\Delta T)^2 (2\omega)^7}{9! D \eta^2} \quad \text{IV-34}$$

Ideal barrier theory equations for parameters H and K in solutions to the transport equation for a column with n equally spaced ideal vertical barriers

$$H_{IB}^n = \frac{\alpha \beta_T \rho g B (\Delta T)^2 (2\omega)^3}{6! \bar{T} \eta (n+1)^4} \quad \text{IV-56}$$

$$K_{CIB}^n = \frac{\beta_T^2 \rho g^2 B (\Delta T)^2 (2\omega)^7}{9! D \eta^2 (n+1)^8} \quad \text{IV-57}$$

where $n = 0, 1, 2, 3 \dots$ IV-58

Equations for parameters H and K in solutions to the transport equation for a thermogravitational column with a single vertical real barrier with hydrodynamic nonideality

$$H_{AB}^1 = H_{IB}^1 + h_{AB} \quad \text{IV-78}$$

$$K_{CAB}^1 = K_{CIB}^1 + k_{AB} \quad \text{IV-79}$$

where

$$h_{AB} = \frac{15 \alpha \beta_T \rho g B (\Delta T)^2 (2\omega)^3 FL^2}{6! \bar{T} [\rho g_C (2\omega)^3 + 16 \eta FL^2]} \quad \text{IV-80}$$

$$k_{AB} = \frac{26 \beta_T^2 g^2 \rho_B (\Delta T)^2 (2\omega)^7 F^2 L^4}{8! D \left[\rho g_C (2\omega)^3 + 16 \eta FL^2 \right]^2} + \frac{\beta_T^2 g^2 \rho_B (\Delta T)^2 (2\omega)^7 FL^2}{(384) 6! D \eta \left[\rho g_C (2\omega)^3 + 16 \eta FL^2 \right]}$$

IV-81

in which F is a coefficient of macroscopic bulk flow of material through the barrier.

It should be emphasized again that the ideal and real barrier theory H and K values are quite general. They may be used in any of the conventional solutions to the transport equation.

CHAPTER V

DISCUSSION OF RESULTS

This chapter is presented in five parts. A brief summary of the experimental sets of data taken and results obtained is followed by a discussion of qualitative (trend) comparisons with theory. The degree of quantitative agreement with theory is presented, followed by additional work which is not directly related to the problem of vertical barriers in steady-state continuous-flow thermal diffusion columns. Finally, a short resume of the chapter is given.

Resume of Experimental Sets of Data

As mentioned previously in Chapter III, an experimental "set" of data was normally a series of steady-state separation (Δ) versus flow rate (σ) data taken with the thermogravitational column, treating as parameters the temperature difference (ΔT), plate spacing (2ω), and of course the barrier type. The mean temperature level ($\bar{T}$), column length, and physical system were never varied.

Detailed data for all steady-state continuous-flow runs are presented in Appendix B. Column and system parameters for all experimental sets are given as Appendix C.

The flow patterns used in all sets of runs are diagrammed in Appendix E. An estimate of the reliability of each set of runs is given as Appendix G.

Experimental Sets of Runs Made Without Barriers.---

Experimental Sets A, B, C and D were straightforward runs made without barriers. These sets of data were taken to try to eliminate defects from the experimental equipment, to develop experimental technique, and for comparison with sets taken with vertical barriers. Results were satisfactory and in agreement with other investigators. Sets E and F were taken without barriers; but with unequal product flow rates, and are discussed under Additional Work.

Experimental Sets of Runs Made With Vertical

Barriers.--Experimental Sets G, H, I, J, K, L and M were taken with single vertical barriers of various types installed in the thermogravitational column. Sample data sheets are shown as Appendix L. Detailed specifications and arrangements of the barriers are presented as Appendix D. The installation of vertical barriers in the working space of the thermal diffusion column has been described in Chapter III. Multiple barriers were not tested because of the mechanical problems involved.

Set G was taken with a vertical perforated aluminum foil barrier. This set was a failure. Wrinkles in the barrier could not be eliminated, so the barrier was somewhat loose and touched the hot and cold plates. Experimental

results were completely nonreproducible.

Set H was obtained with a vertical perforated Mylar barrier. The barrier was uniformly perforated with 0.124 cm diameter round holes, such that the barrier had an open area of 10.7 per cent. The system was severely nonideal; both hydrodynamically and with respect to diffusion. Separations were reduced below those obtained under similar conditions without a barrier because of these nonidealities.

As a check on the "worst" type of barrier, Set I was obtained. The barrier used was an impervious Mylar sheet with a large horizontal slot at the top and bottom. Thus this barrier should be totally nonideal with respect to both diffusion and bulk flow. Such was the case. Within experimental error, zero separation was obtained at every flow rate.

Set J was obtained using a tracing paper vertical barrier. The flow pattern used in this set was not deemed satisfactory (see explanation of flow modification for barriers in Chapter III and the flow patterns of Appendix E), and a minute leak developed in the system, so this set was essentially repeated as Set L using a suitable flow pattern. However, the data of Set J show a good increase in separation at low flow rates.

The data of Set K were obtained using a vertical tracing paper barrier and a large plate spacing. This set also showed an increase in separation at low flow rates over

a comparable set taken without a barrier.

Set L made use of a vertical tracing paper barrier and showed a good increase in separation at low flow rates compared to similar data obtained with no barrier. Sets K and L will later be compared from the standpoint of the effect of plate spacing with a vertical barrier in place.

Set M was similar to Set L, but at a different level of temperature difference. Again a vertical tracing paper barrier was used and exhibited an increase in separation at low flow rates over comparable data obtained without a barrier.

Shown as Figure 29 are some steady-state separation (Δ) versus flow rate (σ) data to illustrate the variations noted with different types of barriers. The sets of data were all taken at approximately the same plate spacings (2ω) and temperature differences (ΔT). Trend lines have been sketched in for convenience of comparison, but have no theoretical basis in this particular figure.

"Ideality" Tests Made on the Tracing Paper Used as Barrier Material.--The paper used was a Keuffel and Esser prepared tracing paper, designated as ALBANENE 195 MX. This paper was subjected to ordinary diffusion and bulk flow tests previously described in Chapter III. The results of these tests are presented as Appendices H and I.

Ordinary diffusion tests were carried out in a small batch cell with and without tracing paper separating the two

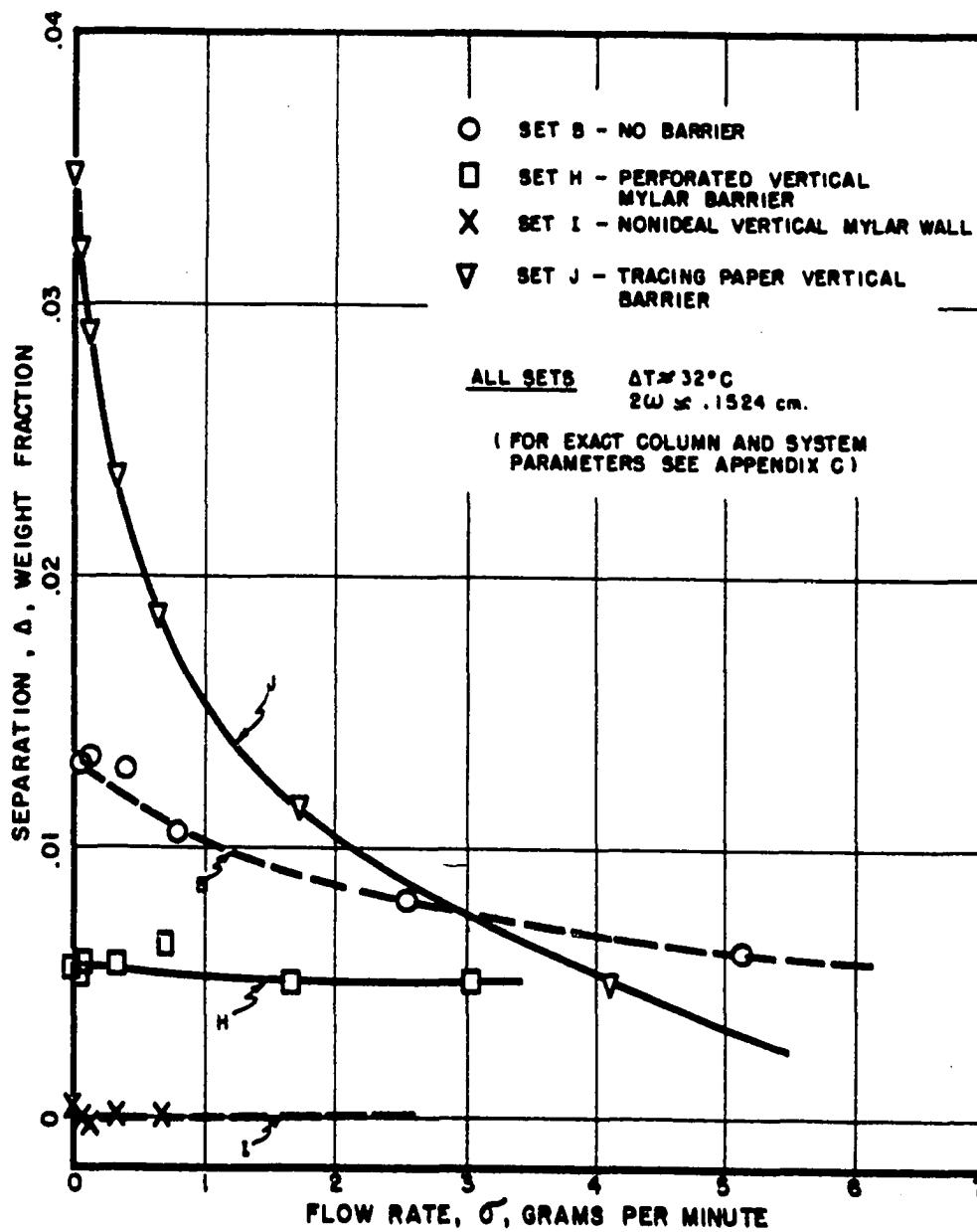


Figure 29 - Qualitative Comparative Separations for Different Types of Barriers Under the Same Conditions

halves of the cell. Within experimental error, no difference could be detected in the ordinary diffusion rates. On this basis it is assumed that the paper barriers were very nearly "ideal" with respect to diffusion impedance.

The theoretical developments of Chapter IV assumed a linear flow law of the form

$$Q = Fh \quad \text{IV-63}$$

where Q is the volumetric flow rate per unit area through the barrier,

h is the driving force in terms of liquid head, and

F is a coefficient of flow.

Tests were made on the tracing paper used for vertical barriers to determine the coefficient of flow, F . The resulting value was $F = 4.02 \times 10^{-6} \text{ cm}^3\text{-gm-m/cm}^2\text{-sec-gm-f-cm}$. Appendix H and the Sample Calculations, Appendix M, show how this figure was obtained.

Since an "ideal" barrier has an F of zero, the tracing paper rates rather high in hydrodynamic ideality. Thus in the following section, qualitative comparisons with theory will be made assuming F is equal to zero (truly "ideal"). The measured F will be discussed more fully in later quantitative comparisons with theory.

Miscellaneous.--To try to alter the flow pattern with vertical barriers in place, external circulating loops were attached to the top and bottom of the column (See Figure 52, Appendix E). These runs were erratic, due to vapor locks in

the upper loop, and are considered unreliable.

Some transient data were obtained in the course of this work. These data are discussed in some detail in a later section on Additional Work. The transient work with barriers is significant in that it supports the idea that some modification of the thermogravitational theory of Furry, Jones, and Onsager may be applied to columns containing a vertical barrier.

Qualitative Comparisons With Theory

Method of Comparison.--To compare experimental thermogravitational continuous-flow steady-state separation data with theory, Equation IV-41 previously developed will be used

$$\Delta = \frac{H}{2\sigma} (1 - e^{-\frac{cL}{2K}}). \quad \text{IV-41}$$

This equation shows that for a given column length (L), the separation (Δ) versus flow (σ) data should be correlated by the two column constants, H and K. For a given set of separation versus flow data, H and K can be determined empirically to best fit the data. Then the empirically determined H and K values can be theoretically corrected for various parameters to qualitatively compare theory with experiment at low flow rates.

Powers (237) has devised a new method of fitting separation versus flow data to empirically determine H and K for low flow rates. If the previously developed equation for

steady-state batch separation

$$\Delta_0 = \frac{HL}{4K} \quad \text{IV-42}$$

is divided into Equation IV-41, the result is an equation of the form

$$\frac{\Delta}{\Delta_0} = \frac{2K}{\sigma L} \left(1 - e^{-\frac{\sigma L}{2K}}\right). \quad \text{V-1}$$

Such an equation represents the steady-state flow separation normalized with respect to the maximum batch separation.

Equation V-1 can be rewritten in the form

$$\frac{\Delta}{\Delta_0} = \frac{1}{Z} (1 - e^{-Z}) \quad \text{V-2}$$

where

$$Z = \frac{\sigma L}{2K} . \quad \text{V-3}$$

A plot of the normalized general flow-separation Equation V-2 is presented as Figure 30.

To use a generalized plot of the type shown in Figure 30, it is necessary to assume values of Δ_0 and K . Then a set of processed Δ vs σ (separation versus flow rate) data can be plotted on the graph (L , the column length is known). Then the values of Δ_0 and K are adjusted to obtain the best fit. When a satisfactory fit is achieved, H can be calculated from Δ_0 using Equation IV-42. Thus "best" empirical values of H and K for experimental sets are

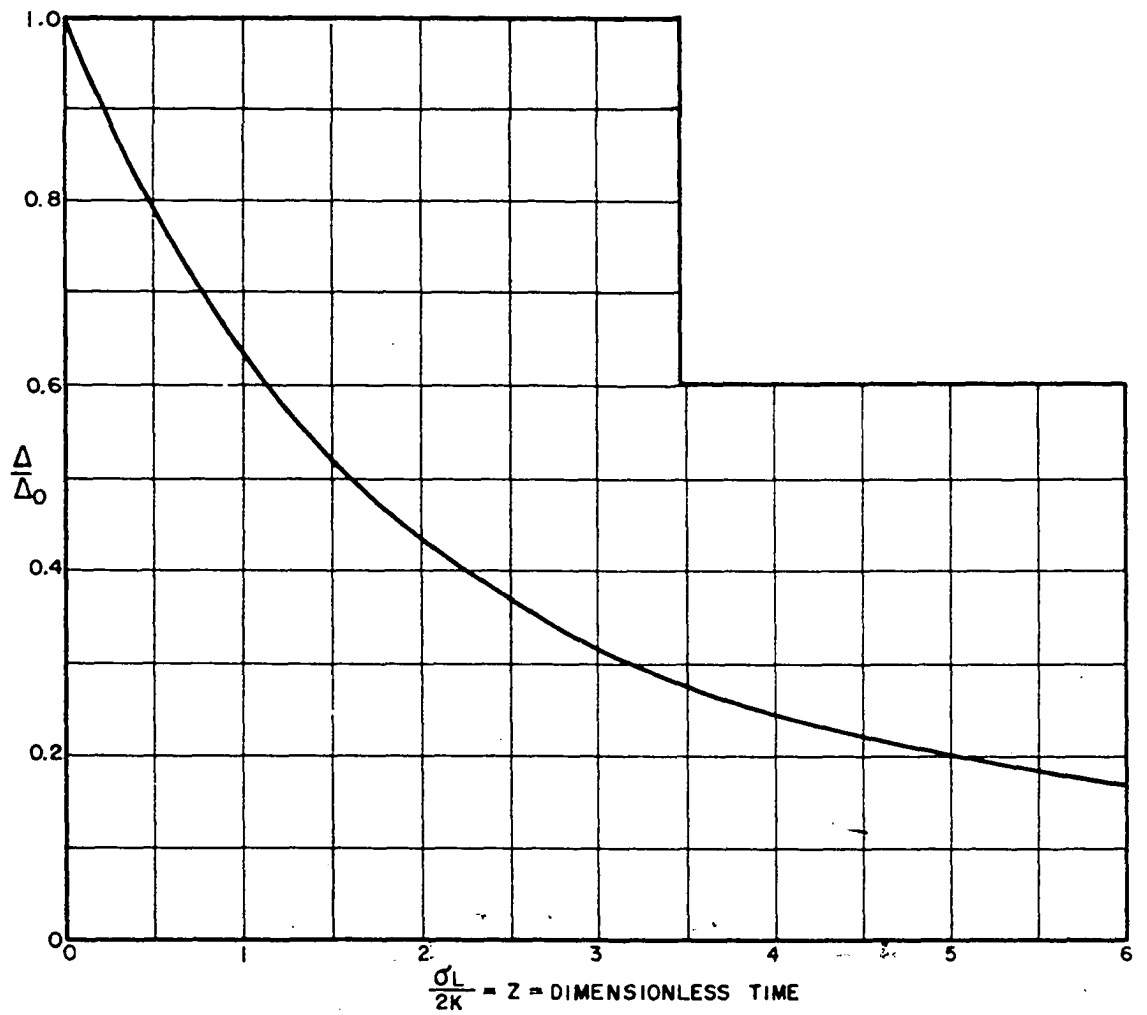


Figure 30 - Powers' Method of Generalized Theoretical
Separation Versus Flow Rate Plot

determined. This method of determining empirical H and K values from steady-state data is used exclusively in this work. The method is illustrated step by step in the Sample Calculations, Appendix M.

Effect of Flow Rate.--Equation IV-41 should predict the effect of flow rate on separation if the proper H, K and L values are used (H and K empirically determined by the method just previously described). The prediction of separation versus flow rate is excellent as shown by Figure 31 without barriers. Deviations from the semi-theoretical curve begin to occur at higher flow rates because the assumption that the net flow through the column is small compared to the internal convective flow is violated. However, Figure 31 definitely shows that the form of Equation IV-41 is correct for low flow rates. Powers (58) devised elaborate correction factors for higher flow rates. However, in this work we will only be concerned with the degree of agreement at low flow rates.

Figure 32 shows the effect of flow rate on separation with a single vertical tracing paper barrier in place. Again Equation IV-41 predicts the separation versus flow rate data well for low flow rates when H and K are determined empirically. This is expected because the ideal and actual barrier theory developed affect only H and K, and not the form of Equation IV-41.

Effect of Temperature Difference (ΔT).--According to

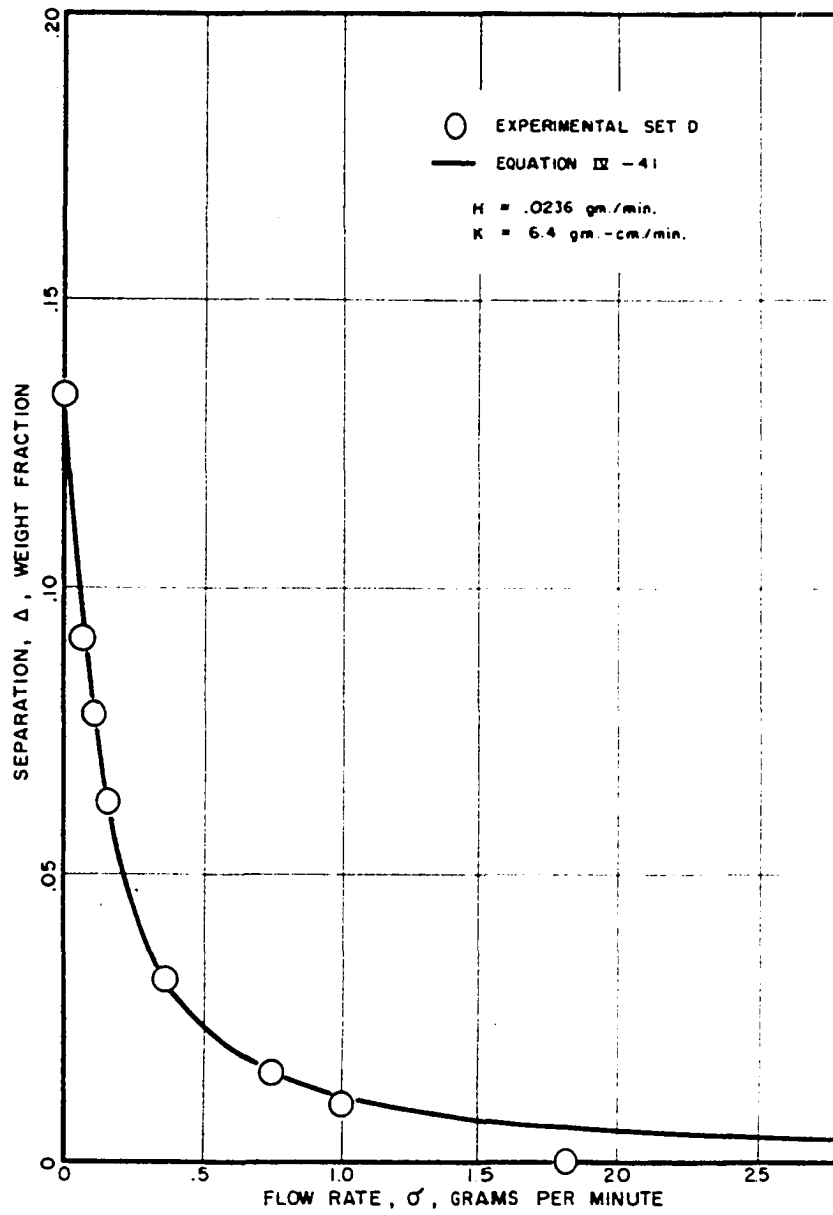


Figure 31 - Effect of Flow Rate on Separation--No
Barrier

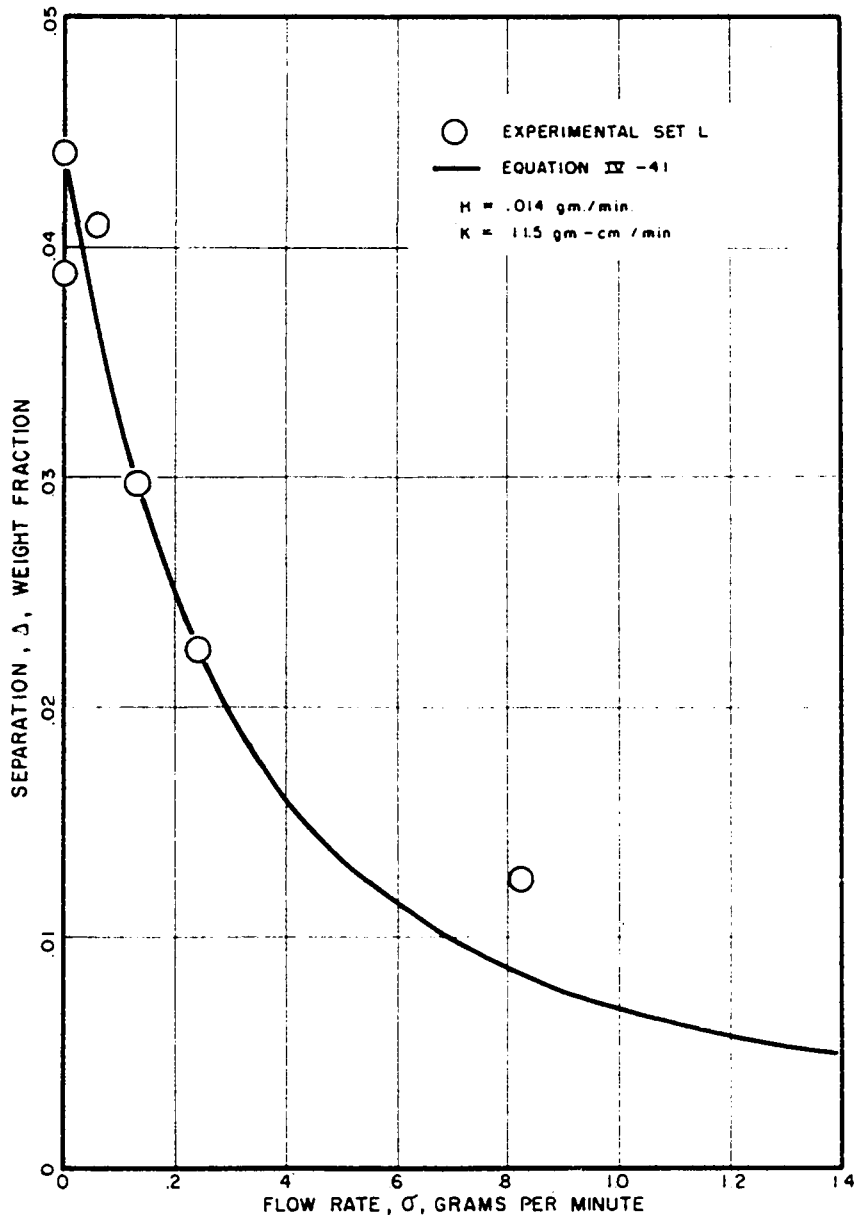


Figure 32 - Effect of Flow Rate on Separation--Tracing
 Paper Barrier

Equations IV-33 and IV-34, both H and K should be proportional to the square of the temperature difference, $(\Delta T)^2$, with no barriers. Values of H and K should be capable of being represented by $H = a(\Delta T)^2$ and $K = b(\Delta T)^2$ where a and b are constants. Thus, empirical H and K values for a given plate spacing can be corrected by ratios of the square of the temperature differences to account for varying temperature differences. Figure 33 shows fair agreement with this reasoning without barriers at low flow rates. This substantiates the results of a number of previous workers (58,180, 190). However, a definite trend in batch separation as a function of temperature difference is evident, contrary to theory. The discrepancy is of the same order of magnitude as observed by the above cited investigators.

It is shown by Equations IV-56 and IV-57 that for an ideal vertical barrier--with all other parameters the same--that H and K should again be proportional to the square of the temperature difference. Experimental data taken at two levels of temperature difference with a single vertical barrier in place are shown on Figure 34. H and K values are determined empirically for one set, theoretically corrected for temperature difference, and used in Equation IV-41. Agreement is fairly good at low flow rates.

Effect of Plate Spacing (2ω).--Equations IV-33 and IV-34 for no barriers predict a strong dependence of H and K on plate spacing; $H = a(2\omega)^3$ and $K = b(2\omega)^7$ --all other parameters being equal. Empirical H and K values for one

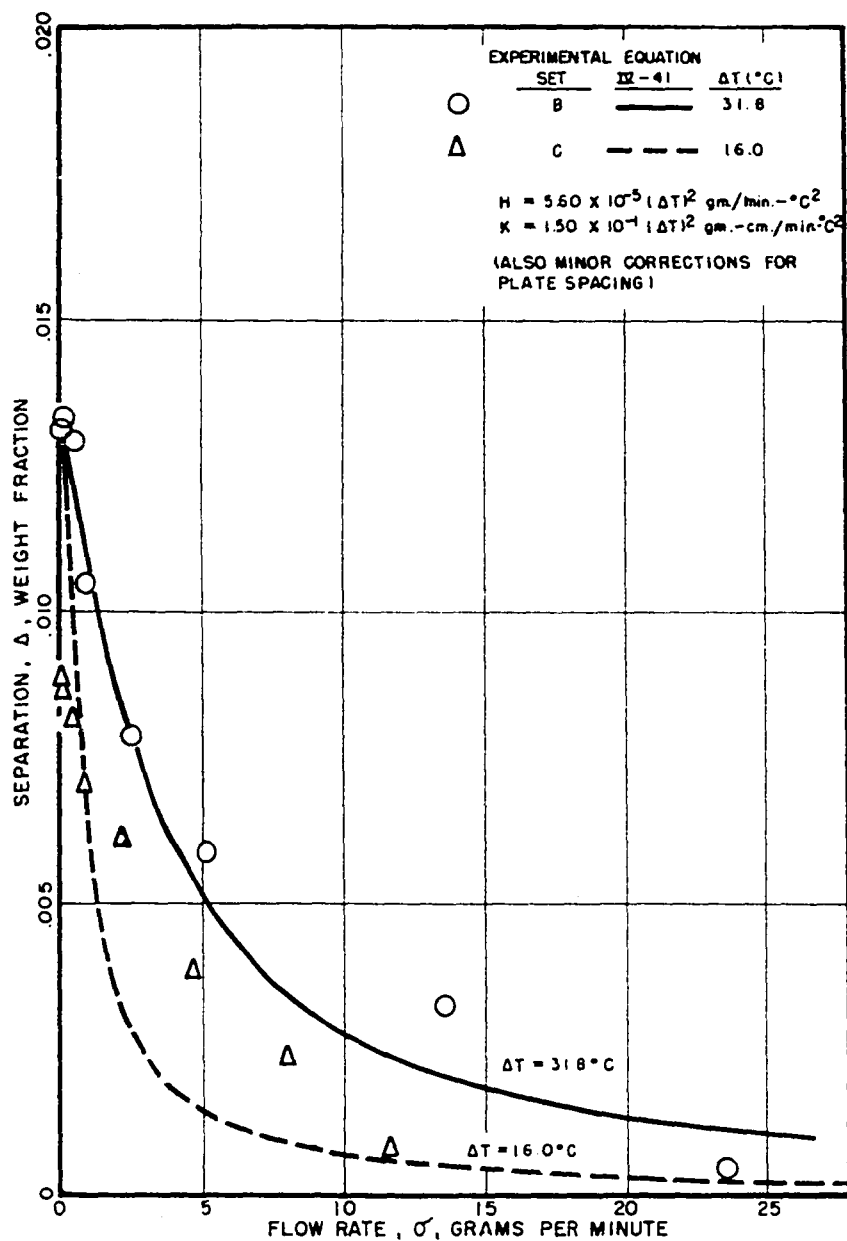


Figure 33 - Effect of Flow Rate on Separation With
Parameters of Temperature Difference--
No Barrier

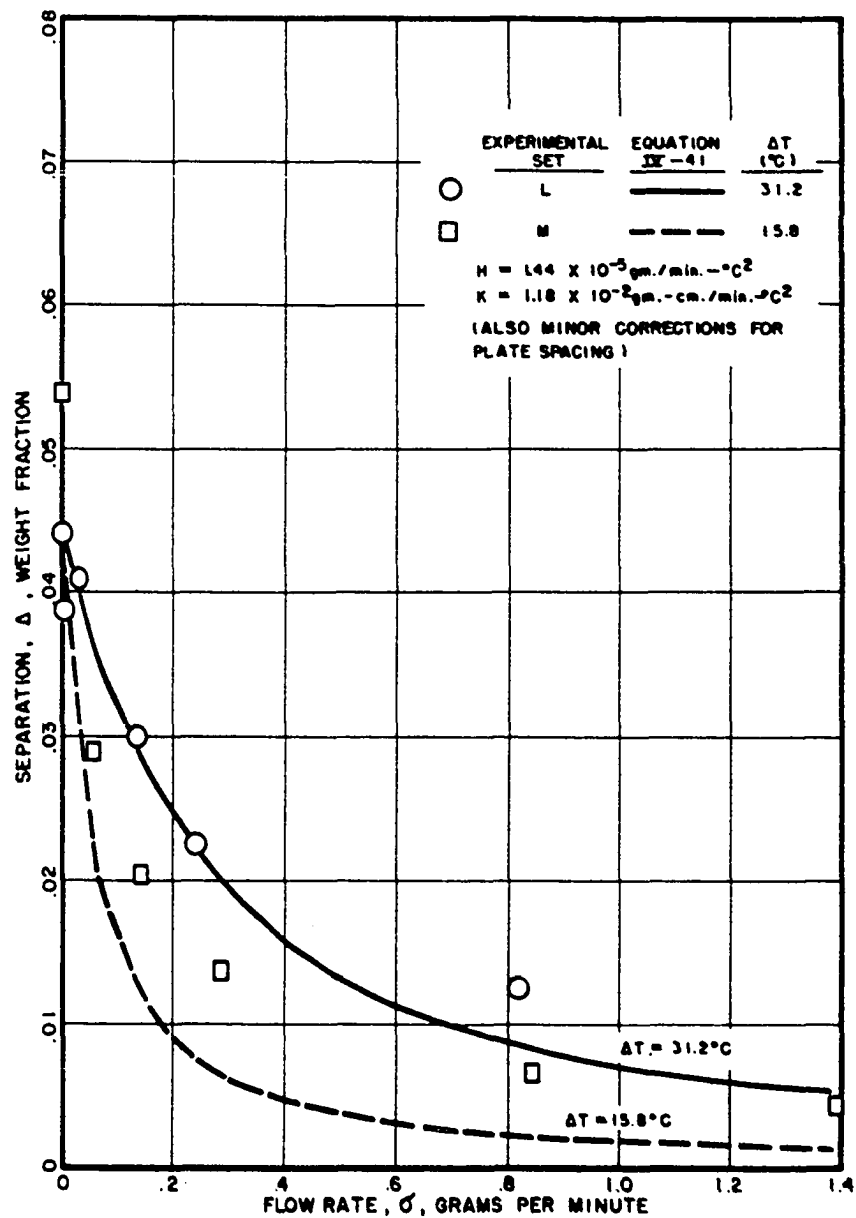


Figure 34 - Effect of Flow Rate on Separation with
Parameters of Temperature Difference--
Tracing Paper Barrier

experimental set have been corrected by these relationships and used in Equation IV-41 to try to represent other experimental sets at differing plate spacings. The agreement is fair to poor as shown in Figure 35 with no barriers at low flow rates. Other workers (58,89,106,185) have also shown only fair agreement between experiment and theory with regard to varying plate spacing. This is probably because of difficulties in precise measurement of the plate spacing, and the severe fashion in which these measurements enter into the theory.

For an ideal vertical barrier, Equations IV-56 and IV-57 predict the same H and K dependence on plate spacing as with no barriers. Therefore qualitative comparisons were made by correcting empirical H and K values by the cube and seventh power of the relative plate spacings respectively for use in Equation IV-41. Figure 36 presents data and semi-theoretical curves for two different plate spacings with a single vertical tracing paper barrier in place (and about the same temperature difference). The measured plate spacings with barriers in place were corrected for the thickness of the barrier used. Again only fair agreement is noted.

Effect of Vertical Barrier.--It is predicted by Equation IV-53 that the H value with a single ideal vertical barrier should be $1/16$ that of the H value for the same column without a barrier. Likewise Equation IV-54 states

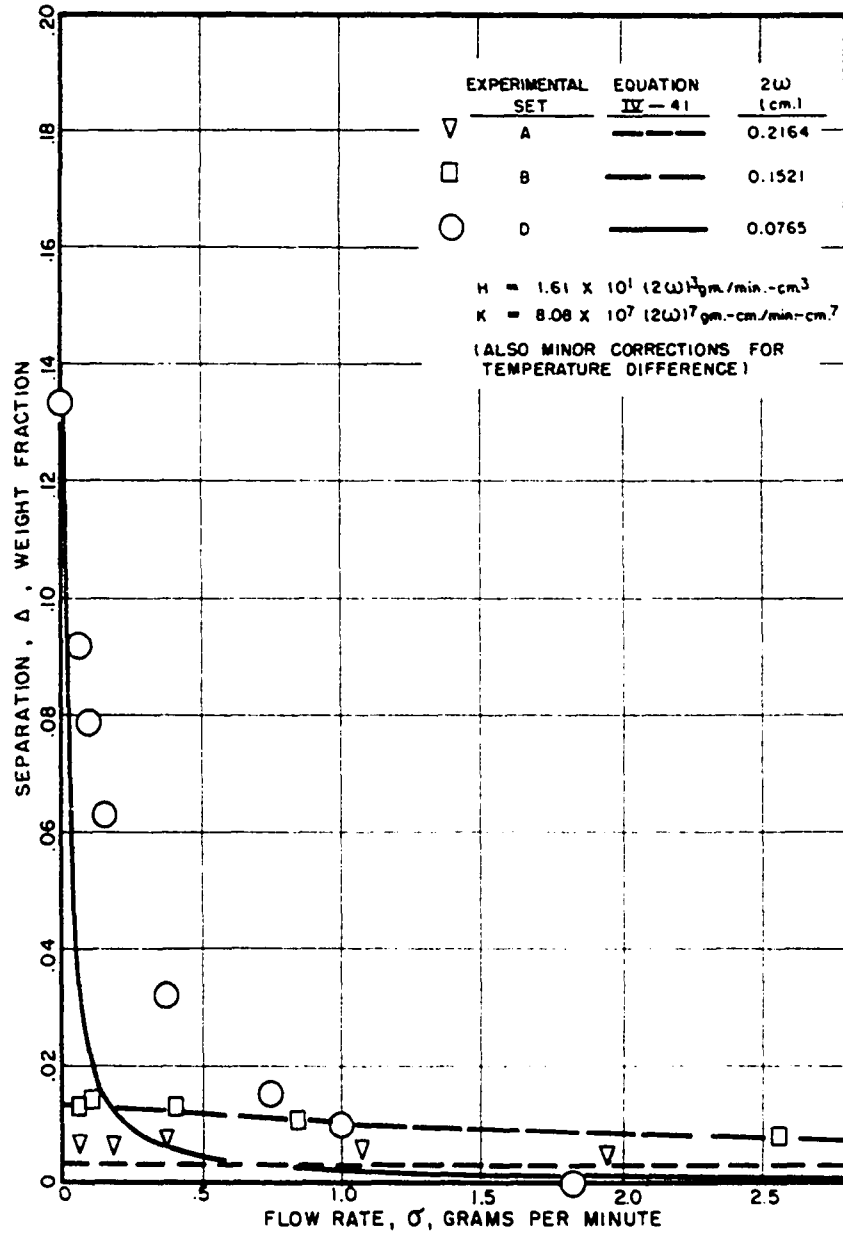


Figure 35 - Effect of Flow Rate on Separation with
Parameters of Plate Spacing--No Barrier

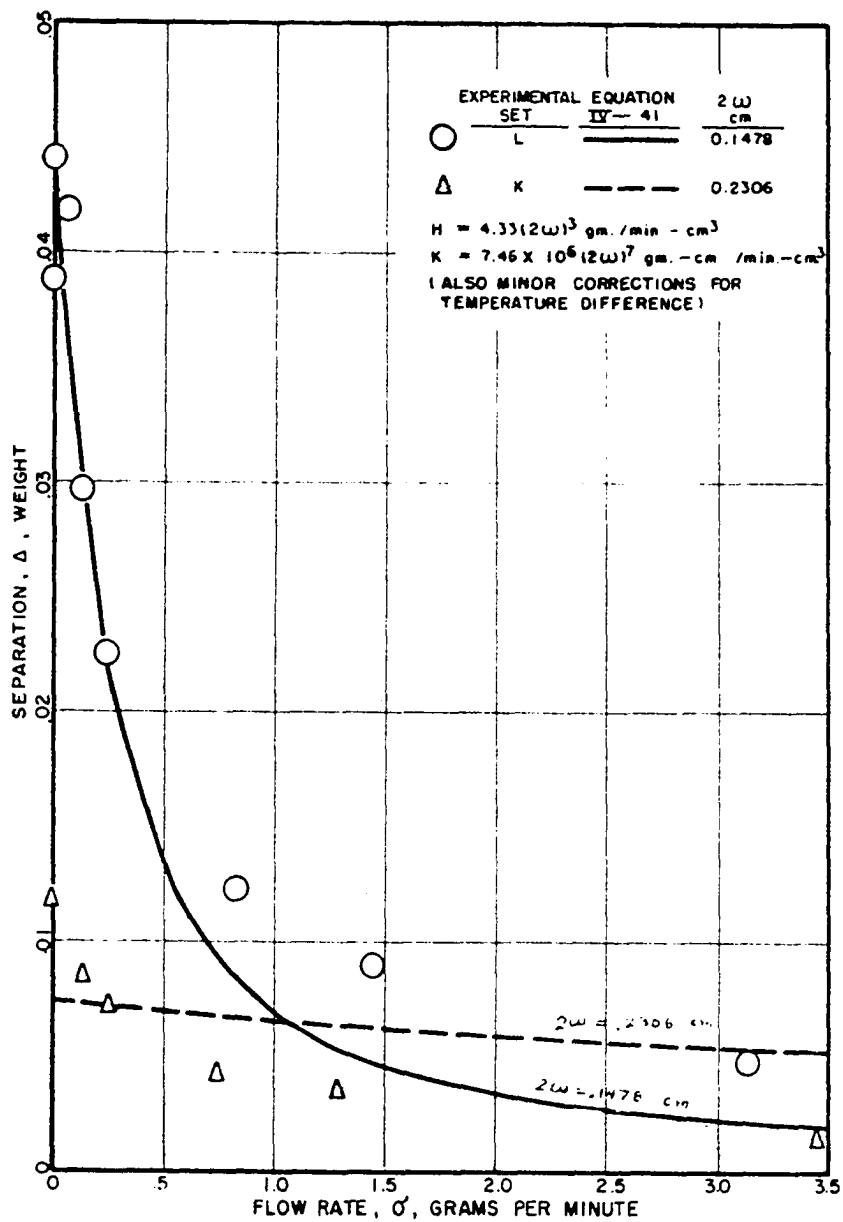


Figure 36 - Effect of Flow Rate on Separation with
Parameters of Plate Spacing--Tracing Paper
Barrier

that K should be reduced by a factor of $1/256$ upon the introduction of a single ideal vertical barrier.

The empirical H and K values for two sets of data without barriers have been corrected as suggested above and used in Equation IV-41 to predict semi-theoretical curves for barrier runs. Two comparisons of sets of data taken with and without a single vertical tracing barrier are shown as Figures 37 and 38. The two sets shown on each graph are at comparable levels of temperature difference and plate spacing, and differ only by the presence or absence of a vertical tracing paper barrier. The trend is correct in each case, but the qualitative agreement is only fair. This is expected because tracing paper is only an approximation of the mathematical model of an ideal barrier. Further discussion of agreement with modified ideal barrier theory will be found in the following section on Degree of Quantitative Agreement With Theory.

Degree of Quantitative Agreement With Theory

Columns Without Barriers.--In previous sections it has been shown that Equation IV-41 fairly successfully predicts trends and the effect of changes in operating conditions on separations if the proper H and K values are used. In the theoretical development, equations are evolved which should yield the correct values of H and K; for instance, Equations IV-33 and IV-34 for no barriers (for liquids K is very nearly equal to K_c). However, many investigators (58,106,180,186,

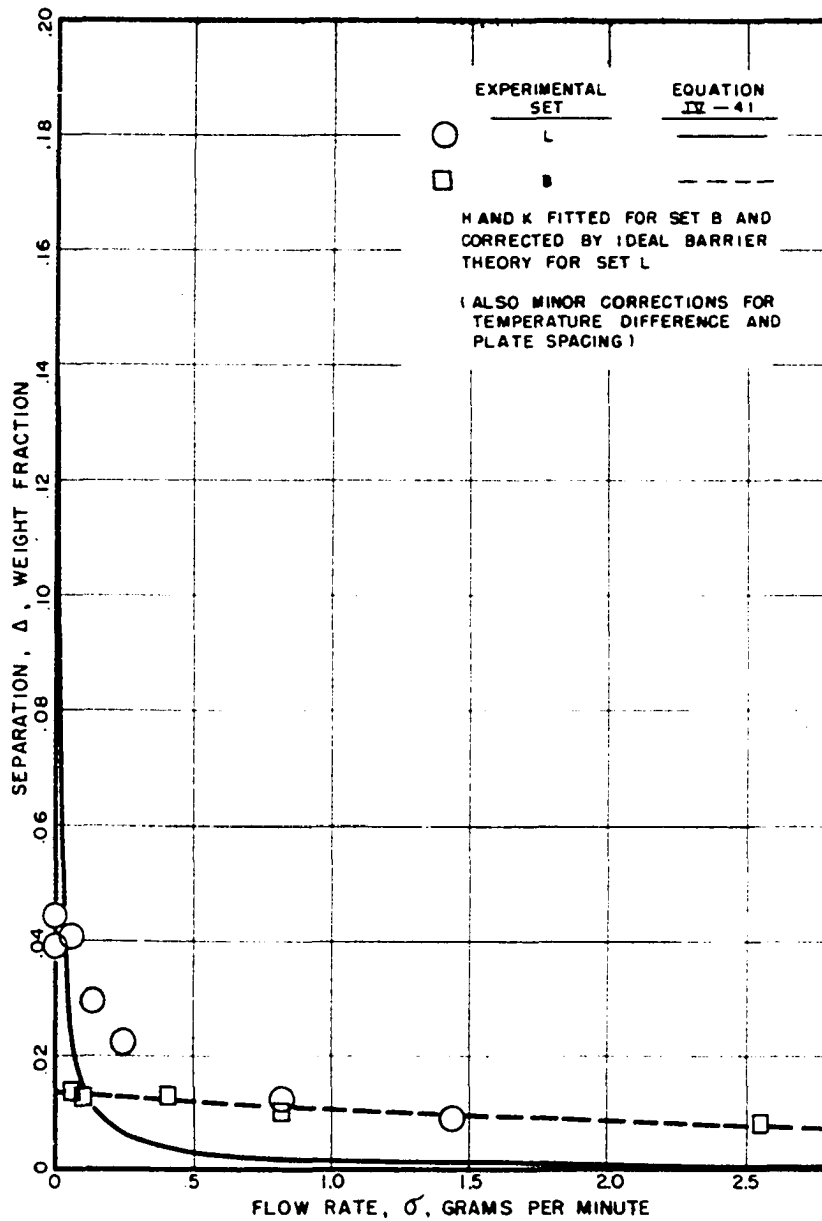


Figure 37 - Effect of Flow Rate on Separation--

Theoretical and Experimental Comparisons of
Sets With and Without Barrier--Sets B and L

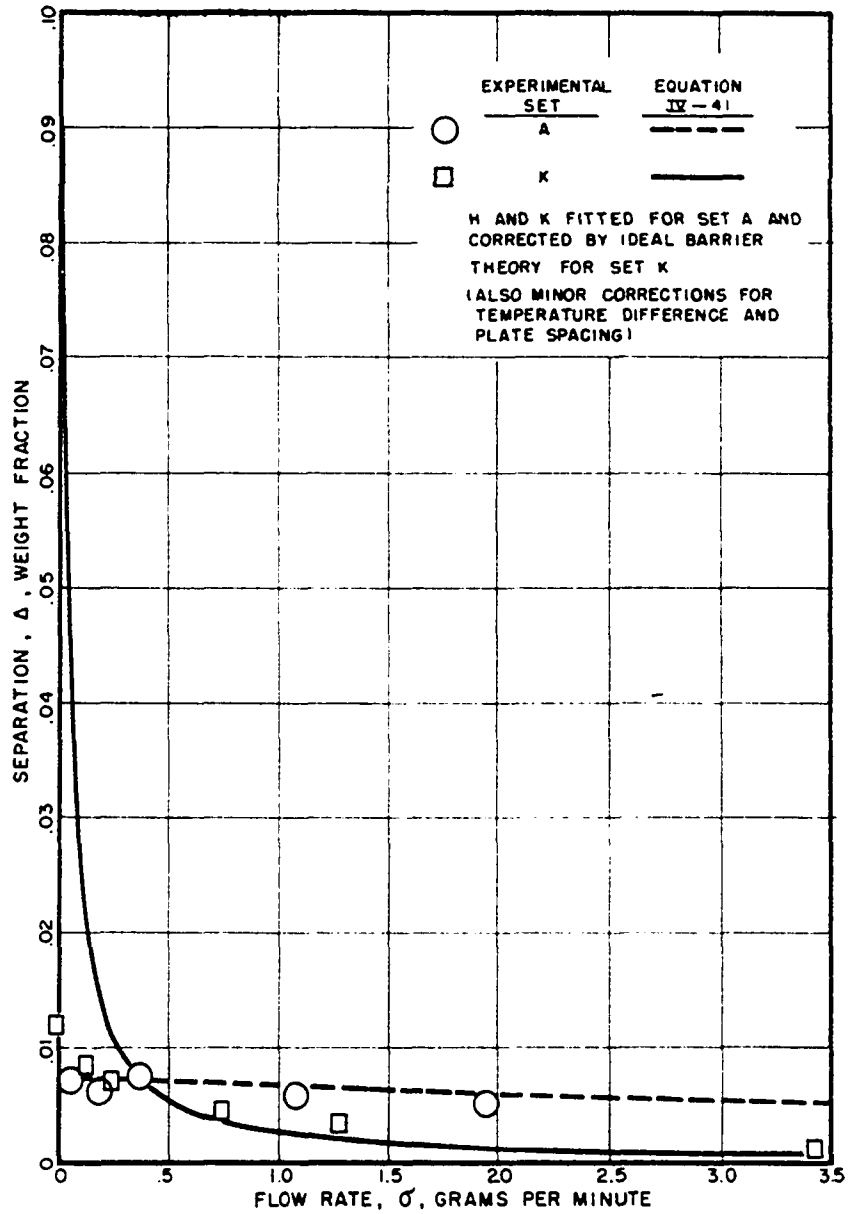


Figure 38 - Effect of Flow Rate on Separation--

Theoretical and Experimental Comparisons of
Sets With and Without Barrier--Sets A and K

208) have found that for liquids, the calculated theoretical values of H and K were not in agreement with experimental values.

Various workers have defined correction factors (58, 206-213). Powers (58) suggests that correction factors be defined as

$$\phi_H = \frac{H_{\text{expt}}}{H_{\text{theor}}} \quad \text{V-4}$$

and

$$\phi_K = \frac{K_{\text{expt}}}{K_{\text{theor}}} , \quad \text{V-5}$$

where the subscripts "expt" and "theor" refer to experimental and theoretical, respectively. Powers presented a correlation of these correction factors based on dimensional analysis. Powers also showed a fair correlation of these correction factors with plate spacing (2ω) for the system ethyl alcohol-water.

In the present work these correction factors can be obtained from experimental Sets A, B, C and D; all obtained without barriers, using the system alcohol-water. The resulting correction factors, together with those of Powers, are shown as Figure 39. A summary of these correction factors is presented as Appendix J. The method of calculation is shown in the Sample Calculations, Appendix M.

Some interesting features of Figure 39 should be pointed out:

- (1) The theory is quantitative at a certain small

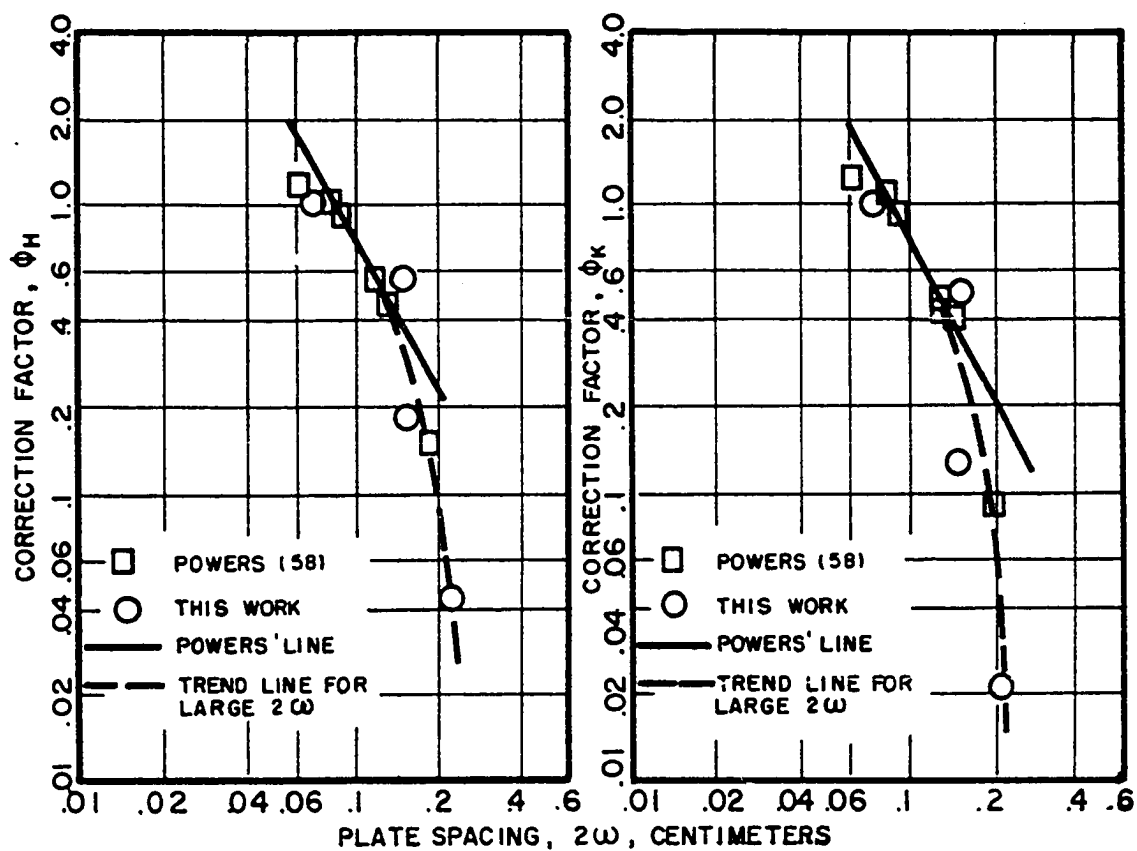


Figure 39 - Correction Factors ϕ_H and ϕ_K as a Function of Plate Spacing for the System Ethyl Alcohol-Water

value of plate spacing ($2\omega \approx 0.085$ cm).

- (2) The theory is in good qualitative agreement over the range of plate spacing ($0.05 < 2\omega < 0.15$ cm) in which appreciable separations occur.
- (3) The correction factors vary rapidly with plate spacing.
- (4) The correction factors fall off extremely rapidly at large plate spacings, probably as a result of turbulent phenomena.
- (5) The correction factors of the present work and those of Powers are in good agreement, even though the column dimensions are widely different.

Determination of the Thermal Diffusion "Constant".--

It has been shown by Powers (58) that the correction factors ϕ_H and ϕ_K are empirically related by the exponential form

$$\phi_K = \phi_H^{1.25} \quad \text{V-6}$$

With this equation, a straightforward method of determining the thermal diffusion "constant," α , is available in connection with previous empirical developments of this chapter plus the theory of Chapter IV.

The method will now be outlined step by step:

- (1) From empirically fitting a set of data by the method described in Qualitative Comparisons, K_{expt} is known.

- (2) By calculation, K_{theor} is known (Equation IV-34).
- (3) By definition (Equation V-5) ϕ_K can be calculated.
- (4) A value of ϕ_H can be obtained by Equation V-6.
- (5) The value of H_{expt} is known from empirical fitting; and, using the defining equation for ϕ_H (Equation V-4), H_{theor} is determined.
- (6) Using Equation IV-33, the only unknown is the thermal diffusion "constant," α .

The method is demonstrated in the Sample Calculations, Appendix M.

The most reliable (in terms of high separation and low analytical error) set of data, Set D, was used for this calculation. The result was a thermal diffusion "constant" of 0.513 for a 40 weight percent ethyl alcohol-water solution. This value, together with values obtained by other thermogravimational workers is shown in Figure 40. The values shown for Powers (58) were obtained in a continuous-flow thermogravimational column. The data of van Veldon et al. (238) and Cabicar and Zatka (239) were obtained in batch thermogravimational columns. The latter two sets of data were corrected at high concentrations by the method recommended by Prigogine and Buess (240). Other values of the thermal diffusion "constant" for the system ethyl alcohol-water determined in static cells are available. But, as pointed out by Powers (58) and Von Halle (50), these values are usually radically different from those determined by the thermogravimational

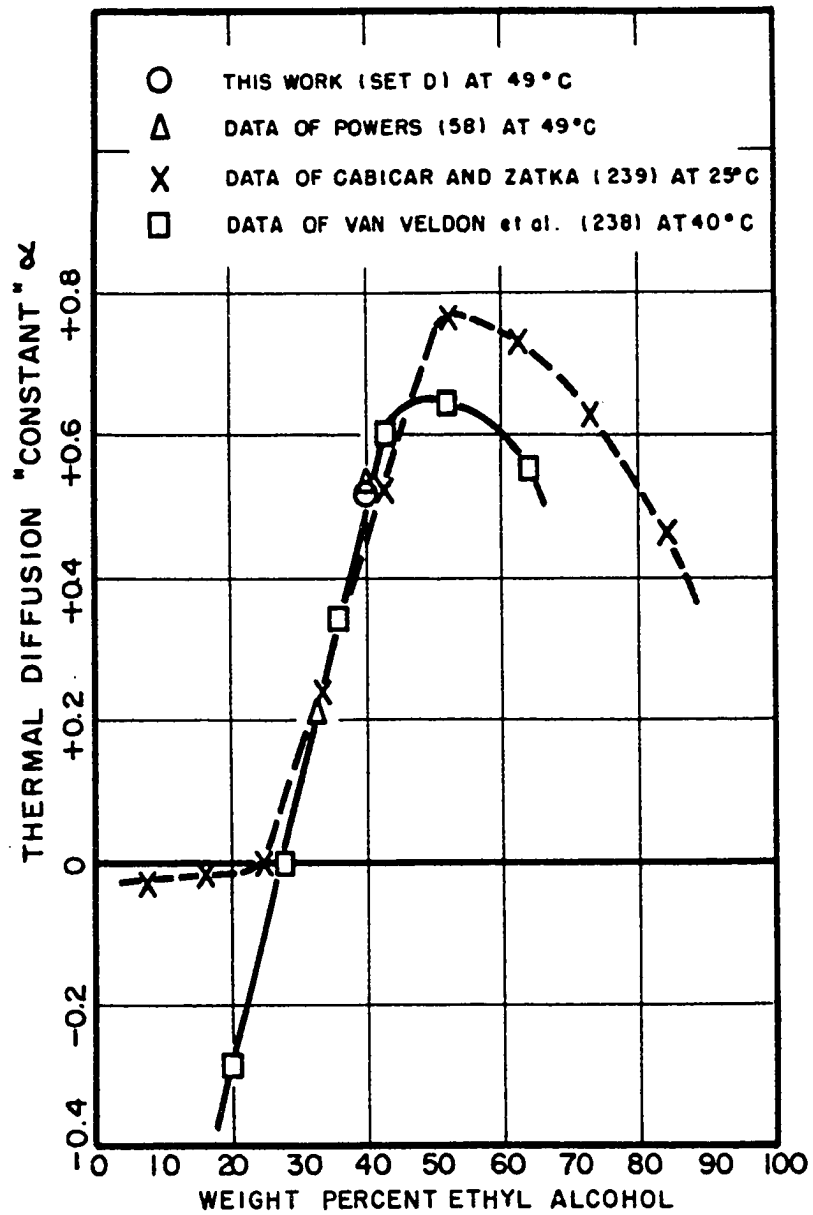


Figure 40 - The Thermal Diffusion "Constant," α , as a Function of Concentration for the System Ethyl Alcohol-Water

method.

Columns With Vertical Barriers.--There are obviously a number of ways of checking the quantitative agreement of the vertical barrier data with the theoretical developments of Chapter IV. However, it must be remembered that the thermogravitational theory without barriers is not quantitative which poses additional complications.

With this in mind, probably the most straightforward comparison is to theoretically calculate H and K values using the theory developed for a real barrier which allows some bulk flow ($F = 4.02 \times 10^{-6} \text{ cm}^3\text{gm-m/cm}^2\text{sec gm-f cm}$ coefficient of bulk flow measured for tracing paper). These theoretical H and K values can then be compared with those derived from empirical fitting. The resulting correction factors ϕ_H and ϕ_K will then be compared with those of Figure 39 developed for no barriers. The method of calculation using Equations IV-78, 79, 80 and 81 is detailed in the Sample Calculations, Appendix M. As suggested early in this chapter, data show the tracing paper to be "ideal" with respect to diffusion.

Experimental Sets K, L and M (tracing paper barriers) were treated as suggested and the results presented as Tables 3 and 4. For the convenience of the reader it is repeated below that the theoretical parameters H and K for a single real vertical barrier are made up of additive terms consisting of the ideal barrier term plus a term to account for bulk flow through the barrier,

TABLE 3

CORRECTION FACTORS ON H WITH REAL SINGLE VERTICAL BARRIER
(TRACING PAPER) IN THERMOGRAVITATIONAL COLUMN

Experimental Set	K	L	M
Plate Spacing, 2ω , cm	.2306	.1478	.1483
h_{AB} , gm/min	.0018	.0013	.0003
H_{IB}^1 , gm/min	.0789	.0169	.0041
H_{AB}^1 , gm/min, (H_{theor})	.0807	.0182	.0047
From Empirical Fit, gm/min, (H_{expt})	.0052	.0140	.0058
By Definition, ϕ_H	.065	.77	1.23
From Figure 39 at $2\omega/2$, ϕ_H	.61	1.26	1.26
From Figure 39 at 2ω , ϕ_H	.043	.43	.43

TABLE 4

CORRECTION FACTORS ON K WITH REAL SINGLE VERTICAL BARRIER
(TRACING PAPER) IN THERMOGRAVITATIONAL COLUMN

Experimental Set	K	L	M
Plate Spacing, 2ω , cm	.2306	.1478	.1483
k_{AB} , gm-cm/min	4.0	.48	.124
K_{CIB}^1 , gm-cm/min	117.8	4.24	1.078
K_{CAB}^1 , gm-cm/min, (K_{theor})	121.8	4.72	1.202
From Empirical Fit, gm-cm/min, (K_{expt})	16.0	11.5	4.0
By Definition, ϕ_K	.131	2.44	3.33
From Figure 39 at $2\omega/2$, ϕ_K	.58	1.30	1.30
From Figure 39 at 2ω , ϕ_K	.010	.36	.36

$$H_{AB}^1 = H_{IB}^1 + h_{AB} \quad \text{IV-79}$$

and

$$K_{CAB}^1 = K_{CIB}^1 + k_{AB} \quad \text{IV-80}$$

Also, the definition of the correction factor, ϕ , should be remembered as the experimental value over the theoretical value.

Presented on Tables 3 and 4 for comparison with the calculated correction factor, are correction factors taken from Figure 39 for both the Experimental Set plate spacing (2ω), and one-half the Experimental Set plate spacing ($2\omega/2$). Probably the latter has more meaning if the required correction factors are attributed to turbulent phenomena.

Upon inspection of the comparative correction factors of Tables 3 and 4 the conclusion--in all fairness--is that the theory is not quantitative. However, the modified real barrier theory (in fact the pure ideal barrier theory) is almost as truly quantitative as the general thermogravitational column theory for liquids.

A number of explanations could be advanced to explain the discrepancies. Probably the most plausible is that the diffusion impedance tests are in error on the barrier material. It would require an error of more than reasonable magnitude in the bulk flow tests to bring k_{AB} values up to appreciable numbers. And, of course, the barrier is not infinitely thin. However, the plate spacing and temperature

difference were corrected for the barrier thickness.

Probably a combination of all these factors, plus the inherent non-quantitative character of the basic theory all contribute to the discrepancy in quantitative agreement between theory and experiment.

Additional Work

Transient Batch Analysis.--The transient batch behavior of liquid thermogravitational thermal diffusion columns has been developed by Powers (178). In the course of the present work, several transient batch runs were made with and without barriers (see Appendix F). It is of interest to see how well H and K values derived from transient batch runs represent steady-state flow experimental sets of data.

Powers (178) has derived an equation of the form

$$\frac{\Delta}{\Delta_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{e^{-\frac{(2m+1)^2 \pi^2 K}{\mu L^2} t}}{(2m+1)^2} \quad \text{V-7}$$

where

Δ_{∞} is the batch separation at infinite time
(comparable to steady-state Δ_0)

and μ is the mass of material per unit length of column.

Powers has defined

$$\frac{\pi^2 K}{\mu L^2} t = \xi \quad \text{V-8}$$

and has presented tables of

$$\frac{\Delta}{\Delta_{\infty}} = f(\xi). \quad \text{V-9}$$

Thus if separation, Δ , versus time, t , transient batch data are available; a two constant fit (Δ_{∞} and K) of the transient batch data can readily be obtained. Noting that

$$\Delta_0 = \Delta_{\infty} = \frac{HL}{4K} \quad \text{IV-42}$$

H can also be calculated, knowing Δ_{∞} and K (and of course the column length, L).

Transient batch data were obtained in Run 36D, and presented in Appendix F. Transient analysis of the data by the above described methods was used to determine values of H and K (Δ_{∞} for this run is taken as 0.1335 weight fraction ethyl alcohol). The transient fit and experimental points of Run 36D are shown in Figure 41. The fit is not exact because too frequent sampling rendered the run not truly batch. The transient derived H and K values were used in Equation IV-41 to see how well these represent steady-state flow data at low flow rates for Set D. Experimental points and the semi-theoretical line are shown as Figure 42. The steady-state data are reasonably well represented.

Identical treatment was given to the data from a set

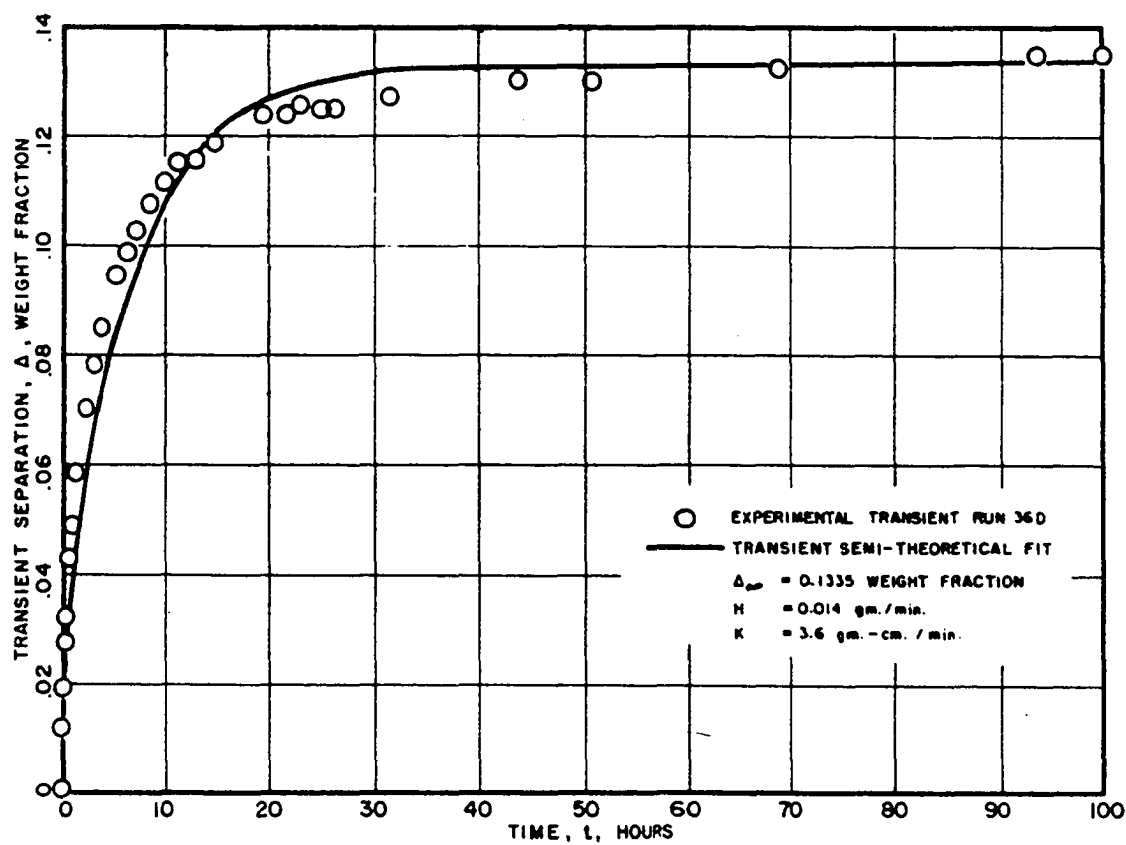


Figure 41 - Separation as a Function of Time in a Batch Thermogravitational Column--No Barrier

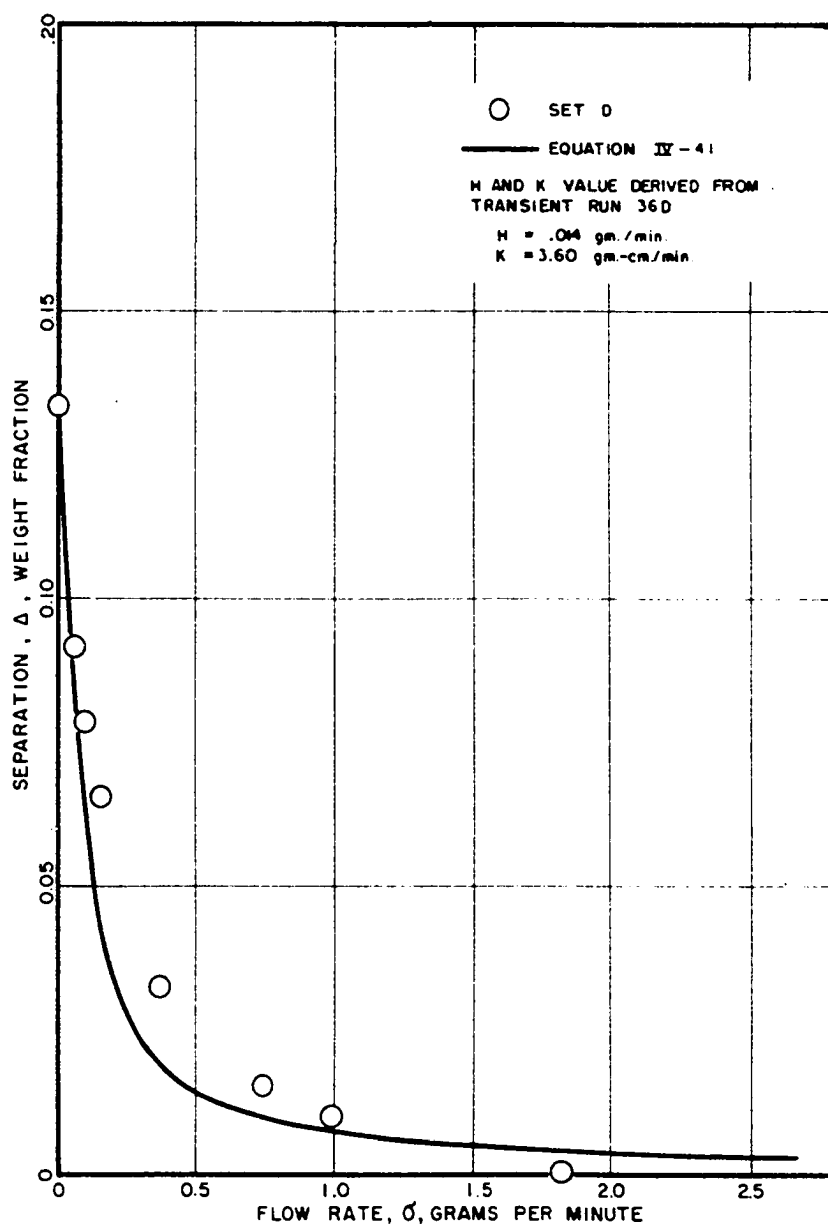


Figure 42 - Effect of Flow Rate on Steady-State Separation Using H and K Values Derived from Batch Transient Data--No Barrier

of runs with a tracing paper barrier in place (Set L). H and K values were derived from transient batch Run 94L, using Δ_{∞} as 0.0440 weight fraction ethyl alcohol. The transient fit and experimental points of Run 94L are shown as Figure 43. The H and K values derived from transient data were then used in Equation IV-41 to see how well these represented the steady-state flow separations of Set L. The semi-theoretical curve and the experimental points are given as Figure 44. Again, the H and K values derived from transient batch analysis represent steady-state flow separations rather well.

The transient fit with a barrier, and the prediction of steady-state continuous-flow results from transient-derived constants is very significant. It definitely lends weight to the hypothesis that a modification of the theory of Furry, Jones, and Onsager may be applied to thermogravitational columns with barriers. That is, the effect of vertical barriers may be accounted for in the H and K values using conventional forms of the solutions to the transport equation.

To summarize the degree of agreement between H and K values derived from transient batch and steady-state continuous-flow analysis, Table 5 has been prepared. Inspection of Table 5 shows the agreement surprisingly good considering the fact that too frequent experimental sampling induced errors in the transient batch data.

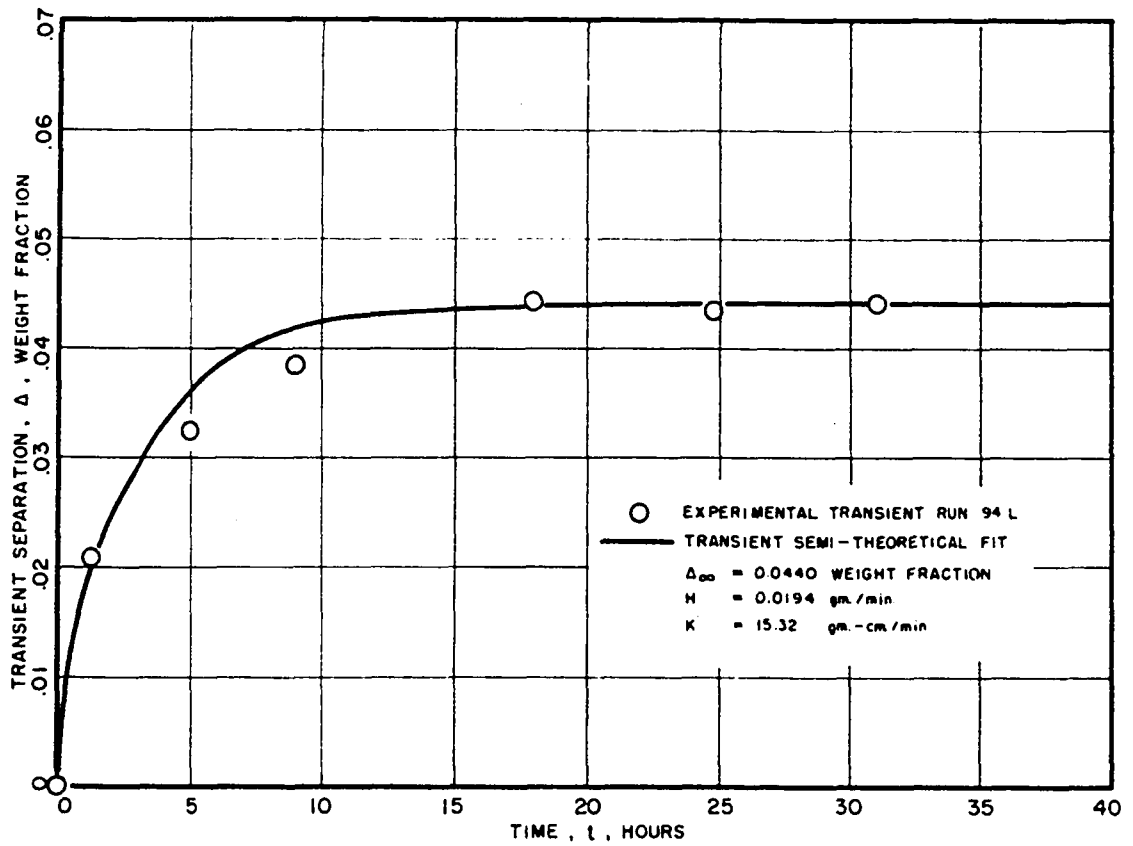


Figure 43 - Separation as a Function of Time in a Batch
 Thermogravitational Column--Tracing Paper
 Barrier

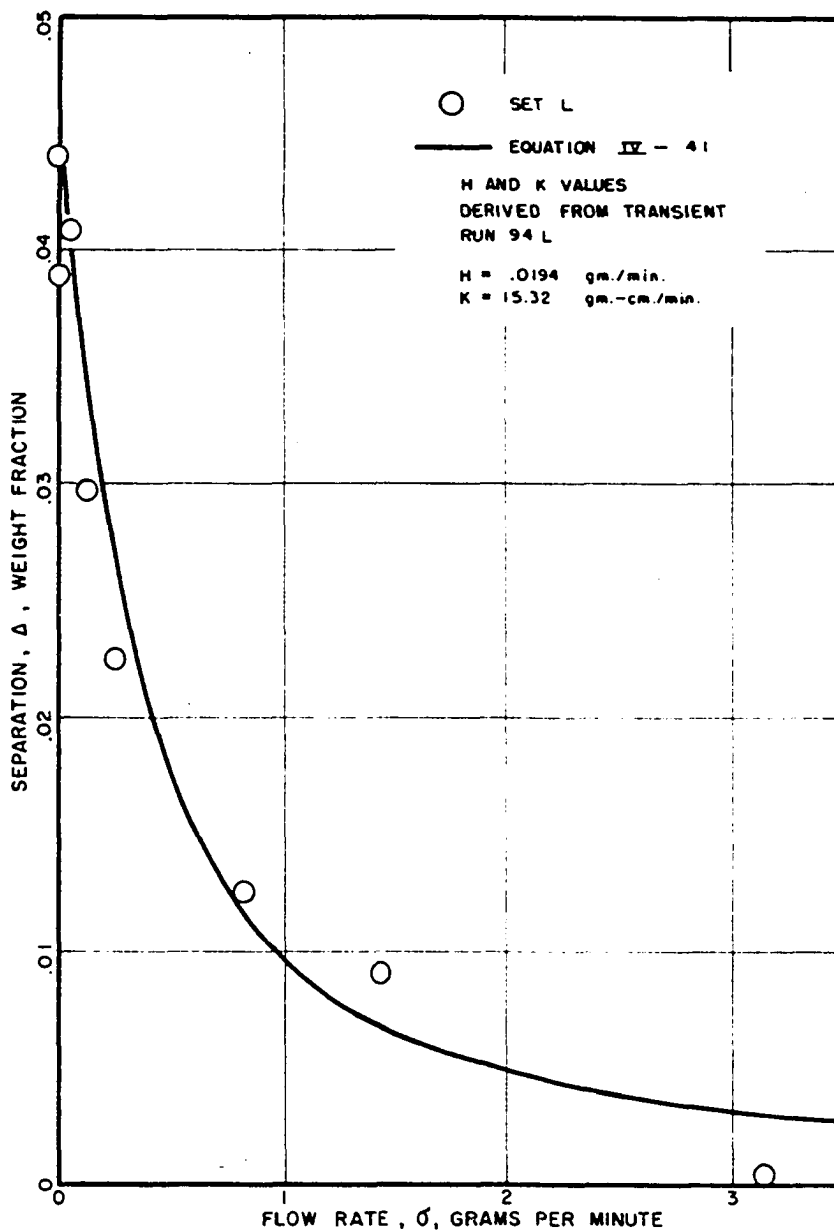


Figure 44 - Effect of Flow Rate on Steady-State Separation Using H and K Values Derived from Batch Transient Data--Tracing Paper Barrier

TABLE 5

COMPARISON OF H AND K VALUES DERIVED FROM TRANSIENT BATCH
ANALYSIS AND STEADY-STATE FLOW ANALYSIS

Derived From	H	K
	gm/min	gm-cm/min
Transient Batch Run 36D	0.014	3.6
Steady-State Flow Set D	0.0236	6.4
Transient Batch Run 94L	0.0194	15.32
Steady-State Flow Set L	0.014	11.5

Note:

Set D was taken without barriers.

Set L was taken with tracing paper vertical barriers.

Transient data under continuous-flow conditions were obtained in a few cases as a matter of interest. These data are reported with the transient batch data in Appendix F.

Unequal Product Flow Rates Without Barriers.--This work and other investigations (58) have qualitatively substantiated the theory of Furry, Jones, and Onsager (35) for center-fed continuous-flow thermogravitational columns with equal enriching and stripping product flow rates. For unequal flow rates the following type of conventional equation was developed in Chapter IV:

$$\Delta = \frac{H}{4\sigma_e} \left(1 - e^{-\frac{\sigma_e L_e}{K}} \right) + \frac{H}{4\sigma_s} \left(1 - e^{-\frac{\sigma_s L_s}{K}} \right). \quad \text{IV-40}$$

Powers (241) has shown that for low flow rates, with the assumption that the column always adjusts to yield its maximum separation, the following type of equation can be developed:

$$\Delta = \frac{H\sigma}{2\sigma_e\sigma_s} \left(1 - e^{-\frac{\sigma_e\sigma_s L}{2\sigma K}} \right). \quad \text{V-10}$$

A very preliminary attempt was made by Powers to test the applicability of Equations IV-40 and V-10. Powers' data showed excellent agreement with Equation V-10 at low ratios of enriching to stripping flows, σ_e/σ_s . However, above σ_e/σ_s equals one, the only data point did not agree with either Equation IV-40 or V-10.

In an attempt to clarify which equation is more applicable, data Sets E and F were obtained in the course of this investigation. Each of these sets was obtained at a fixed arithmetic average flow rate $\left(\frac{\sigma_e + \sigma_s}{2} = \text{Constant} \right)$, but with varying ratios of σ_e/σ_s .

Experimental Sets E and F were taken immediately after Set D (at the same temperature difference and plate spacing) such that empirical H and K values derived from Set D could be used to test the theory in Sets E and F.

The steady-state separations, Δ , as a function of the ratios of enriching to stripping flow rate, σ_e/σ_s were calculated using the H and K values of Set D and Equations IV-40 and V-10. The results of these calculations, with experimental points shown are presented as Figures 45 and 46. The non-symmetry of the curves is due to the fact that the thermal diffusion "constant," α , varies rapidly with concentration for the system ethyl alcohol-water.

Comparison of theory and experiment in Figures 45 and 46 is disappointing, in that the data are inconclusive in choosing between Equations IV-40 and V-10. However, the data do substantiate the conclusion of Powers (241) that the use of an arithmetic average flow rate leads to no appreciable error in calculating separations by Equation IV-41 over a wide range of ratios of enriching to stripping product flow rates (unequal product flows). The suggested range over which the use of an arithmetic average flow rate leads to

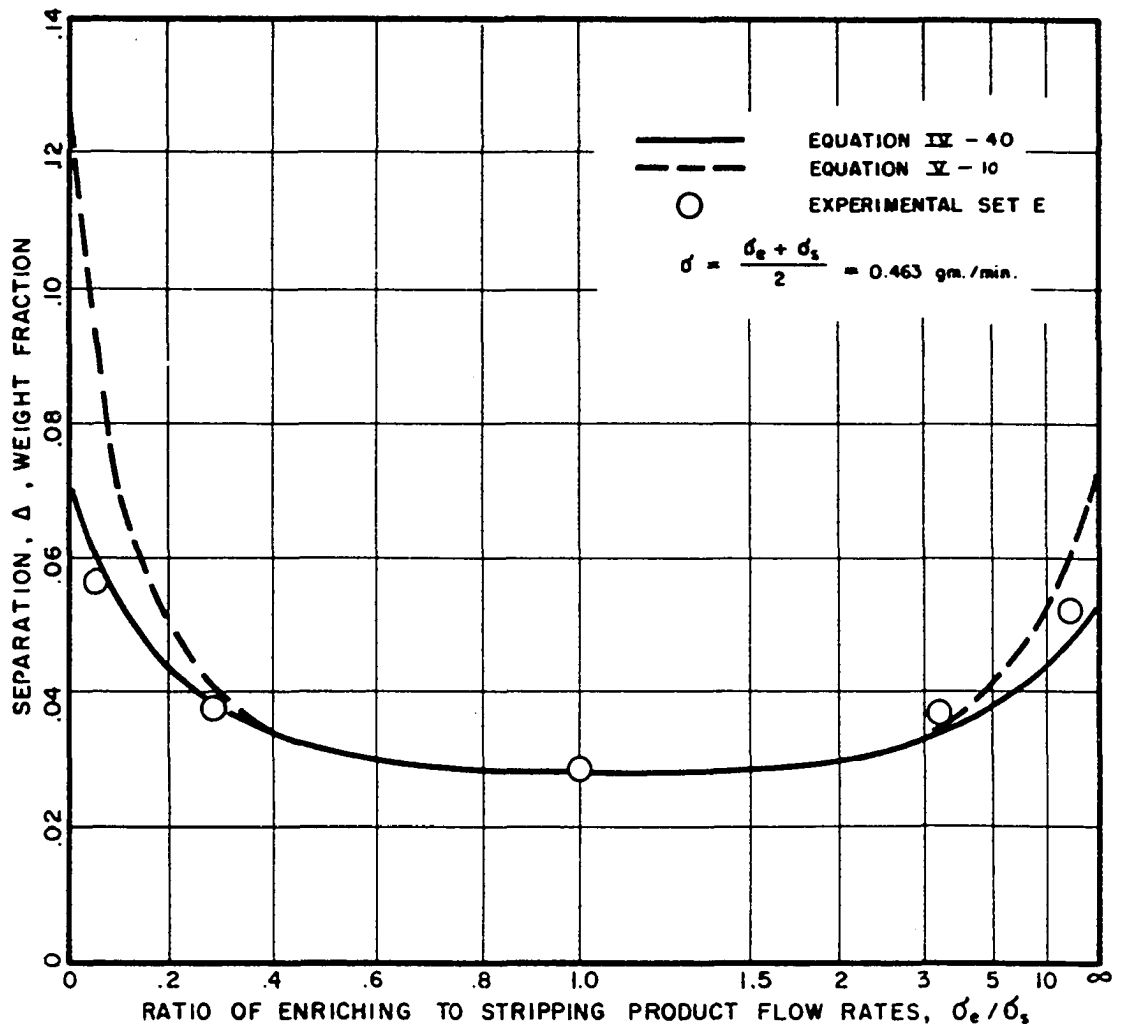


Figure 45 - Separation as a Function of the Ratio of Flow Rates in the Enriching and Stripping Sections of the Thermogravitational Column--Set E (Note change of Scale on Abscissa)

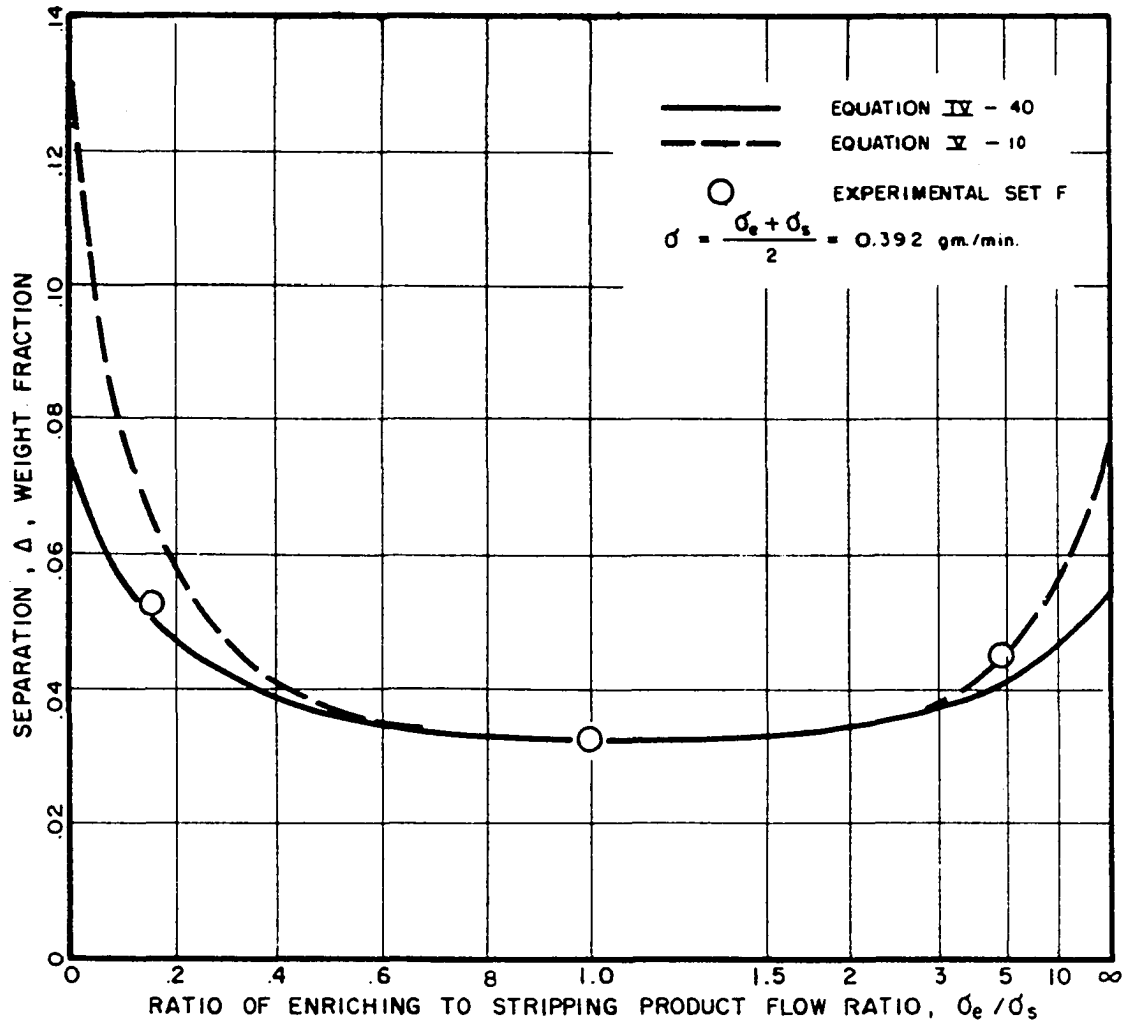


Figure 46 - Separation as a Function of the Ratio of Flow Rates in the Enriching and Stripping Sections of the Thermogravitational Column--Set F
(Note change of Scale on Abscissa)

little error is for ratios of enriching to stripping product flow rates of from $0.5 < \sigma_e / \sigma_s < 2$.

Conclusion

Of the various vertical barrier materials tested, only tracing paper showed increases in separation (at low flow rates) over the separations attained under identical conditions in the same thermogravitational column without barriers. Qualitative agreement with ideal barrier and actual barrier theory developed in Chapter IV is satisfactory. Quantitative agreement is not exact, even when the non-quantitative nature of basic thermogravitational theory without barriers is included.

The restricted integral solutions of the transport equation are excellent correlating (two parameter) expressions for thermogravitational column separation data for both steady-state continuous-flow and transient batch columns. The transient and steady-state data are compatible, and fit column data without and with vertical barriers (tracing paper) equally well.

The effects of temperature difference and plate spacing are predicted as well for thermogravitational columns with barriers (tracing paper) as for columns without barriers. Discrepancies are in agreement with others.

Theoretical ideal barrier equations do not quantitatively predict the data, even when corrected by correlatable correction factors based on columns without barriers.

Modification for hydrodynamic nonidealities (bulk flow through real barriers) shows little improvement, but is in the right direction.

The thermal diffusion "constant" for the system ethyl alcohol-water derived from the present work (without barriers) is in excellent agreement with previous investigators. Data taken with unequal product flow rates in a continuous-flow center-fed column without barriers are inconclusive.

SUMMARY

A thermogravitational thermal diffusion column is a device which effects partial separation of components in mixtures due to the combination of a temperature gradient and the resulting convection currents. Several investigators have reported that separations in thermogravitational columns increase with the introduction of vertical barriers. Almost no theory has been proposed by previous workers to explain the function of vertical barriers. Such theory has been developed in this work. Experimental investigations were carried out to test the new theory.

To explain increases in separation with barriers, the mathematical concept of an "ideal" vertical barrier has been proposed. The "ideal" vertical barrier is infinitely thin and allows free molecular diffusion, but allows no macroscopic bulk flow of material through the barrier. The choice of this model permitted the fundamental thermogravitational column theory of Furry, Jones, and Onsager to be modified to account for the introduction of any number of equally spaced "ideal" vertical barriers in a thermogravitational column. Real barriers allow macroscopic bulk flow of material to some extent, so the theory was further modified to account for

bulk flow for the case of a single vertical barrier.

The theory developed predicts striking increases in separation with an "ideal" vertical barrier in a thermogravitational column at low product flow rates. At increasing flow rates the theoretical barrier advantage decreases; and in fact, the barrier is not advantageous at high throughputs. An important aspect of the theory developed is that it predicts the effect on separation caused by "ideal" barriers is identical to the effect attained by operating multiple columns without barriers in parallel with proportionally reduced temperature differences, plate spacings, and flow rates.

Experimental tests were carried out on various types of vertical barriers. Verification of the reported increases in separation was obtained using membrane-type (paper) vertical barriers. Perforated barriers of plastic film and metal foil were unsatisfactory.

Qualitative experimental confirmation of the new theoretical developments was found for both steady-state continuous-flow and transient batch thermogravitational columns using membrane-type vertical barriers. This type of barrier more nearly approaches the theoretical mathematical model than the others tested. Quantitative confirmation of barrier theory is not entirely satisfactory, because the basic thermogravitational column theory of Furry, Jones, and Onsager is not quantitative for liquids.

In addition to the work with barriers, the fundamental theory of Furry, Jones, and Onsager has again been qualitatively confirmed for steady-state continuous-flow and batch transient liquid thermogravitational columns without barriers. The thermal diffusion "constant" for the system ethyl alcohol-water was determined and is in agreement with other workers. Results using unequal product flow rates are reported for steady-state center-fed continuous-flow thermogravitational columns.

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APPENDIX A
NOMENCLATURE

NOMENCLATURE

a = General constant

A = Designation for numbered assumptions in Chapter IV

b = General constant

B = Column width (in z direction)

$\dot{B}$ = Total volumetric bulk flow rate through one-half the total barrier area

C_1, C_2 = Fraction of component 1,2 in binary mixture

C_e, C_s = Concentration of component 1 leaving enriching, stripping sections of thermogravitational column

$C_{ec}, C_{eh}, C_{sc}, C_{sh}$ = Concentration of component 1 leaving enriching cold side, enriching hot side, stripping cold side, stripping hot side of thermogravitational column with a single vertical barrier using certain special flow patterns

C_F = Concentration of component 1 in feed

$\bar{C}_1$ = Mean concentration of component 1 evaluated at $x = 0$

$\bar{C}_1 \bar{C}_2$ = Mean value of the product of concentrations of components 1,2

D = Ordinary diffusion coefficient

$f(y)$ = Arbitrary function of y

F = Coefficient of bulk flow through actual (real) barrier as defined by Equation IV-63

g = Acceleration of gravity

g_C = Gravitational constant

h_{AB} = Contribution to H_{AB}^1 as defined by Equation IV-80 and IV-78

h_x, h_y = Head loss in x, y direction

H = Parameter defined by Equation IV-15 and evaluated by various refinements of the equation

H_{expt} = Parameter derived by Empirical fit of experimental data

H_{theor} = Parameter calculated from any of the theoretical forms developed

H_e, H_s = Parameter for enriching, stripping sections of thermogravitational column

H_{AB}^1 = Parameter for column with one actual (real) vertical barrier as defined by Equation IV-78

$H_{IB}^1, H_{IB}^2, \dots, H_{IB}^n$ = Parameter for column with 1, 2, ..., n ideal vertical barriers, Equation IV-56

I_1, I_2, I_3 = Constants of integration

J_{x-OD} = Flux of component 1 in the x direction due to ordinary diffusion

J_{y-OD} = Flux of component 1 in the y direction due to ordinary diffusion

J_{x-TD} = Flux of component 1 in the x direction due to thermal diffusion

k_{AB} = Contribution to K_{CAB}^1 as defined by Equations IV-81 and IV-79

K = Parameter defined by Equation IV-18

K_c = Parameter defined by Equation IV-16 and evaluated by various refinements of the equation

K_d = Parameter defined by Equation IV-17

K_p = Parameter appended to theory by Furry, Jones, and Onsager to account for parasitic remixing

K_{expt} = Parameter derived by Empirical fit of experimental data

K_{theor} = Parameter calculated from any of the theoretical forms developed

K_e, K_s = Parameter for enriching, stripping sections of thermogravitational column

K_{CAB}^1 = Parameter for column with one actual (real) vertical barrier as defined by Equation IV-79

$K_{CIB}^1, K_{CIB}^2, \dots, K_{CIB}^n$ = Parameter for column with 1, 2, ..., n ideal vertical barriers, Equation IV-57

$(\overline{1w_f})_x, (\overline{1w_f})_y$ = Lost work due to friction in x, y directions

L = Total length (in y direction) of thermogravitational column

L_e, L_s = Length of enriching, stripping sections of thermogravitational column

m = Summation index in Equation V-7

$\dot{M}(y)$ = Volumetric longitudinal (y direction) flow rate on one side of actual (real) barrier as a function of y

$\bar{\dot{M}}$ = Integrated average $\dot{M}(y)$ with respect to y

$\dot{M}_{\max}$ = Maximum value of $\dot{M}(y)$

n = Generalized number of ideal vertical barriers

P = Pressure

Q = Volumetric bulk flow through an actual (real) barrier per unit area per unit time

t = Time

T = Absolute temperature

$\bar{T}$ = Arithmetic average of hot and cold plate absolute temperatures

$v(x)$ = General batch velocity distribution, velocity a function of x alone

$v_L(x), v_R(x)$ = Representations of the batch velocity distribution function on the left (cold), right (hot) side of a vertical barrier

$v_L(x)_{\text{par}}, v_R(x)_{\text{par}}$ = Representations of the batch parabolic contributions to the velocity distribution on the left (cold), right (hot) sides of a single vertical real barrier with hydrodynamic nonideality

$v_L(x)_{AB}, v_R(x)_{AB}$ = Representations of the batch velocity distribution function on the left (cold), right (hot) sides of a single vertical actual (real) barrier with hydrodynamic nonideality

$\bar{V}$ = Average longitudinal (y direction) velocity of parabolic contribution to the batch velocity distribution function on one side of a single vertical real barrier with hydrodynamic nonideality

x,y,z = Axes of coordinate system (see Figure 23)

Z = Grouping defined by Equation V-3

α = Thermal diffusion "constant" as defined by the flux Equation IV-1

$$\beta^* = - \frac{\partial \rho}{\partial x}$$

$$\beta_T = - \frac{\partial \rho}{\partial T}$$

δ_1, δ_2 = Measured distance between pairs of balls used for determining plate spacing

Δ = Separation as the difference in concentration at the ends of a thermogravitational column ($C_e - C_s$)

Δ_0 = Separation as the difference in concentration at the ends of a thermogravitational column at steady-state batch conditions

Δ_∞ = Limit of separation at infinite time for a transient batch thermogravitational column

Δ_{oIB}^1 = Separation as the difference in concentration at the ends of a thermogravitational column at steady-state batch conditions with a single vertical ideal barrier in place

ΔT = Temperature difference between hot and cold plates

η = Coefficient of viscosity

μ = Mass of liquid per unit length of thermogravitational column

ξ = Grouping defined by Equation V-8

ρ = Density

$\bar{\rho}_C, \bar{\rho}_H$ = Mean density of material on cold (left), hot (right) side of a single vertical barrier

σ = Average mass flow rate, $\frac{\sigma_e + \sigma_s}{2}$

σ_e, σ_s = Mass flow rate from enriching, stripping sections of thermogravitational column

$\sigma_{ec}, \sigma_{eh}, \sigma_{sc}, \sigma_{sh}$ = Mass flow rate leaving enriching cold side, enriching hot side, stripping cold side, stripping hot side of thermogravitational column with a single vertical barrier using certain special flow patterns.

τ = Net transport of component 1 up a thermogravitational column

τ' = Net transport of component 1 up a thermogravitational column with an external impressed flow through the column

ϕ_H = Correction factor on H as defined by Equation V-4

ϕ_K = Correction factor on K as defined by Equation V-5

ω = One-half the distance between the hot and cold plates of a thermogravitational column (plate spacing is 2ω)

APPENDIX B
STEADY-STATE FLOW SEPARATION DATA

TABLE 6

STEADY-STATE FLOW DATA^a

Run and Set No.	σ_e Top Flow Rate	σ_s Bottom Flow Rate	σ^b Average Flow Rate
	<u>grams</u> <u>min.</u>	<u>grams</u> <u>min.</u>	<u>grams</u> <u>min.</u>
1A	1.16	1.00	1.08
2A	1.97	1.93	1.95
3A	4.78	4.66	4.72
4A	0.216	0.152	0.184
5A	13.7	13.0	13.4
6A	0.427	0.321	0.374
7A	35.9	39.0	37.5
8A	0.0649	0.0648	0.0649
9B	0.0690	0.0658	0.0674
10B	0.127	0.110	0.119
11B	0.389	0.423	0.406
12B	0.863	0.780	0.822
13B	2.71	2.40	2.56
14B	5.09	5.19	5.14
15B	13.6	13.6	13.6
16B	24.8	22.4	23.6
17C	0.0694	0.0706	0.0700
18C	0.118	0.112	0.115
19C	0.396	0.399	0.398
20C	1.023	0.783	0.903
21C	2.18	2.21	2.20
22C	4.69	4.47	4.58
23C	11.8	11.5	11.7
24C	8.19	7.81	8.00
25D	0.0611	0.0635	0.0623
26D	0.0974	0.1093	0.103
27D	1.84	1.80	1.82
28D	0.376	0.362	0.369
29D	0.744	0.753	0.749
30D	0.195	0.127	0.161
31D	1.031	0.972	1.00
32E	0.0578	0.897	0.478
33E	0.886	0.0535	0.470
34F	0.112	0.686	0.399
35F	0.635	0.134	0.385
36D	0	0	0
37E	0.205	0.706	0.456
38E	0.686	0.207	0.447

TABLE 6--Continued

Run and Set No.	σ_e Top Flow Rate	σ_s Bottom Flow Rate	σ^b Average Flow Rate
	<u>grams</u> min.	<u>grams</u> min.	<u>grams</u> min.
39G	0.278	0.306	0.292
40G	0.0509	0.9554	0.0532
41G	0.485	0.618	0.552
42G	1.27	1.20	1.24
43G	4.38	4.28	4.32
44G	0.114	0.111	0.113
45H	0	0	0
46H	0.0517	0.0609	0.0563
47H	0.107	0.129	0.118
48H	0.321	0.335	0.328
49H	0.502	0.899	0.701
50H	1.77	1.61	1.69
51H	3.11	2.96	3.04
52H	8.51	8.41	8.46
53H	19.6	19.3	19.4
54I	0.919	0.441	0.680
55I	0.337	0.344	0.346
56I	0.122	0.112	0.117
57I	0.0561	0.0598	0.0580
58I	0	0	0
59J	0	0	0
60J	0.328	0.410	0.369
61J	0.0672	0.0669	0.0671
62J	0.124	0.121	0.123
63J	0.416	0.913	0.665
64J	1.80	1.70	1.75
65J	4.18	4.07	4.13
66J ^c	0	0	0
67J	7.96	7.64	7.80

TABLE 6--Continued

Run and Set No.	σ_{ec} Cold Side Top Flow Rate	σ_{sc} Cold Side Bottom Flow Rate	σ_{eh} Hot Side Top Flow Rate	σ_{sh} Hot Side Bottom Flow Rate	σ_d Average Flow Rate
	<u>grams</u> min.	<u>grams</u> min.	<u>grams</u> min.	<u>grams</u> min.	<u>grams</u> min.
68K	0	0	0	0	0
69K	0.0626	0.0682	0.0750	0.0701	0.138
70K	0.135	0.138	0.107	0.128	0.254
71K	0.456	0.381	0.339	0.304	0.740
72K	0.634	0.655	0.660	0.609	1.28
73K	1.97	1.66	1.65	1.60	3.44
74K	3.25	3.01	3.17	3.15	6.29
75K	6.63	6.57	6.51	6.24	13.0
76K	14.1	14.6	12.7	13.8	27.6
77K ^c	0	0	0	0	0
78L	0.0346	0.0242	0.0333	0.0301	0.0611
79L	0.0697	0.0761	0.0648	0.0622	0.136
80L	0.125	0.133	0.123	0.106	0.244
81L	0	0	0	0	0
82L	1.57	1.66	1.45	1.58	3.13
83L	0.404	0.405	0.417	0.420	0.823
84L	0.744	0.764	0.695	0.668	1.44
85L	3.23	3.48	3.21	3.26	6.59
86L ^c	0	0	0	0	0
87M	0	0	0	0	0
88M	0.0721	0.0731	0.0678	0.0751	0.144
89M	0.0350	0.0171	0.0354	0.0384	0.0630
90M	0.139	0.143	0.142	0.155	0.290
91M	0.426	0.467	0.305	0.504	0.851
92M	0.723	0.719	0.657	0.681	1.39
93M	1.62	1.91	1.53	1.56	3.31
94L	0	0	0	0	0
95M ^c	0	0	0	0	0

^aSee Flow Patterns, Figures 48-52, Appendix E, for explanation of flows.

^bCalculated as $(\sigma_e + \sigma_s)/2$.

^cRuns with External Circulating Loops, See Appendix E.

^dCalculated as $(\sigma_{ec} + \sigma_{sc} + \sigma_{eh} + \sigma_{sh})/2$.

TABLE 7

STEADY-STATE SEPARATION DATA^a

Run and Set No.	C _e Top Composition	C _s Bottom Composition	Δ^b Separation
	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH
1A	0.4028	0.3969	0.0059
2A	0.4022	0.3969	0.0053
3A	0.4022	0.3969	0.0053
4A	0.4028	0.3964	0.0064
5A	0.4015	0.3982	0.0033
6A	0.4026	0.3951	0.0075
7A	0.4022	0.4008	0.0014
8A	0.4043	0.3972	0.0071
9B	0.4072	0.3941	0.0131
10B	0.4067	0.3934	0.0133
11B	0.4066	0.3937	0.0129
12B	0.4048	0.3943	0.0105
13B	0.4043	0.3964	0.0079
14B	0.4030	0.3971	0.0059
15B	0.4020	0.3987	0.0033
16B	0.4008	0.4003	0.0005
17C	0.4045	0.3957	0.0088
18C	0.4040	0.3954	0.0086
19C	0.4041	0.3960	0.0081
20C	0.4037	0.3967	0.0070
21C	0.4030	0.3969	0.0061
22C	0.4020	0.3982	0.0038
23C	0.4005	0.3997	0.0008
24C	0.4005	0.3981	0.0024
25D	0.4482	0.3565	0.0917
26D	0.4421	0.3629	0.0782
27D	0.4008	0.4008	0.0000
28D	0.4159	0.3836	0.0323
29D	0.4077	0.3924	0.0153
30D	0.4263	0.3635	0.0628
31D	0.4057	0.3959	0.0098
32E	0.4559	0.3989	0.0570
33E	0.4060	0.3538	0.0522
34F	0.4471	0.3944	0.0527
35F	0.4087	0.3639	0.0448
36D	0.4752	0.3417	0.1335
37E	0.4298	0.3929	0.0369

TABLE 7--Continued

Run and Set No.	C _e Top Composition	C _s Bottom Composition	Δ^b Separation
	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH
38E	0.4087	0.3723	0.0364
39G	0.4139	0.3984	0.0155
40G	0.3683	0.4256	-0.0573
41G	0.4087	0.4969	0.0118
42G	0.4089	0.3984	0.0105
43G	0.4030	0.4001	0.0029
44G	0.3984	0.4101	-0.0117
45H	0.4034	0.3979	0.0055
46H	0.4035	0.3981	0.0054
47H	0.4035	0.3979	0.0056
48H	0.4047	0.3991	0.0056
49H	0.4050	0.3986	0.0064
50H	0.4020	0.3971	0.0049
51H	0.4013	0.3964	0.0049
52H	0.4001	0.3974	0.0027
53H	0.3995	0.3995	0.0000
54I	0.3993	0.3993	0.0000
55I	0.4006	0.4006	0.0000
56I	0.4001	0.4003	-0.0002
57I	0.4001	0.4001	0.0000
58I	0.3984	0.3982	0.0002
59J	0.4055	0.3708	0.0347
60J	0.4116	0.3880	0.0236
61J	0.4126	0.3806	0.0320
62J	0.4124	0.3836	0.0288
63J	0.4132	0.3947	0.0185
64J	0.4071	0.3958	0.0113
65J	0.4035	0.3986	0.0049
66J ^d	0.4026	0.3868	0.0158
67J	0.4006	0.3979	0.0027

TABLE 7--Continued

Run and Set No.	C _{ec} Cold Side Top Composi- tion	C _{sc} Cold Side Bottom Composi- tion	C _{eh} Hot Side Top Composi- tion	C _{sh} Hot Side Bottom Composi- tion	c Separation
	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH
68K	0.4050	0.3926	0.4067	0.3956	0.0118
69K	0.4025	0.3954	0.4082	0.3989	0.0084
70K	0.4013	0.3947	0.4062	0.3981	0.0071
71K	0.4003	0.3962	0.4060	0.4013	0.0043
72K	0.3991	0.3962	0.4050	0.4013	0.0035
73K	0.3989	0.3969	0.4018	0.4008	0.0014
74K	0.3993	0.3966	0.4001	0.3998	0.0015
75K	0.4001	0.3979	0.4003	0.3996	0.0015
76K	0.3999	0.3991	0.3998	0.3987	0.0009
77K ^d	0.4332	0.3949	0.4059	0.4010	0.0216
78L	0.4286	0.3798	0.4241	0.3900	0.0409
79L	0.4154	0.3843	0.4256	0.3984	0.0297
80L	0.4094	0.3863	0.4208	0.4003	0.0225
81L	0.4215	0.3786	0.4246	0.3899	0.0388
82L	0.4017	0.3949	0.4087	0.4059	0.0048
83L	0.4033	0.3895	0.4139	0.4028	0.0124
84L	0.4030	0.3929	0.4124	0.4050	0.0090
85L	0.4016	0.3967	0.4057	0.4037	0.0036
86L ^d	0.4377	0.3794	0.4215	0.3826	0.0486
87M	0.4271	0.3719	0.4298	0.3772	0.0539
88M	0.4123	0.3894	0.4168	0.3987	0.0204
89M	0.4142	0.3820	0.4187	0.3899	0.0290
90M	0.4057	0.3904	0.4111	0.3989	0.0136
91M	0.4033	0.3952	0.4082	0.4020	0.0066
92M	0.4026	0.3960	0.4061	0.4042	0.0043
93M	0.4008	0.3984	0.4020	0.4020	0.0014
94L	0.4321	0.3788	0.4236	0.3890	0.0440
95M ^d	0.4584	0.3831	0.4378	0.3885	0.0623

^aSee flow patterns, Figures 48-52, Appendix E, for explanation of where these compositions were obtained in the column.

^bCalculated as $\cdot = C_e - C_s$.

$$^c \text{Calculated as } \Delta = \frac{C_{ec}\sigma_{ec} + C_{eh}\sigma_{eh}}{\sigma_{ec} + \sigma_{eh}} - \frac{C_{sc}\sigma_{sc} + C_{sh}\sigma_{sh}}{\sigma_{sc} + \sigma_{sh}}.$$

^dRuns with external circulating loops, see Figure 52, Appendix E.

APPENDIX C
COLUMN AND SYSTEM PARAMETERS

TABLE 8

COLUMN AND SYSTEMS PARAMETERS

Set	Included Runs	Plate ^a Spacing 2ω	Mean ^a Temp. Diff. ΔT	Column Length L	Mean Temp. Level T	Column Width B	Feed Conc. C _F
		cm	°C	cm	°C	cm	Weight Frac. EtOH
A	1-8	0.2164	34.5	145	48.9	10.2	0.4003
B	9-16	0.1521	31.8	145	48.9	10.2	0.4004
C	17-24	0.1519	16.0	145	48.9	10.2	0.4007
D	25-31,36	0.0765	25.4	145	48.9	10.2	0.4005
E	32,33,37,38	0.0762	25.4	145	48.9	10.2	0.4008
F	34,35	0.0762	25.4	145	48.9	10.2	0.4003
G	39-44	0.1565	31.0	145	48.9	10.2	0.4018
H	45-53	0.1448	31.4	145	48.9	10.2	0.4002
I	54-58	0.1526	31.9	145	48.9	10.2	0.4004
J	59-67	0.1476	30.8	145	48.9	10.2	0.4007
K	68-77	0.2306	34.7	145	48.9	10.2	0.4011
L	78-86,94	0.1478	31.2	145	48.9	10.2	0.4024
M	87-93,95	0.1483	15.8	145	48.9	10.2	0.4031

^aCorrected for thickness of barrier in sets where barriers were used.

APPENDIX D
DETAILS AND ARRANGEMENT OF BARRIERS

TABLE 9
BARRIER MATERIALS AND SPECIFICATIONS

Experimental Set(s)	Barrier Material	Barrier Thickness (Dry) cm	Miscellaneous
A,B,C,D,E,F	None	---	---
G	Aluminum foil, Reynolds Wrap	0.00178	Uniformly perforated with 0.124 cm diameter holes, 13.8% open area
H	duPont Mylar Type C	0.00127	Uniformly perforated with 0.124 cm diameter holes, 10.7% open area
I	duPont Mylar Type C	0.00127	No perforations, 0.635 x 7.62 cm horizontal slot at top and bottom
J,K,L,M	Keuffel and Esser prepared tracing paper, ALBANENE 195 MX	0.0071	No perforations, presoaked with water

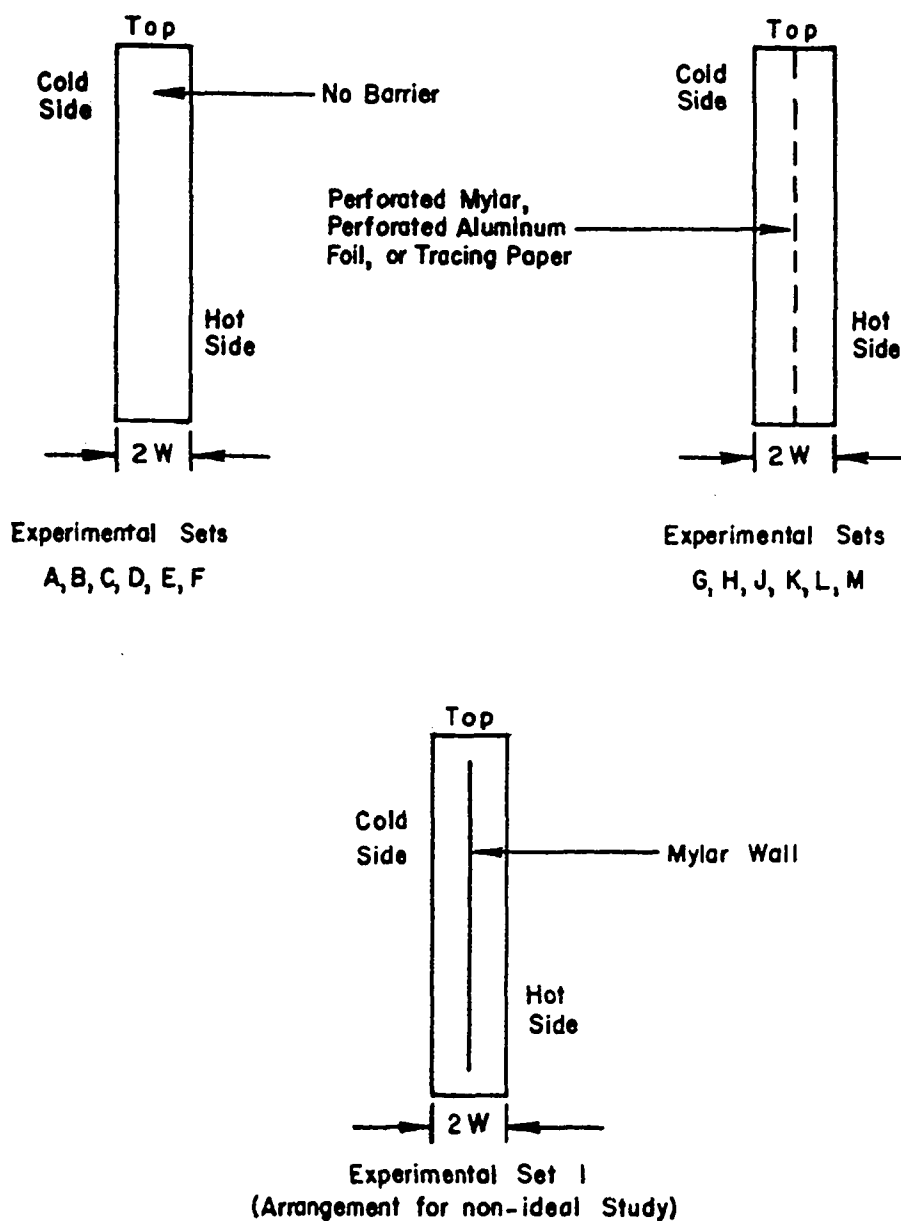
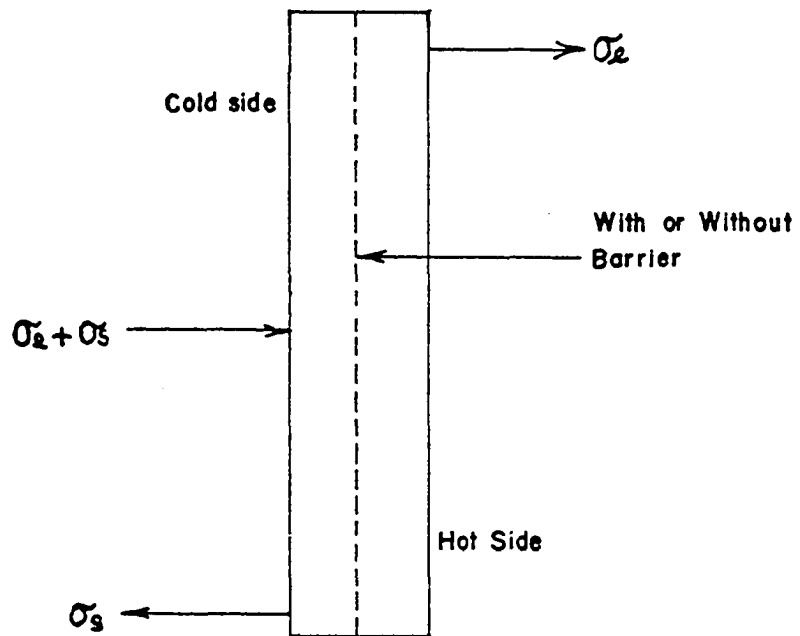


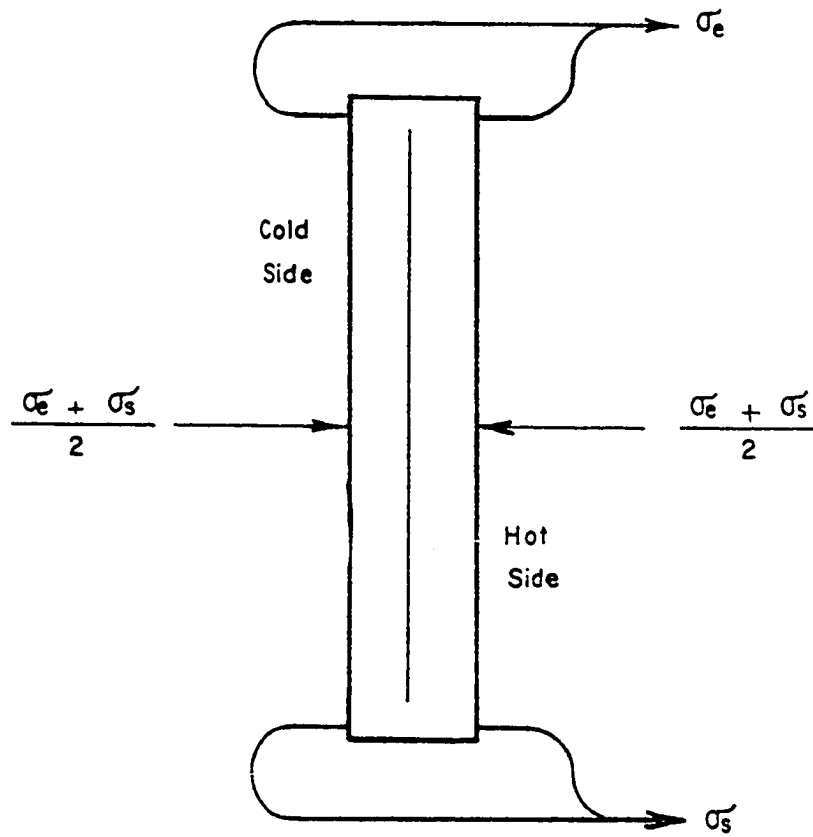
Figure 47 - Cross-Sections of Working Space of Column
for Experimental Sets (Vertical Scale
Greatly Foreshortened)

APPENDIX E
FLOW PATTERNS USED



Experimental Sets A,B,C,D,E,F,G,H

Figure 48 - Flow Pattern Used on Experimental Sets A, B, C, D, E, F, G, H (Vertical Scale Greatly Foreshortened)



Experimental Set I

Figure 49 - Flow Pattern Used on Experimental Set I
(Vertical Scale Greatly Foreshortened)

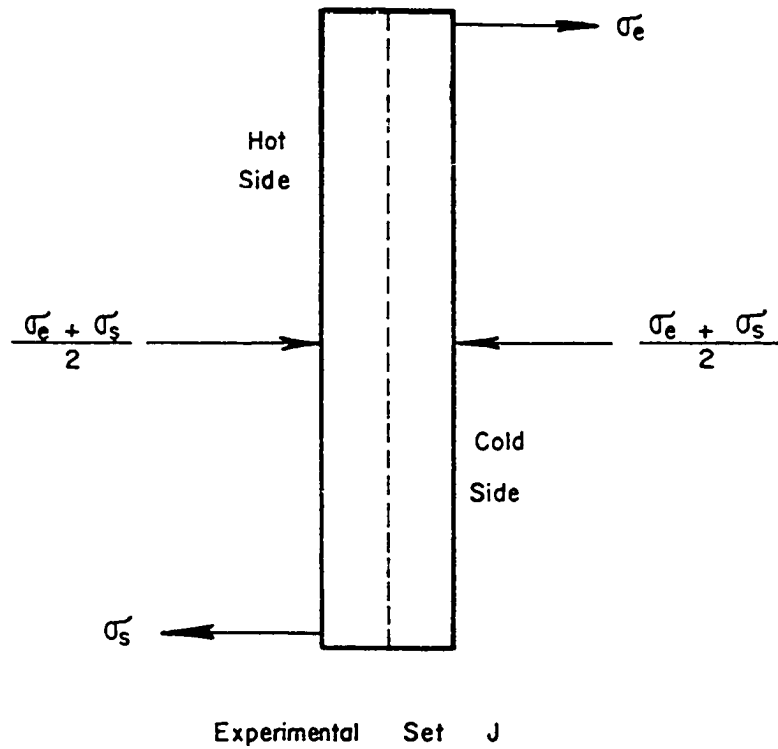
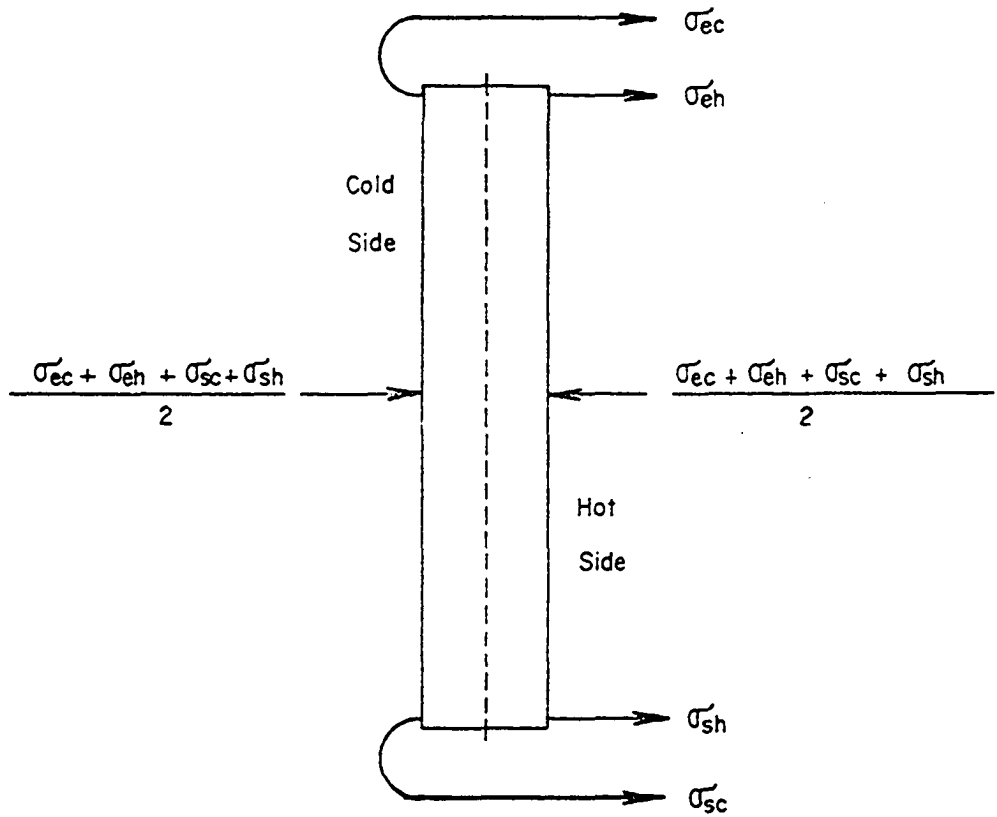
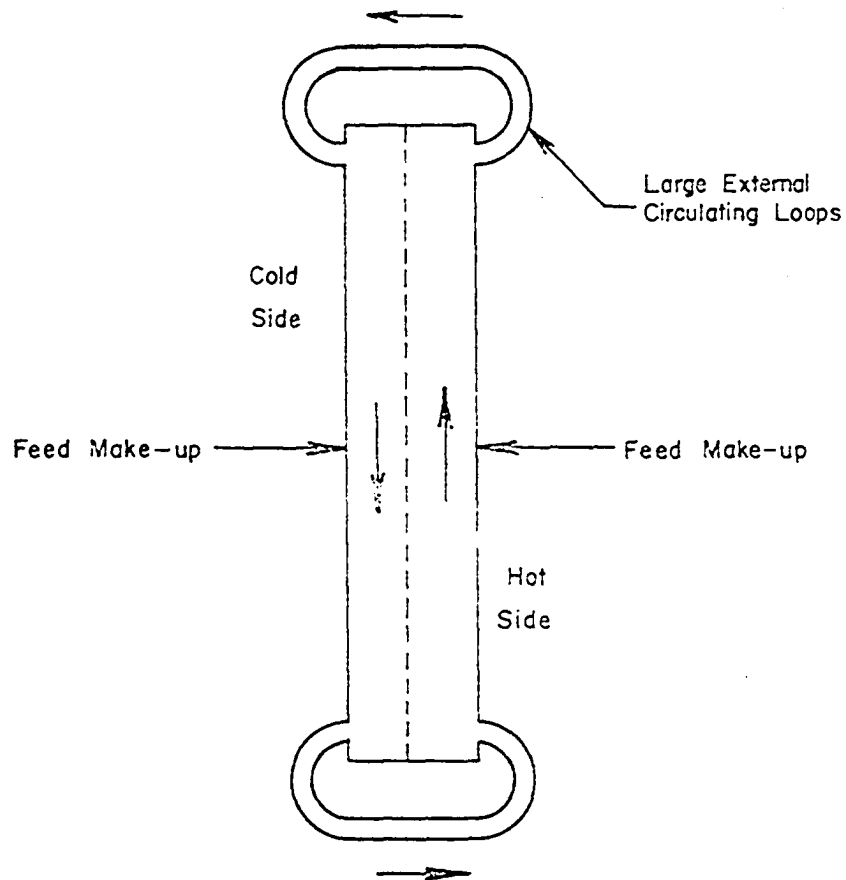


Figure 50 - Flow Pattern Used on Experimental Set J
(Vertical Scale Greatly Foreshortened)



Experimental Sets K, L, M

Figure 51 - Flow Pattern Used on Experimental Sets K, L, M (Vertical Scale Greatly Foreshortened)



Experimental Runs 66J, 77k, 86L, 95M

Figure 52 - Flow Pattern Used on Runs Made With
External Circulating Loops--Experimental
Runs 66J, 77K, 86L, 95M (Vertical Scale
Greatly Foreshortened)

APPENDIX F
TRANSIENT SEPARATION DATA

TABLE 10

TRANSIENT SEPARATION DATA^a

Run and Set No.	t Time	C _e Top Composition	C _s Bottom Composition	Δ ^b Separation
		Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH
	Minutes			
25D	0	0.4006	0.4006	0.0000
	15	0.4094	0.3902	0.0192
	45	0.4215	0.3781	0.0434
	75	0.4253	0.3747	0.0506
	105	0.4283	0.3714	0.0569
	165	0.4343	0.3668	0.1675
	240	0.4384	0.3635	0.0749
	300	0.4416	0.3608	0.0808
	375	0.4433	0.3595	0.0838
	465	0.4457	0.3582	0.0875
	585	0.4465	0.3570	0.0895
	720	0.4474	0.3551	0.0923
	840	0.4490	0.3557	0.0933
	900	0.4482	0.3557	0.0925
	960	0.4482	0.3563	0.0919
28D	0	0.4003	0.4003	0.0000
	5	0.4072	0.3947	0.0125
	15	0.4116	0.3887	0.0229
	25	0.4132	0.3880	0.0252
	40	0.4139	0.3865	0.0274
	60	0.4147	0.3865	0.0282
	90	0.4139	0.3858	0.0281
	120	0.4147	0.3843	0.0304
	315	0.4147	0.3836	0.0311
	405	0.4154	0.3836	0.0318
	600	0.4147	0.3836	0.0311
	645	0.4154	0.3836	0.0318
	675	0.4162	0.3836	0.0326
	705	0.4162	0.3836	0.0326
36D	0	0.4006	0.4006	0.0000
	5	0.4087	0.3969	0.0118
	10	0.4116	0.3932	0.0184
	20	0.4147	0.3872	0.0275
	30	0.4162	0.3843	0.0319
	50	0.4223	0.3801	0.0422

TABLE 10--Continued

Run and Set No.	t	C _e	C _s	Δ ^b
	Time	Top	Bottom	Separation
	Composition	Composition	Composition	Composition
Run and Set No.	Minutes	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH
	Minutes	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH
	70	0.4246	0.3761	0.0485
	100	0.4298	0.3721	0.0577
	150	0.4359	0.3661	0.0698
	205	0.4400	0.3621	0.0779
	250	0.4433	0.3582	0.0851
	335	0.4482	0.3538	0.0944
	400	0.4507	0.3519	0.0988
	450	0.4533	0.3507	0.1026
	525	0.4568	0.3495	0.1073
	600	0.4576	0.3470	0.1106
	700	0.4593	0.3452	0.1141
	800	0.4602	0.3446	0.1156
	900	0.4626	0.3440	0.1186
	1180	0.4651	0.3417	0.1234
	1300	0.4651	0.3417	0.1234
	1400	0.4669	0.3417	0.1252
	1500	0.4669	0.3423	0.1246
	1600	0.4660	0.3417	0.1243
	1905	0.4687	0.3417	0.1270
	2640	0.4714	0.3417	0.1297
	3040	0.4714	0.3417	0.1297
	4125	0.4733	0.3417	0.1316
	5610	0.4762	0.3417	0.1345
	6045	0.4762	0.3417	0.1345

Run and Set No.	t	C _{ec}	C _{sc}	C _{eh}	C _{sh}	Δ ^c
	Time	Cold	Cold	Hot	Hot	Separation
	Composition	Side	Side	Side	Side	Composition
Run and Set No.	Minutes	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH
	Minutes	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH
94L	0	0.4035	0.4035	0.4035	0.4035	0.0000
	75	0.4132	0.3880	0.4169	0.4116	0.0208

TABLE 10--Continued

Run and Set No.	t Time Minutes	Cec Cold Side Top Compo- sition	Csc Cold Side Bottom Compo- sition	Ceh Hot Side Top Compo- sition	Csh Hot Side Bottom Compo- sition	Δ^c Separation
		Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH
	300	0.4231	0.3829	0.4215	0.3976	0.0322
	540	0.4291	0.3808	0.4238	0.3954	0.0384
	1080	0.4367	0.3801	0.4246	0.3924	0.0444
	1485	0.4298	0.3774	0.4231	0.3887	0.0434
	1860	0.4298	0.3788	0.4231	0.3858	0.0442

^aSee flow patterns, Appendix E, for explanation of where these compositions were obtained in the column.

^bCalculated as $\Delta = C_e - C_s$.

^cCalculated as $\Delta = [(C_{ec} - C_{es}) + (C_{eh} - C_{sh})] / 2$.

APPENDIX G
RELATIVE RELIABILITY OF DATA

TABLE 11

RELATIVE RELIABILITY OF DATA

Steady-State Set or Transient Run	Relative Reliability	Comments
A	Fair	Fairly low separation with relatively high analytical errors.
B	Good	---
C	Good	---
D	Good	---
E	Good	Unequal product flow rates.
F	Good	Unequal product flow rates.
G	Worthless	Barrier poorly installed, results very erratic with very poor reproducibility.
H	Good	---
I	Good	---
J	Poor	Leak in system, also unsuitable flow pattern with this type of barrier.
K	Fair	Low separation, relatively high analytical errors.
L	Good	---
M	Good	---
25D	Fair	Too frequent sampling in early part of run.
28D	Fair	Too frequent sampling in early part of run.
36D	Fair	Much too frequent sampling early part of run.
94L	Good	---

APPENDIX H
BARRIER BULK FLOW DATA

TABLE 12
BARRIER BULK FLOW DATA

	Total Flow Through Barrier	Head Across Barrier	Time	Temperature
Reading	Cubic cm	cm of EtOH	Min.	°C
1	28.53	4	450	25.9
2	35.65	7	535	27.9
3	13.11	3	510	27.1
4	14.35	5	420	26.8

Parameters: Liquid composition 0.40 weight fraction ethyl alcohol. Area available for flow 81 square cm.

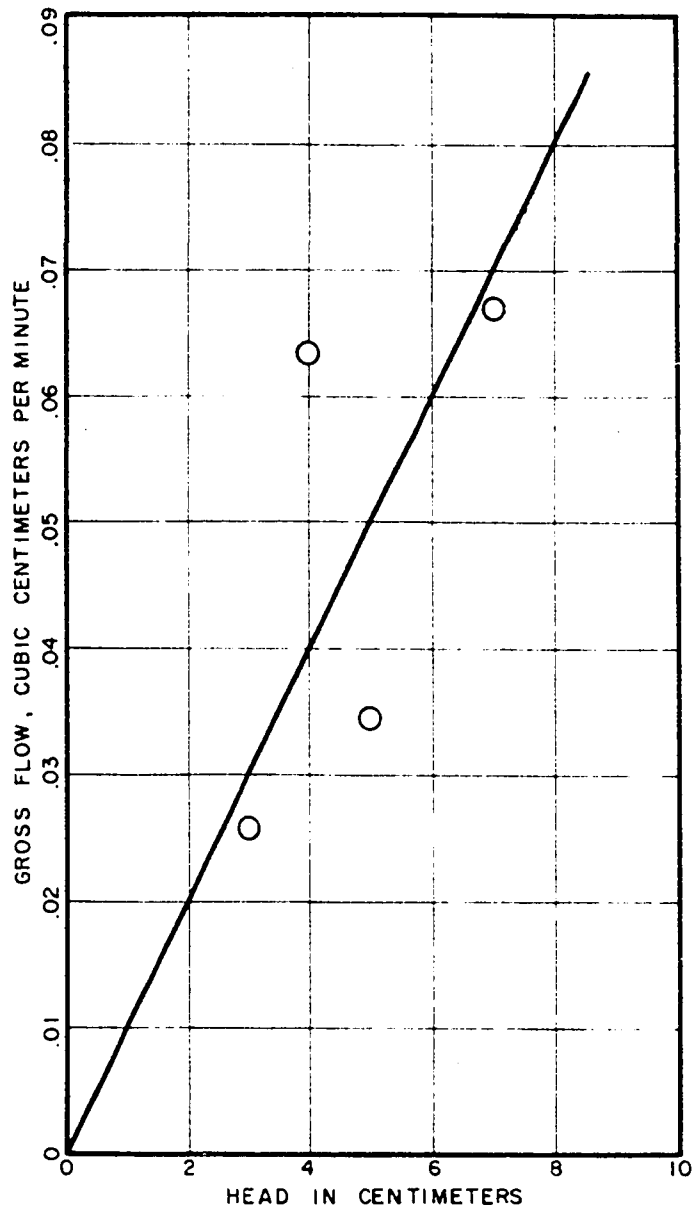


Figure 53 - Plot of Semi-Processed Bulk Flow Data to Determine Actual Barrier Flow Coefficient "F"

APPENDIX I
BARRIER DIFFUSION IMPEDENCE DATA

TABLE 13
BARRIER DIFFUSION IMPEDENCE DATA

	No Barrier	With Barrier
	Weight Frac. EtOH	Weight Frac. EtOH
Top Solution Composition, Initial	0.4490	0.4482
Top Solution Composition, Final	0.4185	0.4208
Bottom Solution Composition, Initial	0.3551	0.3532
Bottom Solution Composition, Final	0.3808	0.3843
Diffusing Time:	48 hours	
Average Temperature:	84°F	
Vertical Diffusion Cell:	Length of Top Half of Cell, 1.91 cm Length of Bottom Half of Cell, 1.91 cm Diameter of Cell, 1.27 cm	
Barrier Specifications:	Kueffel and Esser Prepared Tracing Paper, ALBANENE 195 MX, Presoaked in 0.40 Weight Fraction EtOH Solution.	

APPENDIX J

SUMMARY OF ϕ_H AND ϕ_K VALUES

TABLE 14

SUMMARY OF ϕ_H AND ϕ_K VALUES

Experi- mental Set	Plate Spacing 2ω	H_{expt}	H_{theor}	K_{expt}	K_{theor}	ϕ_H	ϕ_K
	cm	$\frac{\text{gm}}{\text{min}}$	$\frac{\text{gm}}{\text{min}}$	$\frac{\text{gm-cm}}{\text{min}}$	$\frac{\text{gm-cm}}{\text{min}}$		
A	.2164	.0712	1.655	345.	17,590.	.043	.0197
B	.1521	.0566	.308	152.	1,270.	.184	.12
C	.1519	.0373	.0674	150.	314.	.554	.478
D	.0765	.0236	.0216	6.4	6.57	.98	.975
K	.2306	.0052	.0807	16.0	121.8	.064	.131
L	.1478	.0140	.0182	11.5	4.72	.77	2.44
M	.1483	.0058	.0047	4.0	1.202	1.23	3.33
-	.1350	-	-	-	-	.472	.413
-	.1416	-	-	-	-	.538	.404
-	.1344	-	-	-	-	.538	.425
-	.0628	-	-	-	-	1.12	1.18
-	.1928	-	-	-	-	.147	.092
-	.0908	-	-	-	-	.895	.890
-	.0908	-	-	-	-	.895	-
-	.0850	-	-	-	-	1.00	1.00

Notes: (a) All ϕ values for system ethyl alcohol-water.

(b) Sets A, B, C, D, this work with no barriers.

(c) Sets K, L, M, this work with single vertical tracing paper barrier.

(d) Unlabeled sets taken from the work of Powers (58).

APPENDIX K
PHYSICAL PROPERTY DATA USED

TABLE 15
VALUES OF PHYSICAL PROPERTIES USED IN CALCULATIONS^a

Property	Units	Symbol	Value	Reference No.
Density	$\frac{\text{gm mass}}{\text{cu. cm}}$	ρ	0.9125	(229,230)
Diffusion Coefficient	$\frac{\text{sq. cm}}{\text{sec.}}$	D	1.03×10^{-5}	(231-233)
Temperature Coefficient of Expansion	$\frac{\text{gm mass}}{\text{cu. cm-}^{\circ}\text{C}}$	β_T	8.12×10^{-4}	(58)
Viscosity	$\frac{\text{gm mass}}{\text{cm-sec.}}$	η	1.14×10^{-2}	(229)

^aBecause the mean column composition was nearly the same in all sets of data, physical properties were evaluated at the grand average of the feed compositions of all sets, $C_F = 0.4010$ Weight Fraction EtOH.

APPENDIX L
SAMPLE DATA SHEETS

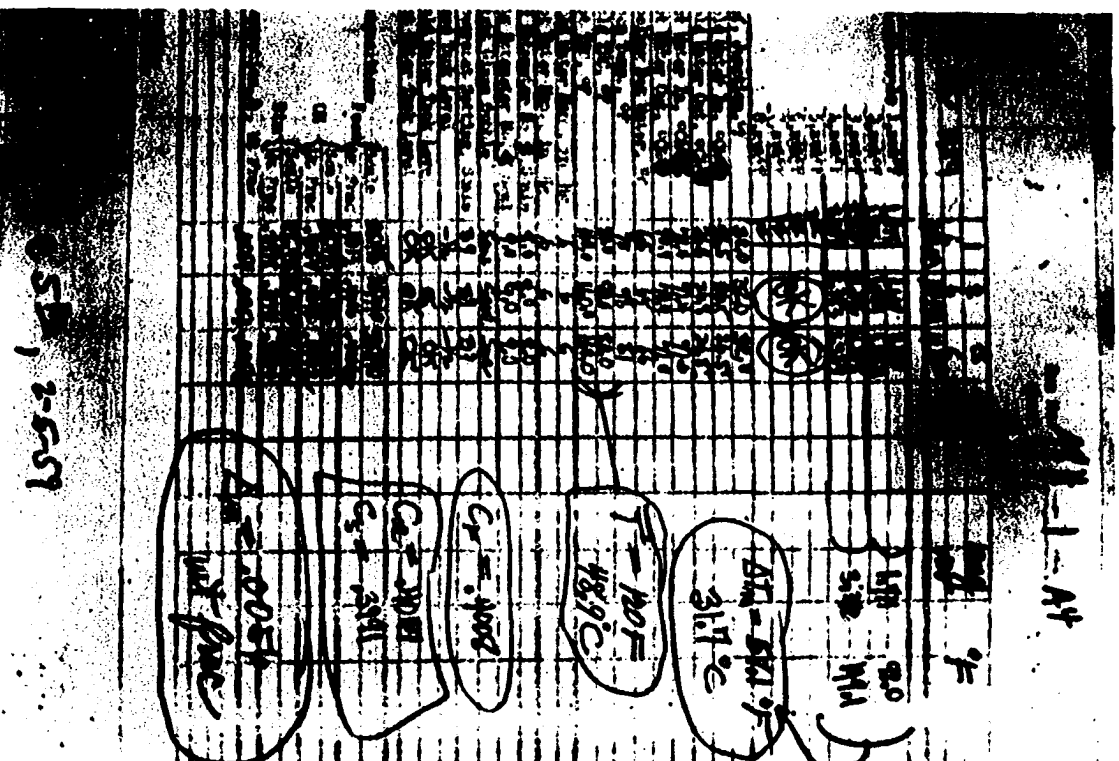


Figure 54 - Sample Data Sheet - Run 48H, Sheet A

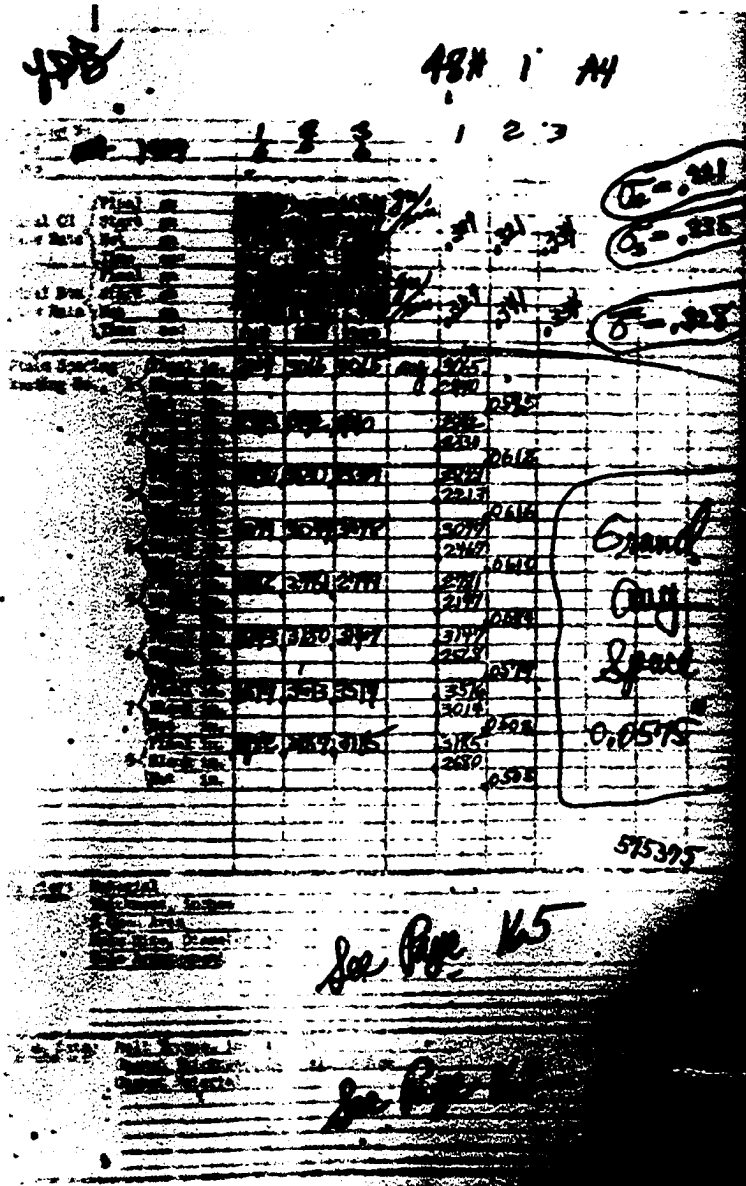


Figure 55 - Sample Data Sheet - Run 48H, Sheet B

APPENDIX M
SAMPLE CALCULATIONS

1. Sample Calculation of H_{expt} and K_{expt} (Set D).--

Using the method of Powers (237) described in Chapter V, values of Δ_0 and K are assumed until a satisfactory fit is achieved.

$$\frac{\Delta}{\Delta_0} = \frac{1}{Z} (1 - e^{-Z}) \quad \text{Eqn. V-2}$$

$$Z = \frac{\sigma L}{2K} \quad \text{Eqn. V-3}$$

After a few preliminary trials, assume

$$\Delta_0 = 0.1335 \text{ wt. fraction}$$

$$\text{and} \quad K = 6.40 \text{ gm.-cm./min.}$$

The column used in this work had a length, $L = 145 \text{ cm.}$

Experimental Data
Set D

Δ Separation, wt. frac.	σ Flow Rate, gm./min.	Computed $\frac{\Delta}{\Delta_0}$	Computed Z
0.1335	0	1.000	0
0.0917	0.0623	0.687	0.706
0.0782	0.103	0.586	1.17
0.0628	0.161	0.471	1.82
0.0323	0.369	0.242	4.18

The computed values of Δ/Δ_0 and Z are plotted on the general graph of Equation V-2 and shown as Figure 56. The excellent fit shows that the assumed values of Δ_0 and K are satisfactory.

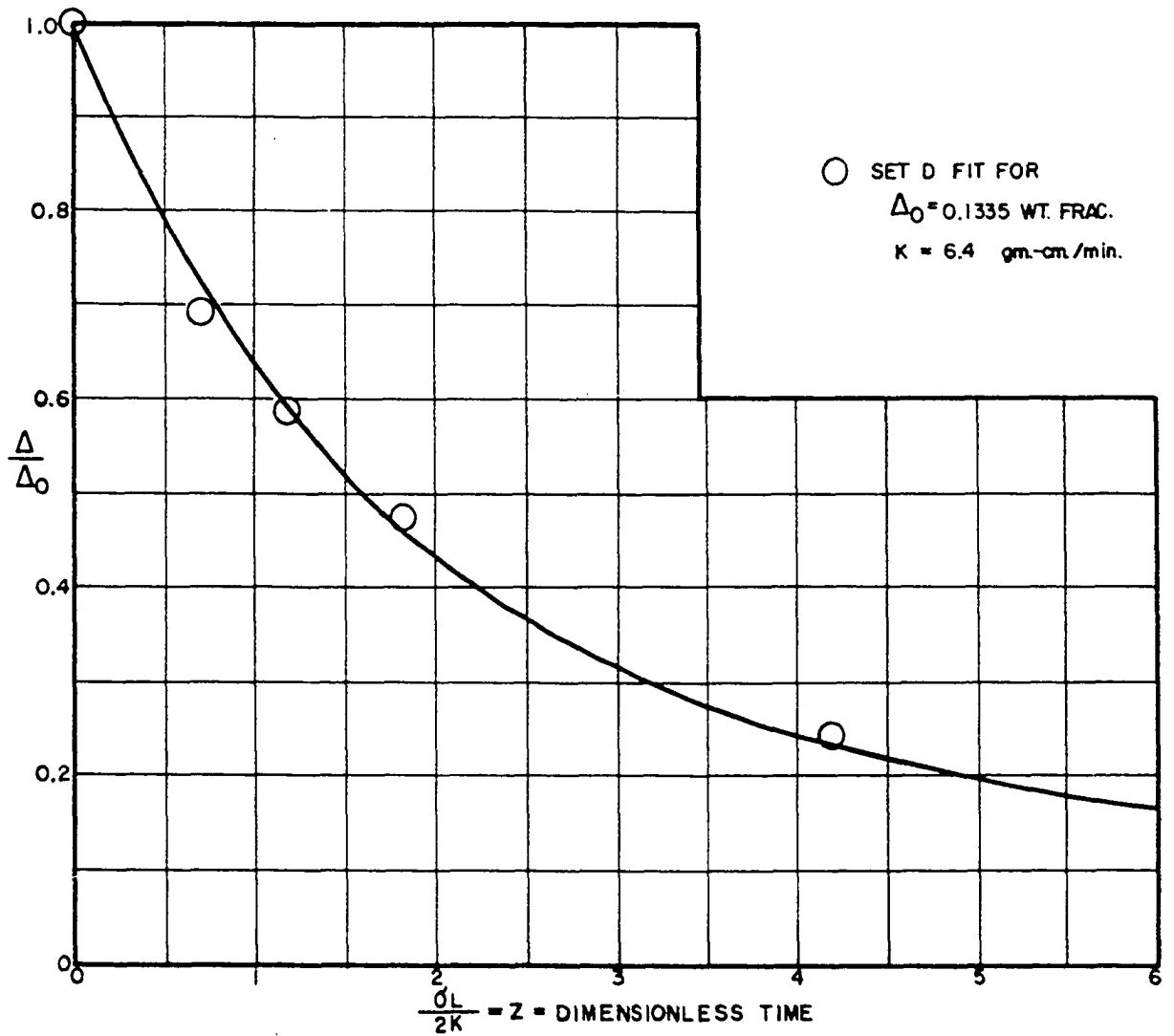


Figure 56 - Sample of Fit Using Powers' Method to
 Determine H and K from Experimental Data--
 Set D

From

$$\Delta_0 = \frac{HL}{4K} \quad \text{Eqn. IV-42}$$

the value of H can be found.

$$0.1335 = \frac{H(145 \text{ cm.})}{(4)(6.40 \text{ gm.-cm./min.})}$$

$$H = 0.0236 \text{ gm./min.}$$

By these calculations it has been determined that for
Experimental Set D:

$$\underline{\underline{H_{\text{expt}} = 0.0236 \text{ gm./min.}}}$$

$$\underline{\underline{K_{\text{expt}} = 6.40 \text{ gm.-cm./min.}}}$$

2. Sample Calculation of ϕ and α Values (Set D).---

Following the method described in Chapter V and using the assumption that $K \approx K_C$

$$K_C = K_{\text{theor}} = \frac{\beta_T^2 \rho g^2 B (\Delta T)^2 (2\omega)^7}{9! D_{rl}^2} \quad \text{Eqn. IV-34}$$

$$\beta_T = 8.12 \times 10^{-4} \text{ gm.-m./cu.cm.-}^\circ\text{C}$$

$$\rho = 0.9125 \text{ gm.-m./cu.cm.}$$

$$g = 980 \text{ cm./sq.sec.}$$

$$B = 10.2 \text{ cm.}$$

$$\Delta T = 25.4^\circ\text{C.}$$

$$2\omega = 0.0765 \text{ cm.}$$

$$D = 1.03 \times 10^{-5} \text{ sq.cm./sec.}$$

$$\eta = 1.14 \times 10^{-2} \text{ gm.-m./cm.-sec.}$$

When these values are substituted in Equation IV-34 along with a factor of 60 sec./min., the result is

$$\underline{\underline{K_{\text{theor}} = 6.57 \text{ gm.-cm./min.}}}$$

From previous Sample Calculation

$$K_{\text{expt}} = 6.40 \text{ gm.-cm./min.}$$

$$\phi_K = \frac{K_{\text{expt}}}{K_{\text{theor}}} = \frac{6.40 \text{ gm.-cm./min.}}{6.57 \text{ gm.-cm./min.}} \quad \text{Eqn. V-5}$$

$$\underline{\underline{\phi_K = 0.975}}$$

Calculation of ϕ_H

$$\phi_K = \phi_H^{1.25} \quad \text{Eqn. V-6}$$

$$0.975 = \phi_H^{1.25}$$

$$\underline{\underline{\phi_H = 0.98}}$$

Calculation of H_{theor}

$$\phi_H = \frac{H_{\text{expt}}}{H_{\text{theor}}} \quad \text{Eqn. V-5}$$

From previous sample calculation

$$H_{\text{expt}} = 0.0236 \text{ gm./min.}$$

$$0.98 = \frac{0.0236}{H_{\text{theor}}}$$

$$\underline{\underline{H_{\text{theor}} = 0.0216 \text{ gm./min.}}}$$

Calculation of α

$$H_{\text{theor}} = H = \frac{\alpha \beta_T \rho g B (\Delta T)^2 (2\omega)^3}{6! \bar{T} \eta} \quad \text{Eqn. IV-33}$$

$$H = 0.0216 \text{ gm./min.}$$

$$\beta_T = 8.12 \times 10^{-4} \text{ gm.-m./cu.cm.-}^\circ\text{K.}$$

$$\rho = 0.9125 \text{ gm.-m./cu.cm.}$$

$$g = 980 \text{ cm./sq.sec.}$$

$$B = 10.2 \text{ cm.}$$

$$\Delta T = 25.4^\circ\text{K.}$$

$$2\omega = 0.0765 \text{ cm.}$$

$$\bar{T} = 322^\circ\text{K.}$$

$$\eta = 1.14 \times 10^{-2} \text{ gm.-m./cm.-sec.}$$

When these values are substituted in Equation IV-33 along with a factor of 60 sec./min., and the equation solved for α , the result is $\alpha = 0.513$ (Thermal Diffusion "Constant") Set D.

3. Sample Calculation of h_{AB} (Set L).---Using

$$h_{AB} = \frac{15 \beta_T \rho g B (\Delta T)^2 (2\omega)^3 FL^2}{6 \bar{T} [\rho g_C (2\omega)^3 + 16 \eta FL^2]} \quad \text{Eqn. IV-80}$$

$$\alpha = 0.513$$

$$\beta_T = 8.12 \times 10^{-4} \text{ gm.-m./cu.cm.-}^\circ\text{K.}$$

$$\rho = 0.9125 \text{ gm.-m./cu.cm.}$$

$$g = 980 \text{ cm./sq.sec.}$$

$$B = 10.2 \text{ cm.}$$

$$\Delta T = 31.2^\circ\text{K.}$$

$$2\omega = 0.1478 \text{ cm.}$$

$$F = 4.02 \times 10^{-6} \text{ cu.cm.-gm.-m./sq.cm.-sec.-gm.-f.-cm.}$$

$$L = 145 \text{ cm.}$$

$$\bar{T} = 322^\circ\text{K.}$$

$$g_C = 980 \text{ cm.-gm.-m./sq.sec.-gm.-f.}$$

$$\eta = 1.14 \times 10^{-2} \text{ gm.-m./cm.-sec.}$$

when these values are substituted in Equation IV-80 along with a factor of 60 sec./min., the result is

$$\underline{\underline{h_{AB} = 0.0013 \text{ gm./min.}}}$$

4. Sample Calculation of H_{IB}^1 (Set L).---From

$$H_{IB}^n = \frac{\alpha \beta_T \rho g B (\Delta T)^2 (2\omega)^3}{6! \bar{T}_L (n+1)^4} \quad \text{Eqn. IV-56}$$

For one ideal vertical barrier

$$n = 1$$

$$\alpha = 0.513$$

$$\beta_T = 8.12 \times 10^{-4} \text{ gm.-m./cu.cm.-}^\circ\text{K.}$$

$$\rho = 0.9125 \text{ gm.-m/cu.cm.}$$

$$g = 980 \text{ cm./sq.sec.}$$

$$B = 10.2 \text{ cm.}$$

$$\Delta T = 31.2^\circ\text{K.}$$

$$2\omega = 0.1478 \text{ cm.}$$

$$\bar{T} = 322^\circ\text{K.}$$

$$\eta = 1.14 \times 10^{-2} \text{ gm.-m./cm.-sec.}$$

when these values are substituted in Equation IV-56 along with a factor of 60 sec./min., the result is

$$\underline{\underline{H_{IB}^1 = 0.0169 \text{ gm./min.}}}$$

5. Sample Calculation of H_{AB}^1 (Set L). --From previous
Sample Calculation for Set L,

$$h_{AB} = 0.0013 \text{ gm./min.}$$

$$H_{IB}^1 = 0.0169 \text{ gm./min.}$$

Using

$$H_{AB}^1 = H_{IB}^1 + h_{AB} \quad \text{Eqn. IV-78}$$

$$H_{AB}^1 = 0.0169 \text{ gm./min.} + 0.0013 \text{ gm./min.}$$

$$\underline{\underline{H_{AB}^1 = 0.0182 \text{ gm./min.}}}$$

(This is H_{theor} for Set L.)

6. Sample Calculation of k_{AB} (Set L).--Using

$$k_{AB} = \frac{26 \beta_T^2 g^2 \rho B (\Delta T)^2 (2\omega)^7 F^2 L^4}{8! D \left[\rho g_C (2\omega)^3 + 16 \eta FL^2 \right]^2} \quad \text{Eqn. IV-81}$$

$$+ \frac{\beta_T^2 g^2 \rho B (\Delta T)^2 (2\omega)^7 FL^2}{(384) 6! D \eta \left[\rho g_C (2\omega)^3 + 16 \eta FL^2 \right]}$$

$$\beta_T = 8.12 \times 10^{-4} \text{ gm.-m./cu.cm.-}^\circ\text{C.}$$

$$g = 980 \text{ cm./sq.sec.}$$

$$\rho = 0.9125 \text{ gm.-m./cu.cm.}$$

$$B = 10.2 \text{ cm.}$$

$$\Delta T = 31.2^\circ\text{C.}$$

$$2\omega = 0.1478 \text{ cm.}$$

$$F = 4.02 \times 10^{-6} \text{ cu.cm.-gm.-m./sq.cm.-sec.-gm.-f.-cm.}$$

$$L = 145 \text{ cm.}$$

$$D = 1.03 \times 10^{-5} \text{ sq.cm./sec.}$$

$$g_C = 980 \text{ cm.-gm.-m./sq.sec.-gm.-f.}$$

$$\eta = 1.14 \times 10^{-2} \text{ gm.-m./cm.-sec.}$$

when these values are substituted in Equation IV-81 along with a factor of 60 sec./min., the result is

$$\underline{\underline{k_{AB} = 0.48 \text{ gm.-cm./min.}}}$$

7. Sample Calculation of K_{CIB}^1 (Set L).---Using

$$K_{CIB}^n = \frac{\beta_T^2 \rho g^2 B (\Delta T)^2 (2\omega)^7}{9! D \eta^{2(n+1)} 8} \quad \text{Eqn. IV-57}$$

For one vertical ideal barrier

$$n = 1$$

$$\beta_T = 8.12 \times 10^{-4} \text{ gm.-m./cu.cm.-}^\circ\text{C.}$$

$$\rho = 0.9125 \text{ gm.-m./cu.cm.}$$

$$g = 980 \text{ cm./sq.sec.}$$

$$B = 10.2 \text{ cm.}$$

$$\Delta T = 31.2^\circ\text{C.}$$

$$2\omega = 0.1478 \text{ cm.}$$

$$D = 1.03 \times 10^{-5} \text{ sq.cm./sec.}$$

$$\eta = 1.14 \times 10^{-2} \text{ gm.-m./cm.-sec.}$$

when these values are substituted in Equation IV-57 along with a factor of 60 sec./min., the result is

$$\underline{\underline{K_{CIB}^1 = 4.24 \text{ gm.-cm./min.}}}$$

8. Sample Calculation of K_{CAB}^1 (Set L).--From previous sample calculations,

$$k_{AB} = 0.48 \text{ gm.-cm./min.}$$

$$K_{CIB}^1 = 4.24 \text{ gm.-cm./min.}$$

Using

$$K_{CAB}^1 = K_{CIB}^1 + k_{AB} \quad \text{Eqn. IV-79}$$

$$K_{CAB}^1 = 4.24 \text{ gm.-cm./min.} + 0.48 \text{ gm.-cm./min.}$$

$$\underline{\underline{K_{CAB}^1 = 4.72 \text{ gm.-cm./min.}}}$$

(This is K_{theor} for Set L.)

9. Calculation of Bulk Flow Factor, F.--The defining equation for F is

$$Q = Fh \quad \text{Eqn. IV-63}$$

where h = head in cm.-gm.f./gm.-m.

Q = volumetric flow in cu.cm./sec.-sq.cm.

so F is in cu.cm.-gm.-m/sq.cm.-sec.-gm.-f.-cm.

From Figure 53, Appendix H, the slope of the line is 0.01 cu.cm.-gm.-m./min.-gm.-f.-cm. However, this slope defined the flow through an area of 81 sq.cm., so at bulk flow test conditions

$$\left(0.01 \frac{\text{cu.cm.-gm.-m.}}{\text{min.-gm.-f.-cm.}}\right) \left(\frac{1 \text{ min.}}{60 \text{ sec.}}\right) \left(\frac{1}{81 \text{ sq.cm.}}\right) = F' =$$

$$2.06 \times 10^{-6} \text{ cu.cm.-gm.-m./sq.cm.-sec.-gm.-f.-cm.}$$

The flow through the pores of the barrier should be extremely laminar so that F' can be corrected to column conditions by a factor of

$$\left(\frac{\rho_{120^{\circ}\text{F}}}{\rho_{80.4^{\circ}\text{F}}}\right) \left(\frac{\eta_{80.4^{\circ}\text{F}}}{\eta_{120^{\circ}\text{F}}}\right)$$

where $120^{\circ}\text{F} = 48.9^{\circ}\text{C} =$ thermogravitational column conditions

$80.4^{\circ}\text{F} =$ bulk flow test conditions.

Applying such corrections yields

$$F = \left(2.06 \times 10^{-6} \frac{\text{cu.cm.-gm.-m.}}{\text{sq.cm.-sec.-gm.f.-cm.}}\right) \left(\frac{0.9125}{0.9330}\right) \left(\frac{2.28 \times 10^{-2}}{1.14 \times 10^{-2}}\right)$$

$$\underline{\underline{F = 4.02 \times 10^{-6} \text{ cu.cm.-gm.-m./sq.cm.-sec.-gm.-f.-cm.}}}$$

for tracing paper barrier at thermogravitational column conditions.

APPENDIX N
CALIBRATION DATA

TABLE 16
HOT AND COLD WATER MANOMETER CALIBRATION DATA

Time	Temp.	Initial Sample Weight	Final Sample Weight	Net Sample Weight	Flow Rate	Density ^a	Flow Rate	Mano- meter Reading
Sec.	°F.	lbs.	lbs.	lbs.	$\frac{\text{lbs.}}{\text{sec.}}$	$\frac{\text{lbs.}}{\text{cu.ft.}}$	$\frac{\text{gal.}}{\text{min.}}$	in. Hg.
75.8	84	39.5	184.0	144.5	1.91	62.3	13.8	1.8
69.2	82	39.5	175.0	135.5	1.96	62.3	14.1	1.9
42.3	81	39.5	158.5	119.0	2.82	62.3	20.3	4.1
43.0	80	39.5	159.5	120.0	2.79	62.3	20.1	4.1
28.8	79	39.0	143.0	104.0	3.61	62.3	26.0	6.7
31.8	79	39.5	154.5	115.0	3.62	62.3	26.1	6.7
42.1	80	39.5	177.5	138.0	3.28	62.3	23.6	5.6
53.5	80	39.5	211.0	171.5	3.21	62.3	23.1	5.3
60.8	80	40.5	184.0	143.5	2.36	62.3	17.0	2.7
65.4	78	42.0	207.0	165.0	2.53	62.3	18.2	3.2
31.0	129	42.5	155.5	113.0	3.65	61.5	26.6	6.7
48.5	129	42.5	180.5	138.0	2.85	61.5	20.8	4.1
28.2	178	--	--	100.0	3.55	60.6	26.3	6.5

^aDensity calculated from Keenan and Keyes (242).

Parameters: "Pipe Taps" used
Sharp-Edged Orifices, Diameter = 0.80
in.

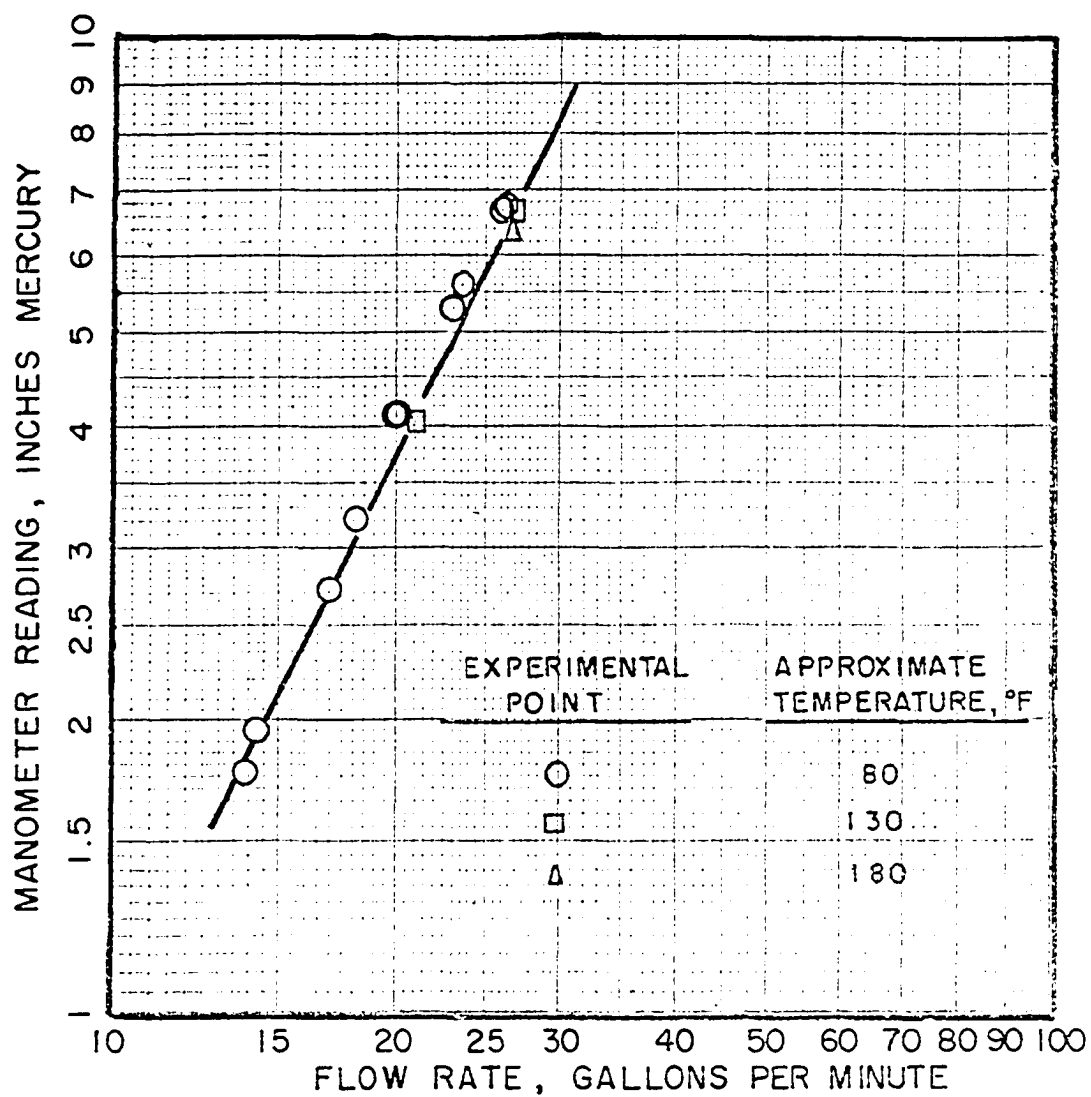


Figure 57 - Hot and Cold Water Manometer Calibration
Curve

Refractometer Calibration

Weighed samples were prepared in sealed sample bottles. Distilled water and U.S.I. absolute pure ethyl alcohol U.S.P.--N.F. (reagent quality) were used in sample preparation. Samples were made up and removed with hypodermic syringes and needles through pharmaceutical rubber stoppers sealing the sample bottles.

Samples were placed in a Bausch and Lomb Precision Refractometer No. 33-45-01 with prism temperature controlled at 25.0°C. The results are shown in Table 17. Repeat readings were made on many samples.

The data of Table 17 were plotted on a large graph (about 3 by 4 feet in size). A smooth curve was drawn through the data, and values read from the curve. The smoothed values were interpolated to the accuracy of the refractometer scale using an IBM 650 computer. The smoothed interpolated data are presented in Table 18, and were used throughout this investigation to determine the composition of ethyl alcohol--water samples taken from the thermal diffusion column.

In the event that index of refraction is desired, Bausch and Lomb provides tables to convert from precision refractometer scale units to index of refraction.

TABLE 17

TABLE 18

INTERPOLATED SMOOTHED REFRACTOMETER CALIBRATION DATA

Composition	Refractometer Reading	Composition	Refractometer Reading
Weight Frac. EtOH	Scale	Weight Frac. EtOH	Scale
0.3013	24.600	0.3189	24.790
0.3017	24.605	0.3195	24.795
0.3021	24.610	0.3200	24.800
0.3025	24.615	0.3205	24.805
0.3029	24.620	0.3210	24.810
0.3034	24.625	0.3216	24.815
0.3038	24.630	0.3221	24.820
0.3042	24.635	0.3226	24.825
0.3046	24.640	0.3231	24.830
0.3050	24.645	0.3236	24.835
0.3055	24.650	0.3242	24.840
0.3059	24.655	0.3247	24.845
0.3064	24.660	0.3252	24.850
0.3068	24.665	0.3258	24.855
0.3072	24.670	0.3263	24.860
0.3077	24.675	0.3268	24.865
0.3082	24.680	0.3274	24.870
0.3086	24.685	0.3279	24.875
0.3091	24.690	0.3284	24.880
0.3095	24.695	0.3290	24.885
0.3100	24.700	0.3295	24.890
0.3105	24.705	0.3300	24.895
0.3109	24.710	0.3306	24.900
0.3114	24.715	0.3311	24.905
0.3119	24.720	0.3317	24.910
0.3124	24.725	0.3322	24.915
0.3129	24.730	0.3328	24.920
0.3134	24.735	0.3333	24.925
0.3138	24.740	0.3339	24.930
0.3143	24.745	0.3344	24.935
0.3148	24.750	0.3350	24.940
0.3153	24.755	0.3355	24.945
0.3158	24.760	0.3361	24.950
0.3164	24.765	0.3366	24.955
0.3169	24.770	0.3372	24.960
0.3174	24.775	0.3378	24.965
0.3179	24.780	0.3383	24.970
0.3184	24.785	0.3389	24.975

TABLE 18--Continued

Composition	Refractometer Reading	Composition	Refractometer Reading
Weight Frac. EtOH	Scale	Weight Frac. EtOH	Scale
0.3394	24.980	0.3641	25.180
0.3400	24.985	0.3648	25.185
0.3406	24.990	0.3654	25.190
0.3411	24.995	0.3661	25.195
0.3417	25.000	0.3668	25.200
0.3423	25.005	0.3674	25.205
0.3429	25.010	0.3681	25.210
0.3434	25.015	0.3688	25.215
0.3440	25.020	0.3694	25.220
0.3446	25.025	0.3701	25.225
0.3452	25.030	0.3708	25.230
0.3458	25.035	0.3714	25.235
0.3464	25.040	0.3721	25.240
0.3470	25.045	0.3727	25.245
0.3476	25.050	0.3734	25.250
0.3482	25.055	0.3741	25.255
0.3488	25.060	0.3747	25.260
0.3494	25.065	0.3754	25.265
0.3501	25.070	0.3761	25.270
0.3507	25.075	0.3767	25.275
0.3513	25.080	0.3774	25.280
0.3519	25.085	0.3781	25.285
0.3525	25.090	0.3788	25.290
0.3532	25.095	0.3794	25.295
0.3538	25.100	0.3801	25.300
0.3544	25.105	0.3808	25.305
0.3550	25.110	0.3815	25.310
0.3557	25.115	0.3822	25.315
0.3563	25.120	0.3829	25.320
0.3570	25.125	0.3836	25.325
0.3576	25.130	0.3843	25.330
0.3582	25.135	0.3851	25.335
0.3589	25.140	0.3858	25.340
0.3595	25.145	0.3865	25.345
0.3602	25.150	0.3872	25.350
0.3608	25.155	0.3880	25.355
0.3615	25.160	0.3887	25.360
0.3621	25.165	0.3894	25.365
0.3628	25.170	0.3902	25.370
0.3635	25.175	0.3909	25.375

TABLE 18--Continued

Composition	Refractometer Reading	Composition	Refractometer Reading
Weight Frac. EtOH	Scale	Weight Frac. EtOH	Scale
0.3917	25.380	0.4215	25.580
0.3924	25.385	0.4223	25.585
0.3932	25.390	0.4230	25.590
0.3939	25.395	0.4238	25.595
0.3947	25.400	0.4246	25.600
0.3954	25.405	0.4253	25.605
0.3962	25.410	0.4260	25.610
0.3969	25.415	0.4268	25.615
0.3976	25.420	0.4276	25.620
0.3984	25.425	0.4283	25.625
0.3991	25.430	0.4290	25.630
0.3998	25.435	0.4298	25.635
0.4006	25.440	0.4305	25.640
0.4013	25.445	0.4313	25.645
0.4020	25.450	0.4320	25.650
0.4028	25.455	0.4328	25.655
0.4035	25.460	0.4336	25.660
0.4042	25.465	0.4343	25.665
0.4050	25.470	0.4351	25.670
0.4057	25.475	0.4359	25.675
0.4064	25.480	0.4367	25.680
0.4072	25.485	0.4375	25.685
0.4079	25.490	0.4384	25.690
0.4087	25.495	0.4392	25.695
0.4094	25.500	0.4400	25.700
0.4101	25.505	0.4408	25.705
0.4109	25.510	0.4416	25.710
0.4116	25.515	0.4424	25.715
0.4124	25.520	0.4432	25.720
0.4132	25.525	0.4441	25.725
0.4139	25.530	0.4449	25.730
0.4147	25.535	0.4457	25.735
0.4154	25.540	0.4465	25.740
0.4162	25.545	0.4474	25.745
0.4169	25.550	0.4482	25.750
0.4177	25.555	0.4490	25.755
0.4185	25.560	0.4497	25.760
0.4192	25.565	0.4507	25.765
0.4200	25.570	0.4516	25.770
0.4208	25.575	0.4524	25.775

TABLE 18--Continued

Composition	Refractometer Reading	Composition	Refractometer Reading
Weight Frac. EtOH	Scale	Weight Frac. EtOH	Scale
0.4533	25.780	0.4900	25.980
0.4542	25.785	0.4910	25.985
0.4550	25.790	0.4920	25.990
0.4559	25.795	0.4930	25.995
0.4568	25.800	0.4940	26.000
0.4576	25.805	0.4950	26.005
0.4585	25.810	0.4960	26.010
0.4593	25.815	0.4970	26.015
0.4602	25.820	0.4981	26.020
0.4610	25.825	0.4991	26.025
0.4618	25.830	0.5001	26.030
0.4626	25.835	0.5012	26.035
0.4635	25.840	0.5022	26.040
0.4643	25.845	0.5032	26.045
0.4651	25.850	0.5043	26.050
0.4660	25.855	0.5054	26.055
0.4669	25.860	0.5065	26.060
0.4678	25.865	0.5077	26.065
0.4687	25.870	0.5088	26.070
0.4696	25.875	0.5100	26.075
0.4705	25.880	0.5112	26.080
0.4714	25.885	0.5123	26.085
0.4724	25.890	0.5135	26.090
0.4733	25.895	0.5148	26.095
0.4743	25.900	0.5160	26.100
0.4752	25.905	0.5172	26.105
0.4762	25.910	0.5184	26.110
0.4772	25.915	0.5196	26.115
0.4781	25.920	0.5208	26.120
0.4791	25.925	0.5221	26.125
0.4801	25.930	0.5233	26.130
0.4810	25.935	0.5245	26.135
0.4820	25.940	0.5258	26.140
0.4830	25.945	0.5270	26.145
0.4840	25.950	0.5283	26.150
0.4850	25.955	0.5295	26.155
0.4860	25.960	0.5307	26.160
0.4870	25.965	0.5319	26.165
0.4880	25.970	0.5331	26.170
0.4890	25.975	0.5343	26.175

TABLE 18--Continued

Composition	Refractometer Reading	Composition	Refractometer Reading
Weight Frac. EtOH	Scale	Weight Frac. EtOH	Scale
0.5354	26.180	0.5903	26.380
0.5366	26.185	0.5918	26.385
0.5378	26.190	0.5933	26.390
0.5389	26.195	0.5948	26.395
0.5401	26.200	0.5963	26.400
0.5414	26.205	0.5980	26.405
0.5427	26.210	0.5997	26.410
0.5440	26.215	0.6014	26.415
0.5454	26.220	0.6032	26.420
0.5468	26.225	0.6050	26.425
0.5482	26.230	0.6068	26.430
0.5496	26.235	0.6086	26.435
0.5510	26.240	0.6104	26.440
0.5525	26.245	0.6122	26.445
0.5540	26.250	0.6140	26.450
0.5553	26.255	0.6157	26.455
0.5567	26.260	0.6175	26.460
0.5580	26.265	0.6192	26.465
0.5593	26.270	0.6208	26.470
0.5606	26.275	0.6225	26.475
0.5616	26.280	0.6243	26.480
0.5632	26.285	0.6261	26.485
0.5645	26.290	0.6280	26.490
0.5657	26.295	0.6299	26.495
0.5670	26.300	0.6318	26.500
0.5684	26.305	0.6337	26.505
0.5698	26.310	0.6357	26.510
0.5712	26.315	0.6377	26.515
0.5726	26.320	0.6397	26.520
0.5740	26.325	0.6417	26.525
0.5755	26.330	0.6437	26.530
0.5769	26.335	0.6458	26.535
0.5784	26.340	0.6478	26.540
0.5798	26.345	0.6499	26.545
0.5814	26.350	0.6520	26.550
0.5829	26.355	0.6540	26.555
0.5843	26.360	0.6560	26.560
0.5858	26.365	0.6580	26.565
0.5873	26.370	0.6600	26.570
0.5888	26.375	0.6620	26.575

TABLE 18--Continued

Composition	Refractometer Reading	Composition	Refractometer Reading
Weight Frac. EtOH	Scale	Weight Frac. EtOH	Scale
0.6641	26.580	0.6816	26.620
0.6661	26.585	0.6840	26.625
0.6682	26.590	0.6862	26.630
0.6704	26.595	0.6885	26.635
0.6725	26.600	0.6907	26.640
0.6747	26.605	0.6928	26.645
0.6770	26.610	0.6950	26.650
0.6816	26.615		

Parameters: Bausch and Lomb Precision Refractometer
No. 33-45-01. Prism Temperature
25.0°C.

APPENDIX O
SUPPLEMENTARY BIBLIOGRAPHY

SUPPLEMENTARY BIBLIOGRAPHY

The following bibliography was assembled in connection with the dissertation, An Experimental and Theoretical Investigation of Vertical Barriers in Liquid Thermal Diffusion. All phases of non-isothermal solution behavior in gases, liquids, and solids are included. References were obtained by carefully searching Chemical Abstracts, checking bibliographies of articles read, and by periodically reviewing the table of contents of current journals.

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