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SEPARATION OF LIQUIDS BY THERMAL DIFFUSION

John Edward Powers

(Thesis)

August, 1954

Berkeley, California

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SEPARATION OF LIQUIDS BY THERMAL DIFFUSION

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August, 1954

ABSTRACT

The separation of liquid mixtures in continuous flow thermogravitational columns was investigated experimentally and theoretically. Two continuous-flow thermogravitational columns were built and operated to determine the effect of changing several operating variables.

The data obtained are in qualitative agreement with the theory of Furry, Jones and Onsager as modified in this thesis. Three additional corrections are necessary to bring the theory into quantitative agreement with the data. In the laminar-flow range individual corrections are required for both low and high convective flow rates without turbulence. A third correction is necessary when turbulence is encountered. A correlation of the correction necessary at high convective flow rates without turbulence (the only region investigated) is proposed which includes data on both liquid and gas systems.

Design procedures to aid in the development of thermal diffusion plants are developed and summarized. A plant to treat 1,000 barrels per day of a liquid aromatic-aliphatic mixture is designed and costs are estimated.

Data obtained in a small glass-diaphragm thermal diffusion cell were not consistent with data from the continuous-flow thermogravitational column.

An extensive review of the literature on all phases of thermal diffusion is included.

SEPARATION OF LIQUIDS BY THERMAL DIFFUSION

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I. INTRODUCTION

During the past quarter century the need for new separation methods has given strong impetus to the investigation of irreversible processes. For example, most of the work done in the field of irreversible processes involving nonisothermal solution behavior has been reported in the last several decades, although this effect was first noted almost one hundred years ago. The possibility of commercial application of separation methods based on these particular irreversible processes has stimulated some of the most recent investigations.

Nonisothermal solution behavior has two manifestations, one the inverse of the other. If two gases of different composition and initially at the same temperature are allowed to diffuse together, a transient temperature gradient results from the ordinary diffusion process. This phenomenon was first noted by Dufour in 1873,²⁰ and bears his name. Conversely, if a temperature gradient is applied to a homogeneous solution, a concentration gradient is usually established. The name thermal diffusion (or thermodiffusion) is generally applied to this second effect.

Obviously only the nonisothermal solution phenomena relating to thermal diffusion can be used for the separation of solutions, as the Dufour effect is the result of a mixing process. Two methods of utilizing thermal diffusion for the separation of solutions have

been proposed. In the static method the thermal gradient is established in such a manner that convection is eliminated and there is no bulk flow. When applied to liquid or solid solutions the static method is called the Ludwig-Soret or the Soret effect. No special name has been given to the phenomenon in gases. The extent of the separation obtainable by the static method is generally very slight. The thermogravitational method multiplies the separation achieved in the static method by utilizing convection currents to produce a cascading effect. The apparatus that is used to produce the cascading effect is called a thermogravitational column or, commonly, a Clusius-Dickel column (in honor of the inventors). This type of apparatus is described in more detail in Chapter IV. Thermogravitational columns have been used to bring about separations in both gas and liquid solutions, and have been operated in both batch (not to be confused with static) and continuous manners. The terms "continuous" and "batch" indicate, respectively, the presence or absence of a net bulk flow through the thermogravitational column.

Figure 1 diagrammatically illustrates the relations between the various phases of nonisothermal solution behavior.

In 1922, Mulliken²⁴ demonstrated that the static method of thermal-diffusion separation could not compete with other well-known separation methods. Benedict,¹⁵² in 1947, compared the thermogravitational method with other multistage separation processes and concluded that the method is relatively expensive and that possible application is limited to processes with very special requirements. Because thermal diffusion is such a special and expensive process, it is desirable to establish adequate design procedures in order to obtain accurate estimates of minimum costs for use in comparison of thermal diffusion with other separation processes. The development of such a design

Figure 1

Classification of Nonisothermal Solution Behavior

procedure could be greatly simplified by a theory that would quantitatively predict the effect of thermogravitational-column variables on the magnitude of separation. Various column theories, as well as design procedures based on these theories, have been proposed in the literature, although there have been insufficient data presented either to substantiate the theories or to define their limits of applicability. This is especially true of continuous-column operation, which would most certainly be utilized in any large-scale commercial application of thermal diffusion.

Objectives

In view of the fact that a continuous-flow thermogravitational process ought to have advantages over the corresponding batch process in commercial application, an extensive investigation of the performance of continuous-flow columns was initiated. The effects of a large number of column variables were to be determined in a coordinated manner. The results of these investigations could be used to evaluate the original column theory and any theoretical or empirical modifications. A design procedure based on experimental facts as well as on theory could then be developed.

II. REVIEW OF LITERATURE ON THERMAL DIFFUSION

A Brief History

Thermal diffusion was first noted by Ludwig¹ in 1856 and then investigated independently by Soret² in the period 1887-1890. Ludwig and Soret, as well as other early investigators,³⁻¹¹ conducted their experiments with aqueous solutions. The several theoretical treatments¹²⁻¹⁹ of thermal diffusion in liquids that were proposed in this early period were inadequate to explain the experimental results.

Dufour²⁰ noted the inverse of the thermal diffusion effect in gases as early as 1872. It was not until Enskog²¹ in 1911 and Chapman²² independently in 1916 predicted thermal-diffusion phenomena in gases on the basis of kinetic theory that Chapman and Dootson²³ in 1917 experimentally verified the existence of thermal diffusion in gases.

All of the early investigators used the static method. This method is not a practical means of separating materials, as was pointed out by Mulliken.²⁴ Measurements made with gases could be used to determine the nature of intermolecular forces because of the high degree of development of the gas theory. The effect in liquids remained largely a laboratory curiosity.

In 1938 Clusius and Dickel²⁵ introduced the hot-wire thermogravitational column, which increased the possibility of use of thermal diffusion as a method of separating gases. Brewer and Bramley²⁶ suggested the use of concentric cylinders rather than hot-wire apparatus. Korsching and Wirtz²⁷ and Clusius and Dickel²⁸ used columns in the form of parallel flat plates in some of the earliest applications of the thermogravitational method to liquids.

In the several years after the introduction of the thermogravitational technique a variety of theories²⁹⁻³⁵ were published to explain the functioning of the column. Although the approach to the solution varies somewhat with different authors, the results can be shown to be very similar.³⁶

So many investigators have used the thermogravitational method to investigate thermal diffusion in gases and liquids that no attempt is made to list them all here.

Published Reviews

Numerous reviews on thermal diffusion are available.³⁷⁻⁵³ The diversity of nationality represented by these publications attests to the widespread attention given to the subject. Several of these reviews merit particular discussion.

The article by R. C. Jones and W. H. Furry⁴⁷ (hereafter referred to as JF) contains a resume of the theories and experimental work published prior to 1946. Their article is especially noteworthy because of its excellent summary of column theory. Theoretical treatments of hot-wire, concentric-cylinder, and flat-plate columns are included. The transient and steady-state behavior of batch columns with and without reservoirs are discussed. The results obtained from the theoretical treatment of a batch column are extended to continuous-flow apparatus, and both single- and multi-stage processes are considered. The authors point out how the equations developed by Furry, Jones and Onsager³¹ for gas separations are equally applicable to the treatment of liquids.

In reviewing the experimental literature, JF illustrate that the effect of pressure on the amount of separation obtained in a thermogravitational column provides a convenient method for checking column theory. If the fundamental thermal diffusion phenomena are independent of pressure, and the properties (other than thermal diffusion) of a Maxwellian gas are assumed, the theory predicts the pressure dependence described by

$$\ln q = \frac{a}{p^2} \left[\frac{1}{1 + p + \frac{b}{p^4}} \right], \quad (2.1)$$

where q is the column equilibrium separation factor $\frac{(C_1/C_2)_{\text{top}}}{(C_1/C_2)_{\text{bottom}}}$

for a binary mixture of components 1 and 2, and a and b are theoretical values independent of pressure. The term p represents the magnitude of the parasitic remixing effects and must be evaluated empirically. JF found that the majority of data available to them could be satisfactorily correlated by empirically evaluating the effect of parasitic remixing.

S. R. deGroot⁴² has presented a very comprehensive study of thermal diffusion in condensed phases (liquids and solids). His review of the theories that have been applied to the fundamental problem of the Soret effect is excellent. These theories have met with very limited success, a fact recognized by deGroot. He begins the chapter dealing with the kinetic theory of the Soret effect with the following note attributed to Chapman,¹² who was instrumental in developing the theory of thermal diffusion in gases:

"The prospect of arriving at an even approximately correct theory seems rather remote. This is not only because of the additional difficulties present in every branch of the kinetic theory of liquids, as compared with the corresponding theory of gases, but because the

theory of thermal diffusion even in gases is unusually complex.

"Though it is depressing thus to dwell on the difficulties which appear to beset the theoretical treatment of the Soret phenomenon, a proper estimation of them may prevent waste of effort on unduly simple methods that are foredoomed to failure."

deGroot also develops the phenomenological theories of the static method and the batch thermogravitational method as they apply to the condensed phases. The experimental data reviewed in deGroot's thesis are in qualitative agreement with the phenomenological theories.

The monograph by Grew and Ibbs⁴¹ contains an excellent review of the theory and experiments dealing with the static effect in gases. One chapter of their book is devoted to the thermogravitational column and another to the effect in liquids. Both chapters are qualitative in nature, and the authors conclude that the column theory has not been sufficiently perfected that separations obtained in thermogravitational columns can be used to study the fundamentals of either the gas or the liquid state.

Recent Publications

The static method in gases continues to serve as a handy tool in the investigation of intermolecular forces in gases,⁵⁴⁻⁵⁸ although such measurements are sensitive to small experimental errors.⁵⁹ New attempts at theoretical interpretation of thermal diffusion in liquids⁶⁰⁻⁷³ only serve to illustrate that knowledge of the liquid state is still very limited. As it appears that thermal diffusion in liquids must be investigated experimentally, several authors⁷⁴⁻⁷⁷ have suggested new apparatus that should increase the speed of measurement of the Soret effect.

The thermogravitational method has been used more than the static method by recent investigators. The ease in measurement afforded by the large separations obtained in thermogravitational columns is offset by the fact that the theoretical treatment of the column performance is not quantitative. It is therefore not surprising that measurements made in thermogravitational columns generally agree only as to order of magnitude with values calculated from gas theory or obtained by static measurements.⁷⁸⁻⁸⁷ This is especially true if the parasitic remixing effects, which can only be evaluated empirically, are not taken into account.

Of the several methods used to test column theory, the investigation of the effect of pressure on the separation is still the most popular. Many of the experimentalists⁸⁸⁻⁹² working in the laminar region have been able to obtain reasonable correlations of their data by employing equations of the form predicted by theory. The effect of pressure on the separation is illustrated in Figure 2 with the data of Drickamer, O'Brien, Bresee and Ochert.⁹⁰ The solid curve represents the separation predicted from the theory neglecting the effects of parasitic remixing.

Even though the theory is supported by data obtained in the laminar region, it cannot account for the fact that as the pressure in the column is increased and the convective flow becomes turbulent⁹³ the separation obtained in the column is equal to or greater than that which would be predicted assuming conditions of laminar flow! Simon⁹⁴ and Donaldson and Watson⁸⁹ noted this in the course of their experiments. Several other investigators⁹⁵⁻¹⁰⁴ have made extensive studies of column behavior at elevated pressures and have tried to interpret their results in the light of theory. Becker⁹⁵ was able to approximate his experimental results by assuming that the effective plate spacing was decreased by

Fig. 2. Separation of a Gas Mixture in a Thermo-gravitational Column as a function of pressure.

the presence of turbulence. Becker also found that the initial rate of separation of the gaseous components in the column was reduced because the effective distance between the walls was diminished.

Drickamer and his coworkers⁹⁷⁻¹⁰³ have carried out an extensive investigation of thermal diffusion in gases with and without turbulence. While Becker's work was done with one column, operated at different pressures, Drickamer et al, used several columns of different dimensions in investigating pressure effects. The latter investigators assumed the thermal diffusion constant to be independent of pressure for all pressures, and were able to correlate their data by using two empirical correction factors.^{99,102} Becker⁹⁶ disagrees with the application of these correction factors to a column operated in the laminar flow region, but finds that his own results are in agreement with Drickamer's modification for turbulent flow.

Hiroto and Koboyashi¹⁰⁴ have presented some experimental results to support Drickamer's modification. Data were obtained from a column with continuous flow. The fact that they use a faulty equation* to interpret their results and then apply Drickamer's modification

*Equation (2) presented by Hirota and Koboyashi¹⁰⁴ cannot be obtained from the analysis developed by Furry, Jones and Onsager.³¹ The equation of Hiroto and Koboyashi appears similar to but is radically different from Eq.(224) of Ref. 47 and Eq.(4.42) appearing in Chapter IV of this thesis.

incorrectly* seems to invalidate their support of the method.

The effect of turbulence is not the only peculiarity in column performance that has been found experimentally. As early as 1939 Clusius and Dickel¹⁰⁵ and Brewer and Bramley¹⁰⁶ found that the performance of their thermogravitational columns was improved by the introduction of spacers placed at intervals in the annular space of the columns. JF disagreed with the conclusions of Brewer and Bramley that the increase in separation was due to swirls in the gas. Subsequent work^{89,107-110} has substantiated the fact that baffling or packing can improve column performance and that swirls do exist in the gas. Several patents^{111,112} have been issued which mention the effects of packing and baffling. The results of such investigations are very important and may well serve to increase the range of application of thermal diffusion. However, since such factors represent a further complication of an already complex problem, this subject will not be considered further in this thesis.

*Hirota and Koboyashi make the following corrections in order to obtain consistent results:

$$H_{\text{Expt.}}^{(\phi)} = \phi^{1/2}(\phi^1)^3 H_{\text{Calc.}}^{(\phi)}, \quad \left[K_c^{(\phi)} \right]_{\text{Expt.}} = \phi^{3/2}(\phi^1)^6 \left[K_c^{(\phi)} \right]_{\text{Calc.}} \text{ and} \\ \left[K_d \right]_{\text{Expt.}} = \phi^{1/2} \left[K_d \right]_{\text{Calc.}} \quad \text{The relations developed by Tung}^{102} \text{ are:}$$

$$H_{\text{Expt.}}^{(\phi)} = (\phi^1)^3 H_{\text{Calc.}}^{(\phi)}, \quad \left[K_c^{(\phi)} \right]_{\text{Expt.}} = \phi(\phi^1)^6 \left[K_c^{(\phi)} \right]_{\text{Calc.}} \text{ and } \left[K_d \right]_{\text{Expt.}} =$$

$\left[K_d \right]_{\text{Calc.}}$ This discrepancy in the use of the factor ϕ is especially serious as ϕ generally represents a much bigger correction than ϕ^1 .

The pressure dependence of the separation in thermogravitational columns is undoubtedly one of the most convenient methods of testing the column theory because only one column and one fluid system need be used. The effective gravitational field causing convective flow can also be varied and this variation used to check the theory. The predicted effect of a change in the gravitational field on the separation is given by Eq.(2.2), which is remarkably similar to Eq.(2.1).

$$\ln q = \frac{a}{g} \left[\frac{1}{1 + p + \frac{b}{g^2}} \right] \quad (2.2)^*$$

The effective gravitational field g may be varied in either of two ways. Farber and Libbey¹¹³ and Tilvis¹¹⁴ devised methods of rotating their columns and thus increasing the convective flow. Both the experimental procedure and theoretical treatment¹¹⁴ are necessarily complicated by this technique. The results of Farber and Libbey, however, are in definite agreement with the relation given by Eq(2.2).

deGroot⁴² has pointed out that the effective gravitational field can be varied by changing the angle of the plates from the vertical. Carr¹¹⁵ has made a qualitative investigation of this effect and his results are in substantial agreement with theory.

*The symbols a , b and p are used throughout the text to indicate functional dependences similar to those indicated in Eqs. (2.1) and (2.2). It might perhaps be better to use different symbols for different functional dependences, but one soon runs out of practical symbols.

This type of investigation is necessarily restricted in application to apparatus consisting of parallel flat plates.

JF concluded that for gas separations a change in pressure is just as effective as and more practical than a change in the gravitational field. A variation of the effective gravitational field may prove practical in application to liquids, however.

Data on the approach to steady state in a thermogravitational column can also be used to evaluate the theory. Numerous investigators^{88,91,92,114-117} have shown that the transient behavior determined experimentally agrees with theory. Lauder⁹¹ and Tilvis¹¹⁴ have verified the predictions, based on theory, that the rate of approach to equilibrium in a column can be increased by varying the pressure and (or) effective gravitational field during operation. deGroot, Gorter and Hoogenstraaten¹¹⁸ further showed that experimental data on transient column behavior obtained with columns of different plate spacings (distance between walls) was in accordance with theory. Prigogine, deBrouchere, and Amand¹¹⁹ used data on the transient behavior in columns to illustrate emphatically that the concentration gradient that exists between the walls of a thermogravitational column can play an important role in the separation of liquid mixtures (the "forgotten effect."¹²⁰).

The effect of flow rate on the separation brought about in a continuous-flow column is a convenient experimental method that has received very little attention. This may be because the correction applied to the treatment of batch columns to deal with continuous-flow systems is without much theoretical justification and few data have been published to support the assumptions made. Many authors have, however, reported the use of continuous or intermittent-flow columns for the separation of isotopes. It is encouraging that several authors¹²¹⁻¹²³

have been able to predict continuous-flow separations accurately from experimental results obtained by operating the same columns in a batchwise manner. Few have actually studied the effect of flow rate as a variable. Hirota and Koboyashi¹²⁴ have published the most extensive data on this subject to date. A. L. Jones¹²⁵ and A. L. Jones and Foreman¹²⁶ have published empirical conclusions based on an extensive investigation of the continuous separation of liquids. A. L. Jones and Hughes¹²⁷ have secured a patent for a continuous method of separating material by liquid thermal diffusion. Treacy¹¹⁰ has reported unusual effects of flow in a column equipped with baffles.

Other experimental work of a less coordinated nature has been reported in the literature and can be used to evaluate certain aspects of the column theory. Docherty and Ritchie¹²⁸ have made an extensive investigation of initial rates of separation. Their data support the conclusion based on the theory of Debye³⁰ that the initial rate is independent of the height of the column. Data reported on the effect of temperature difference^{94,113,117} seem to substantiate the theory. Debye and Bueche¹⁰⁹ and Hirota and Kimura¹²⁹ individually report that their data are in substantial agreement with the dependence on plate spacing and height predicted by theory.

The above paragraphs have been primarily devoted to reviewing the comparisons of column theory and experimental data reported in the literature. To make the treatment as simple as possible, the discussion has been limited to the consideration of binary mixtures. Both theoretical¹³⁰⁻¹³⁷ and experimental^{109,128,138-145} investigations of thermal diffusion in multicomponent systems have been attempted, but this author is in no position to evaluate the results.

It is interesting to note that chemical reactions have been used to enhance separations in thermogravitational columns^{146,147} and conversely, thermogravitational columns have been used to promote chemical reactions.¹⁴⁸⁻¹⁵¹

Summary

On the basis of the literature reviewed above the following conclusions are drawn:

- (1) The fundamental thermal diffusion phenomena in liquids cannot be predicted theoretically but must be determined experimentally.
- (2) The column theory is fundamentally correct and can be used to predict the results of changes in operation if the fluid in the column is in laminar flow.
- (3) If turbulence exists or if obstructions are placed in the separation space the unmodified theory cannot be applied.

III. EXPERIMENTS

Continuous Flow Thermogravitational Column

Equipment. The two thermogravitational columns used in the course of this investigation were constructed in the form of parallel plates (rather than concentric cylinders) in order to facilitate changes in the plate spacing ($2w$) and to permit operation of the column at angles other than vertical. The working space between the plates measured approximately 6 inches by 4 feet in the smaller column and 6 inches by 8 feet in the larger. Details of column construction are shown in Figure 3. The transfer plates (1) were constructed of 1/8-in. stainless steel sheet that was relatively free of scratches. The surfaces of these plates were given no special finishing treatment, as grinding caused excessive warpage of the plates. Two thermocouples (2) were located on the surface of each transfer plate. A thermocouple fixture is shown in detail in Figure 4. The column was supported on an iron frame by means of support arms (3). A pointer attached to one of the support arms indicated the angle of the column on a large metal protractor attached to the frame. Figure 5 shows the 4-foot column in the vertical position on the metal frame. Figure 6 is a view of the 4-foot column inclined at an angle of $+45^\circ$ and Figure 7 is a photograph of the 8-foot column.

The gravity-flow feed system that provided steady flows through the columns is diagramed in Figure 8. All material other than the gasket contacted by the feed was either stainless steel, glass or teflon. The feed supply was kept in a barrel (1) 14 feet above the floor. The liquid level in the barrel could be seen in a glass side

MU-7876

Fig. 3 Details of Column Construction.

- 1) Transfer Plate
- 2) Thermocouples
- 3) Support Arms
- 4) Feed Entrance
- 5) Top Product Exit
- 6) Thermocouple Wire Seals

MU-7877

Fig. 4 Detail of Transfer Plate Thermocouple.

ZN-1003

Fig. 5a Thermogravitational Column (4 ft) in
the Vertical Position.
Front View

ZN-1005

Fig. 5b Thermogravitational Column (4 ft)
in the Vertical Position.
Side View.

ZN-1004

Fig. 6 Thermogravitational Column (4 ft) at an Angle of $+45^{\circ}$.

ZN-1008

Fig. 7. Thermogravitational Column (8 ft) in the Vertical Position.

MU-7878

Fig. 8. Gravity-Flow Feed System.

1) Feed Barrel	7) Control Value
2) Out-Gasser	8) Product Coolers
3) Feed Cooler	9) Rotameters
4) Feed Sample Tap	10) Control Value
5) Therogravitational Column	11) Shunted Capillary Tubes
6) Product Sample Taps	12) Product Barrel

tube. The feed was raised to the temperature of the heating water in a one-liter glass cylinder (2) just below the feed barrel. The gases released by this heating process were periodically vented from the cylinder. The feed was cooled on passing through a small heat exchanger (3), and a sample tap (4) was located between the feed cooler and the thermogravitational column (5). The feed entered the column through holes drilled centrally in both transfer plates. The top product was removed through the hot plate and the bottom product through the cold plate. Product sample taps (6) were located as close to the working space as possible. Details of a sample tap are given in Figure 9. A 1/4-in. needle valve (Hoke No. 343) (7) was located on the bottom product line just downstream from the sample tap. Sufficient heat-exchange surface was provided in the product coolers (8) to bring the temperatures of both product streams below room temperature. Two banks of three rotameters each (9) indicated flow rates from 0.01 to 50 grams per minute. A needle valve (10) identical to the one located on the bottom product line (7) was placed downstream from the rotameters on the top product line. Two series of shunted capillary tubes (1/2 mm) (11), similar in application to an electrical resistance box, were used for flow-rate control at low flow rates (0.02-1.0 grams per minute). The needle valves gave satisfactory control at flow rates larger than 1 gram per minute. The processed material was collected in a product barrel (12) and returned to the feed barrel when needed.

The high-heat-capacity, hot-and-cold water system diagramed in Figure 10 limited the drop in water temperature through the column to less than 1.0°C, and damped temperature fluctuations to less than 0.1°C. Two 55-gallon barrels (1), treated with 4A plastic and

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Fig. 9. Detail of Sample Tap.

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Fig. 10. Heating and Cooling Water System.

1) 55-Gal. Barrels	6) Centrifugal Pumps
2) Overflow Lines	7) Orifices and Monometers
3) Diaphragm Motor Valves	8) Globe Valves
4) Temperature Recorder-
Controllers	9) Thermometers
5) Thermocouples	10) Thermogravitational Column

insulated with several sheets of asbestos paper, were mounted at the same level as the feed barrel. Overflow lines (2) were provided one foot below the tops of the barrels. Steam was mixed with the heating water through a sparge near the bottom of the hot-water barrel and tap water was similarly introduced into the cooling-water barrel. The steam and tap-water rates were regulated by Honeywell air-operated diaphragm motor valves (3), which were activated by Brown circular-chart Electronik potentiometric temperature recorder-controllers (4). (A view of the control panel is given in Fig. 11). Brown pencil-type iron-constantan thermocouples (5) served as sensing elements and were located in the pipeline 6 inches below the bottoms of the barrels. Two 1/3 hp. Ingersoll-Rand Model D motor pumps (6) provided flow rates up to 25 gallons per minute. Rubber hose connections were provided between the pumps and the column but did not eliminate all vibrations. Square-edged orifices (7) were calibrated in place and served to measure water flow rates. Standard globe valves (8) were used to regulate water flows. The hot water entered the top of the column and flowed countercurrent to the cold water. The temperatures of the water streams were measured at the inlets and outlets of the column (10) by means of standardized thermometers (9), with 0.1°C divisions, immersed to a depth of about 5 inches. The water was recirculated to the barrels. The water lines were made of 1-1/2-in. standard pipe and were lagged with Asbestocel insulation.

Procedure. In experiments with the continuous-flow thermogravitational columns, the separation was determined as a function of flow rate. The plate spacing ($2w$), column length (L_T), angle of plates from the vertical (θ), and temperature difference between the plates (ΔT) were treated as parameters. Changes in θ and ΔT could be made easily. Two separate

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Fig. 11. Control Panel.

columns were used to investigate the effect of column length. The plate spacing was varied by using gaskets of different thicknesses between the transfer plates. After a new gasket had been installed the plate spacing had to be determined accurately before the more useful experimental data could be taken. As the plate spacing appears in the theory as $(2w)^3$, $(2w)^4$, and $(2w)^7$, interpretation of the data is extremely sensitive to any error in this measurement. The method of measuring the plate spacing is discussed in detail in the next paragraph.

The column was assembled with very little tension in the gasket-compressing bolts and placed on the supporting frame. Water flow was started through the cooling and heating jackets and set at a rate large enough to give turbulence in the water jackets. The temperature recorder-controllers were adjusted to maintain the desired ΔT and temperature level, $\bar{T}$. After the system had attained thermal equilibrium the gasket-compressing nuts were tightened equally with a torque wrench. A period of several days was allowed for the gasket to compress, and dry air was blown through the column to remove any liquid from the working space as well as from the feed and product headers. When the drying process was completed the working space was filled with distilled water from a weighed bottle. After disturbances in the water-temperature control were eliminated, the weight of water in the working space and headers was determined by again weighing the distilled-water bottle. The density of the water was obtained from a standard source¹⁵³ and the volume of the working space calculated by subtracting the volume of the headers from the total volume. The inner dimensions of the gasket had been measured during column assembly and thus an average column-plate spacing was obtained. This measured plate spacing was larger than the gasket

thickness owing to a slight outward bowing of both transfer plates.

It was necessary to take the following precautions in order to obtain reproducibility in the measurement of the plate spacing:

(1) A gasket material had to be used that would not change under the alternate wet and dry conditions required to determine the plate spacing. This effect accounts for the uncertainty in value of the plate spacings reported for experiments 34-93 and 176-184. Vegetable fiber (Velumoid) gaskets were used during experiments 34-93, and they apparently shrank when dried. The benzene used in experiments 176-184 caused the binder in the compressed asbestos gasket (Garlock No. 7021) to swell and then shrink when dried. The compressed asbestos gaskets were satisfactory for use with ethyl alcohol-water mixtures and gaskets formed from annealed copper wire with a soft soldered joint were employed for the remainder of the n-heptane-benzene experiments.

(2) Both the compressed asbestos and the copper gaskets exhibited plastic flow over a long period of time. The most rapid compression occurred during the first week and only negligible changes occurred after this period. Plate-spacing determinations were made before and after a series of runs and the average was reported.

(3) The water-flow rates were maintained as constant as possible in order to minimize changes of pressure across the transfer plates.

(4) The distilled water bottle used to fill the working space was placed at the same height in successive plate-spacing determinations. In order to duplicate conditions existing during actual column operation, the distilled water bottle was placed at a height calculated to give a head equivalent to the mixture in the feed barrel. The liquid level in the feed barrel was kept within several inches of the reference level during the course of the experiments.

After several plate-spacing determinations had been made, a series of experiments was conducted to determine the separation as a function of the flow rate. The column and all lines were purged with the mixture to be investigated. The rotameters were used to set approximate flow rates through the working space, and samples from both product streams were analyzed periodically. Sufficient time was allowed between sets of samples to purge the headers and eliminate any disturbances introduced by the sampling procedure. The separation was plotted as a function of the time to determine the steady-state separation when the relaxation time was large compared to the time between samples. Several analyses were made with the column operating under steady-state conditions and the average of these analyses was reported. During the time interval between samples taken under steady-state conditions, rotameter readings were taken, and the actual product-flow rates were measured by collecting and weighing samples. Other readings taken at this time included the temperatures of the water entering and leaving the column, manometer readings (water flow rate), controller readings, index of refraction of the feed, feed-barrel level, and the potentials of the four thermocouples located at the surfaces of the transfer plates. A record of these four potentials was made by a Brown electronic multipoint recorder.

Results. The data taken to determine the separation as a function of the flow rate are given in Table I for the ethyl alcohol-water system and in Table II for the n-heptane-benzene mixtures. Table III lists the values of the parameters 2ω , L_T , ΔT_{ave} and Θ as well as average values of the feed composition and column width. All experiments with the ethyl alcohol-water system were made at a mean temperature level of 120°F, and those made with the n-heptane-benzene mixtures were at

a mean temperature of 108°F. These mean temperatures were taken as the average of the temperatures indicated on the temperature recorder-controllers. Table IV lists the data used to determine the thermal conductivity of 40% ethyl alcohol-water mixtures and Table V contains data on the approach to steady state in the column. In Chapter V the data are compared with theory and with the results found by other investigators. Tables of data appear in the appendix.

Glass-Diaphragm Cell

Equipment. The glass-diaphragm cell used to obtain a measurement of the thermal diffusion constant by the static method is shown in Figure 12. The cell is similar to that described by Huse, Trevoy and Drickamer.⁷⁵ The temperature-measuring technique employed was different from that reported by these authors. Copper-constantan thermocouple leads were sealed with Epon resin into small glass tubes which extended into the cell through the ground glass joints. The thermocouples were placed as close to the surface of the diaphragm as possible. The cell was suspended in a bath similar to that used by Huse et al. A photograph of the glass-diaphragm cell and constant temperature baths is reproduced in Fig. 13.

Procedure. The constant-temperature baths were brought to the desired temperature and the diaphragm cell was immersed between them. The apparatus was operated for several days, and a record of the thermocouple potentials was kept on the Brown electronic multipoint recorder. Owing to mechanical difficulty the cells were operated without the benefit of mechanical stirring. After a period of several days samples were taken and analyzed.

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Fig. 12. Details of Glass-Diaphragm Cell.

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Fig. 13. Glass-Diaphragm Cell and Constant-Temperature Baths.

Results. Some of the more reproducible results obtained in the glass-diaphragm cell are given in Tables VI and VII. In Chapter V these results are compared with data of other investigators and with the data obtained in the thermogravitational column.

Materials Used and Methods of Analysis

Ethyl alcohol-water system. The ethyl alcohol-water mixtures used in the experiments were prepared from azeotropic ethyl alcohol (95 wt %) and distilled water. Density and viscosity data for this system were taken from the International Critical Tables.¹⁵⁴ The ICT density data were extended to elevated temperatures by using the data of Rakshit.¹⁵⁵ Values of the expansion coefficient, β_T , were obtained graphically from plots of the density data. Values of the diffusion coefficient were obtained from data reported by Smith and Starrow,¹⁵⁶ Lemonde,¹⁵⁷ and Franke.¹⁵⁸ The data of these three observers were generally in good agreement. Values of the physical properties used in the calculations are given in Table VIII.

The ethyl alcohol-water mixtures were analyzed with the aid of a Bausch and Lomb immersion refractometer. Analyses were made at 15.0°C and the refractometer was calibrated with ethyl alcohol solutions at this temperature. As the separations obtained in the glass-diaphragm cell were very small, these samples were analyzed in a Zeiss portable interferometer with a 40-mm cell. The optical instruments used for analysis of solutions are shown in Fig. 14.

n-Heptane-Benzene. The n-heptane-benzene mixture was prepared from Baker reagent grade (ACS specification) benzene and Phillips pure grade (99+ mol %) n-heptane. The density and expansion coefficient for the

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Fig. 14. Optical Instruments Used for Analysis of Solutions.

mixture were calculated from values for the pure materials obtained from the International Critical Tables based on the assumption of ideal solution behavior. The viscosity and diffusion data for this system have been reported by Trevoy and Drickamer.^{159,160} Values of the physical properties used in the calculations are listed in Table VIII.

The analyses of the n-heptane-benzene mixtures were made with an Abbey refractometer. Measurements were made at 15.0°C and the refractometer was calibrated with n-heptane-benzene mixtures at this temperature. Hydrochloric acid. The aqueous hydrochloric acid solutions that were used for testing the glass-diaphragm cells were prepared from Baker and Adamson reagent grade (ACS specification) hydrochloric acid. The hydrochloric acid concentration was measured by titration with 0.1 N NaOH.

IV. COLUMN THEORY

Mathematical Formulation of the Problem

The temperature gradient applied between the plates of a thermogravitational column has two effects: (1) a flux of one component of the solution relative to the other (or others) is brought about by thermal diffusion, (2) convective currents are produced parallel to the plates due to density differences. The combined result of these two effects is to produce a concentration difference between the two ends of the column which is generally much greater than that obtainable by the static method.

In an ideal column, a temperature gradient exists only in the direction normal to the plates. The flux of component 1 due to thermal diffusion, J_{x-TD} , is given by (See Ref. 47)

$$J_{x-TD} = + \frac{\alpha D}{T} C_1 C_2 \frac{dT}{dx}, \quad (4.1)$$

where

α is the thermal diffusion "constant",

D , the ordinary diffusion coefficient,

T , the absolute temperature,

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

x , the axis normal to the plates.

The choice of sign is arbitrary and is taken as positive in order to be consistent with the notation of Jones and Furry.⁴⁷ Equation (4.1) was developed to represent the behavior of isotopic gas mixtures. In this case α is essentially independent of temperature, pressure and composition. Although nonisotopic liquid solutions bear little or no

resemblance to isotopic mixtures of gases, Eq. (4.1) can be used to define the thermal diffusion "constant", α , for liquids.

The concentration gradient produced by the combined effects of thermal diffusion and convection acts to oppose thermal diffusion and limits the separation. Two equations, (4.2) and (4.3) can describe this flux completely, as any variation in the direction normal to the x-y plane can generally be neglected.

$$J_{x-OD} = -D \frac{\partial c_1}{\partial x}, \quad (4.2)$$

$$J_{y-OD} = -D \frac{\partial c_1}{\partial y} \quad (4.3)$$

where J_{x-OD} is the flux of component 1 in the x direction due to ordinary diffusion,

J_{y-OD} , the flux of component 1 in the y direction due to ordinary diffusion, and

y, the axis parallel to the transfer plates in the direction of normal convective flow.

Figure 15 illustrates the flows existing in a thermogravitational column and the coordinate system that is used in the mathematical description.

Equations (4.1), (4.2) and (4.3) can be combined with a function that represents the convective velocity to obtain a partial differential equation which will describe the concentration as a function of the time and the two coordinates x and y. The resulting equation is greatly simplified if the coefficients D and α as well as the temperature level T are treated as constants and the velocity distribution is considered to be a function of x only. Equation (4.4) is the partial differential equation obtained from Eqs. (4.1), (4.2) and (4.3) by applying the

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Fig. 15. Schematic Diagram of a Continuous-flow Thermogravitational Column.

continuity conditions and the assumptions listed above.

$$\frac{\partial c_1}{\partial t} = D \left[\frac{\partial^2 c_1}{\partial x^2} + \frac{\partial^2 c_1}{\partial y^2} \right] - \frac{\alpha D}{T} \frac{dT}{dx} \frac{\partial(c_1 c_2)}{\partial x} - v(x) \frac{\partial c_1}{\partial y} \quad (4.4)$$

Only the steady-state solution of this equation ($\partial c_1 / \partial t = 0$) is considered in this thesis.

The net flow due to thermal diffusion and ordinary diffusion must be zero at both walls. Therefore a solution to Eq. (4.4) must be found subject to the boundary conditions,

$$-D \frac{\partial c_1}{\partial x} + \frac{\alpha D}{T} c_1 c_2 \frac{dT}{dx} = 0 \quad \text{at } x = \pm \omega. \quad (4.5)$$

Aside from the conditions expressed in Eq. (4.5), a solution to Eq. (4.4) must satisfy material balances made around any section of the column. Eq. (4.6) represents a material balance made around the end of the enriching section.

$$\sigma_e c_e = + B_e \int_{-\omega}^{+\omega} \rho c_1 v(x) dx - B_e \int_{-\omega}^{+\omega} \rho D \frac{\partial c_1}{\partial y} dx \quad (4.6)$$

where σ_e is the mass flow rate out enriching section,

c_e , the fraction of component 1 in the product stream exiting from the enriching section,

B_e , the column width in the enriching section, and

ρ , the density.

Equation (4.7) expresses a similar condition existing in the stripping section:

$$- \sigma_s c_s = + B_s \int_{-\omega}^{+\omega} \rho c_1 v(x) dx - B_s \int_{-\omega}^{+\omega} \rho D \frac{\partial c_1}{\partial y} dx \quad (4.7)$$

Equations (4.4)-(4.7) provide an accurate mathematical description of the processes occurring within the column. Since Eq.(4.4) is a partial differential equation of second order in x and y with a coefficient $v(x)$, that is in general a complicated function, a rigorous mathematical solution to the problem would be tedious to find and of doubtful value unless expressed in a closed form. Furry, Jones and Onsager³¹ (hereafter referred to as FJO) have shown how an ordinary differential equation of first order in y with constant coefficients can be obtained from Eqs. (4.4)-(4.7). Their development is based on the conditions existing in a batch-operated column. Their method of reducing the partial differential equation to an ordinary differential equation (called the transport equation) is acceptable because the total concentration change in the x direction is small compared to the total concentration change in the y direction. The treatment of a continuous-flow column by applying the transport equation obtained in considering conditions in a batch column is subject to some restrictions. In the treatment presented here the transport equation is derived by considering conditions that exist in a continuous-flow column. This is accomplished by making a slight modification in the method proposed by FJO. The mathematical treatment is given in detail in the following section. The results obtained by use of this modification are comparable to those given by FJO. Assumptions and results are tabulated at the end of this chapter.

Derivation of the Transport Equation for a Continuous-Flow Column

Equation (4.4) can be simplified by neglecting the second-order term in y . By inspection it appears reasonable to neglect the effect

of vertical diffusion, $D \frac{\partial^2 c_1}{\partial y^2}$, in relation to the mass flow due to convection, $v(x) \frac{\partial c_1}{\partial y}$. If one is further willing to restrict the solution to conditions of laminar flow, the temperature gradient dT/dx can be replaced by $\Delta T/2\omega$ where ΔT is the temperature difference and 2ω the distance between the plates. With these assumptions and the condition of steady state, Eq. (4.4) reduces to

$$D \frac{\partial^2 c_1}{\partial x^2} - \frac{\alpha D}{T} \frac{\Delta T}{2\omega} \frac{\partial(c_1 c_2)}{\partial x} - v(x) \frac{\partial c_1}{\partial y} = 0. \quad (4.8)$$

Similar assumptions modify the boundary conditions, Eq. (4.5) to

$$D \frac{\partial c_1}{\partial x} - \frac{\alpha D}{T} \frac{\Delta T}{2\omega} c_1 c_2 = 0 \quad \text{at } x = \pm\omega. \quad (4.9)$$

An integration of Eq. (4.8) with respect to the variable x yields

$$D \frac{\partial c_1}{\partial x} - \frac{\alpha D}{T} \frac{\Delta T}{2\omega} c_1 c_2 - \int_{-\omega}^x v(x) \frac{\partial c_1}{\partial y} dx = f(y). \quad (4.10)$$

From the conditions existing at $x = -\omega$, it follows that $f(y) = 0$.

Now if a function $G(x, y)$ is defined by

$$\frac{\partial c_1}{\partial y} G(x, y) = -D \frac{\partial c_1}{\partial x} + \frac{\alpha D}{T} \frac{\Delta T}{2\omega} c_1 c_2 \quad (4.11)$$

and if $\partial c_1 / \partial y$ is assumed to be independent of x , then Eq. (4.10) reduces to

$$-G(x, y) = \int_{-\omega}^x v(x) dx = 0. \quad (4.12)$$

It is now obvious that $G(x, y)$ does not depend on y . Further, it follows from the definition of $G(x)$, Eq. (4.11), and the boundary conditions, Eq. (4.9), that $G(x) = 0$ at $x = \pm\omega$. From (4.12) this can only be true if

$$\int_{-\omega}^{+\omega} v(x) dx = 0$$

that is, only for batch column coporation. This method can be modified to treat the case of a continuous-flow column by assuming a linear dependence of $\frac{\partial c_1}{\partial y}$ on x as a second approximation:

$$\frac{\partial c}{\partial y} = \psi(y)(1 + \gamma x). \quad (4.13)$$

A function $G^*(x, y)$, analogous to $G(x, y)$, is defined by

$$\psi(y)G^*(x, y) = -D \frac{\partial c_1}{\partial x} + \frac{\alpha D}{T} \frac{\Delta T}{2\omega} c_1 c_2 \quad (4.14)$$

The combination of Eqs. (4.8), (4.13) and (4.14) produces

$$-G^*(x, y) - \int_{-\omega}^x v(x)(1 + \gamma x) dx = 0 \quad (4.15)$$

The left hand side of Eq. (4.15) was found to be equal to zero by considering the conditions existing at $x = -\omega$. Inspection of Eq. (4.15) reveals that $G^*(x, y)$ is a function of x only. The boundary condition at $x = +\omega$ serves to define γ in terms of the velocity distribution as indicated by

$$\gamma = - \frac{\int_{-\omega}^{+\omega} v(x) dx}{\int_{-\omega}^{+\omega} x v(x) dx} \quad (4.16)$$

From the velocity-distribution function developed later [Eq. (4.36)] it can be shown that γ is a measure of the ratio of the net flow through the column to the convective flow.

Since $v(x)$ is different in the enriching and stripping sections, separate solutions must be obtained for $y > 0$ and $y < 0$. The complete

solution is obtained by a suitable combination of the two solutions. For $y > 0$ (the enriching section), Eq. (4.6) gives the relation that must be satisfied. If mean values of the density ρ and the diffusion coefficient D are used, Eq. (4.6) simplifies to

$$\sigma_e C_e = + B_e \rho \int_{-w}^{+w} C_1 v(x) dx - B_e \rho D \int_{-w}^{+w} \frac{\partial C_1}{\partial y} dx. \quad (4.17)$$

Equation (4.17) can be transformed to an ordinary differential equation by some mathematical "sleight of hand". The velocity distribution as related through Eq. (4.15) to $G^*(x)$ is given by

$$v(x) = - \frac{1}{(1 + \gamma x)} \frac{d G^*(x)}{dx}. \quad (4.18)$$

Equation (4.19) results from substituting Eq. (4.18) into Eq. (4.17).

$$\sigma_e C_e = + B_e \int_{-w}^{+w} \frac{C_1}{(1 + \gamma x)} d G^*(x) - B_e \rho D \int_{-w}^{+w} \frac{\partial C_1}{\partial y} dx \quad (4.19)$$

If the first term on the right-hand side of Eq. (4.19) is integrated by parts, Eq. (4.20) results from the fact that $G^*(x) = 0$ at $x = \pm w$:

$$\sigma_e C_e = - B_e \gamma \int_{-w}^{+w} \frac{G^*(x)}{(1 + \gamma x)} \left\{ \frac{\partial C_1}{\partial x} - \frac{C_1 \gamma}{(1 + \gamma x)} \right\} dx - B_e \rho D \int_{-w}^{+w} \frac{\partial C_1}{\partial y} dx \quad (4.20)$$

The term $\frac{\partial C_1}{\partial x}$ can be obtained from the definition of $G^*(x)$, Eq. (4.14), and when substituted into Eq. (4.20) yields

$$\sigma_e C_e = \rho B_e \int_{-\omega}^{+\omega} \left\{ \frac{\alpha}{T} \frac{\Delta T}{2\omega} C_1 C_2 - \psi(y) \frac{G^*(x,y)}{D} - \frac{C_1 \gamma}{(1+\gamma x)} \right\} dx - B_e \gamma D \int_{-\omega}^{+\omega} \frac{\partial C_1}{\partial y} dx \quad (4.21)$$

An ordinary differential equation describing the y dependence of the concentration can be obtained from Eq. (4.21) by using mean values of the concentrations, $\bar{C}_1$ and $\bar{C}_2$. In using these mean values it is assumed that the small but important variation of the concentration in the x direction has been described by the terms retained under the integral sign. Equation (4.22) results from this substitution and application of Eq. (4.13).

$$\begin{aligned} \sigma_e C_e = & \frac{\alpha}{T} \frac{\Delta T}{2\omega} \rho B \bar{C}_1 \bar{C}_2 \int_{-\omega}^{+\omega} \frac{G^*(x)}{(1+\gamma x)} dx - \frac{\rho B}{D} \frac{1}{(1+\gamma x)} \frac{d\bar{C}_1}{dy} \int_{-\omega}^{+\omega} \frac{[G^*(x)]^2}{(1+\gamma x)} dx \\ & - \bar{C}_1 \gamma \rho B \int_{-\omega}^{+\omega} \frac{G^*(x)}{(1+\gamma x)^2} dx - \frac{2\omega B \rho D}{(1+\gamma x)} \frac{d\bar{C}_1}{dy} \end{aligned} \quad (4.22)$$

Such a development yields mean concentration values and thus the term $(1+\gamma x)^{-1}$ outside the integral sign can be replaced by 1.0, i.e., $\bar{C}_1 = C_1$ at $x = 0$. Then Eq. (4.22) can be written in the form

$$\sigma_e C_e = H \bar{C}_1 \bar{C}_2 - \left\{ K_c + K_d \right\} \frac{d\bar{C}_1}{dy} - E \bar{C}_1. \quad (4.23)$$

Equations (4.22), (4.23) and (4.15) define the parameters H, $K = K_c + K_d$, and E in terms of the velocity distribution, $v(x)$:

$$H = \frac{\alpha}{T} \frac{\Delta T}{2\omega} \rho B \int_{-\omega}^{+\omega} \frac{G^*(x)}{(1+\gamma x)} dx, \quad (4.24)$$

$$K_c = \frac{\rho B}{D} \int_{-\omega}^{+\omega} \frac{[G^*(x)]^2}{(1+\gamma x)} dx, \quad (4.25)$$

$$K_d = 2\omega D B \rho, \text{ and} \quad (4.26)$$

$$E = \gamma \rho B \int_{-\omega}^{+\omega} \frac{G^*(x)}{(1+\gamma x)^2} dx. \quad (4.27)$$

A convenient form of the velocity distribution $v(x)$ can be obtained from the Navier-Stokes relations describing laminar flow. A simplified form of these relations is

$$\frac{dP}{dy} + g \cos \theta \rho = \eta \frac{d^2 v(x)}{dx^2} \quad (4.28)$$

where

P is the pressure,

g , the acceleration due to gravity,

θ , the angle of plates from the vertical (an addition to the treatment suggested by deGroot⁴² and

η , the coefficient of viscosity.

By differentiating Eq. (4.28) with respect to x and treating the viscosity coefficient as a constant, an equation of this form is found:

$$g \cos \theta \frac{\partial \rho}{\partial x} = \eta \frac{d^3 v(x)}{dx^3} \quad (4.29)$$

If the term $\frac{\partial \rho}{\partial x}$ can be replaced by the constant term, $-\beta^*$, successive integrations of Eq. (4.29) yield

$$v(x) = -g \frac{\cos \theta \beta^* x^3}{6\eta} + \frac{I_1}{2} x^2 + I_2 x + I_3. \quad (4.30)$$

The I 's represent constants of integration. At the walls the velocity must be zero, and when these conditions are applied Eq. (4.30) reduces

to

$$v(x) = \frac{-g \cos \theta \beta^*}{6 \eta} (x^3 - \omega^2 x) + \frac{I_1}{2} (x^2 - \omega^2). \quad (4.31)$$

Now for the enriching section,

$$B_e \rho \int_{-\omega}^{+\omega} v(x) dx = \sigma_e. \quad (4.32)$$

and when this condition is applied to Eq. (4.31) the following form of the velocity distribution is obtained:

$$v(x) = \frac{g \cos \theta \beta^*}{6 \eta} (\omega^2 x - x^3) + \frac{3 \sigma_e}{4 B_e \rho \omega^3} (\omega^2 - x^2). \quad (4.33)$$

Thus the velocity distribution is composed of two independent terms, one describing the convective velocity and the other describing the velocity due to the net flow through the column.

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

$$\frac{\partial \rho}{\partial x} = \frac{\partial \rho}{\partial T} \frac{dT}{dx} + \frac{\partial \rho}{\partial C_1} \frac{\partial C_1}{\partial x} \quad (4.34)$$

In many cases the second term on the right can be neglected. This is not always a good assumption, as is discussed later in this chapter. In the development that follows the density is assumed to be a function of the temperature only. Under these conditions

$$\beta^* = \beta_T \frac{\Delta T}{2\omega} \quad (4.35)$$

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

The velocity distribution is thus described by

$$v(x) = \frac{\beta_T g \cos \theta \Delta T}{12 \omega \eta} (\omega^2 x - x^3) + \frac{3}{4} \frac{\sigma_e}{B_e \rho \omega^3} (\omega^2 - x^2) \quad (4.36)$$

When Eq. (4.36) is used to evaluate Eq. (4.16) and thus Eqs. (4.24) = (4.27), the following relations are obtained:

$$H = H^{(0)} h(\omega \gamma), \quad (4.37)$$

$$H^{(0)} = \frac{\alpha \beta_T \rho g \cos \Theta (2\omega)^3 B_e (\Delta T)^2}{6! \eta \bar{T}}, \quad (4.37a)$$

$$h(\omega \gamma) = 1 - 18 \sum_{\lambda=0}^{\infty} \frac{(\omega \gamma)^{2\lambda}}{(2\lambda-1)(2\lambda+1)(2\lambda+3)(2\lambda+5)} \quad (4.37b)$$

$$K_c = K_c^{(0)} k(\omega \gamma). \quad (4.38)$$

$$K_c^{(0)} = \frac{\beta_T^2 \rho g^2 \cos^2 \Theta (2\omega)^7 B_e (\Delta T)^2}{9! D \eta^2} \quad (4.38a)$$

$$k(\omega \gamma) = 1 - 0.39636(\omega \gamma)^2 + 0.09844 (\omega \gamma)^4 \sum_{\lambda=0}^{\infty} (\omega \gamma)^{2\lambda} \sum_{n=0}^6 \frac{\binom{6}{n} (-1)^n}{2n + 2\lambda + 1} \quad (4.38b)$$

$$K_d = 2\omega D B_e \rho, \quad (4.39)$$

$$E = -\sigma_e, \text{ and} \quad (4.40)$$

$$\gamma = \frac{-6! \eta \sigma_e}{(2\omega)^4 \beta_T \rho g \cos \Theta B_e \Delta T} \quad (4.41)$$

The infinite series in Eqs. (4.37b) and (4.38b) converge in the interval $|\omega \gamma| \leq 1$.

If Eq. (4.40) is substituted into Eq. (4.23), the final form of the transport equation is given by

$$\sigma_e (C_e - \bar{C}_1) = H \bar{C}_1 \bar{C}_2 - K \frac{d\bar{C}_1}{dy}. \quad (4.42)$$

Solutions of the Transport Equation

Equation (4.42) has exactly the same form as the equation used by Jones and Furry⁴⁷ to describe a thermogravitational column that is operated in a continuous manner. The only differences between their transport equation and Eq. (4.42) are the corrections $h(\omega \gamma)$ and $K(\omega \gamma)$, and an empirical term, K_p , which JF added to K_c and K_d to account for the effects of parasitic remixing. Jones and Furry have obtained a general solution to this transport equation as well as several useful approximate solutions. Their results can be applied directly to Eq. (4.42).

The liquid mixtures investigated in connection with this thesis existed in the concentration range $0.7 > C_1 > 0.3$. Under these conditions the solution of Eq. (4.42) is simplified by making the approximation $C_1 C_2 \approx 1/4$ (which is correct to within 16% over the range of C_1). For this case the solution of Eq. (4.42) is given by

$$C_e - \bar{C}_i = \frac{H}{4\sigma_e} \left(1 - \exp. \frac{-\sigma_e L_e}{K} \right) \quad (4.43)$$

where $\bar{C}_i$ is the mean concentration at the feed point and L_e is the length of the enriching section.

The development described above applies only to the enriching section. The treatment of the stripping section is entirely analogous. The following equations are the end result of a development for the stripping section:

$$\bar{C}_i - C_s = \frac{H_s}{4\sigma_s} \left(1 - \exp. \frac{-\sigma_s L_s}{K_s} \right), \quad (4.44)$$

$$\gamma_s = \frac{+ 45 \eta \sigma_s}{\omega^4 \beta_T \rho g \cos \theta B \Delta T} \quad (4.45)$$

The flow rates σ_e and σ_s are always positive numbers. The difference in sign between Eqs. (4.41) and (4.45) is of little significance, as γ appears only to even powers in the functions $h(\omega \gamma)$ and $k(\omega \gamma)$. The equations for H_s and K_s are obtained from Eqs. (4.37) and (4.38) by substituting dimensions and properties relating to the stripping section. The total column separation can be obtained by adding Eqs. (4.44) and (4.45):

$$\Delta \equiv C_e - C_s = \frac{H}{4\sigma_e} (1 - \exp. \frac{-\sigma_e L_e}{K}) + \frac{H_s}{4\sigma_s} (1 - \exp. \frac{-\sigma_s L_s}{K_s}). \quad (4.46)$$

This equation is further simplified to

$$\Delta = \frac{H}{2\sigma} (1 - \exp. \frac{-\sigma L_T}{2K}) \quad (4.47)$$

if $\sigma_e = \sigma_s \equiv \sigma$, $L_e = L_s = L_T/2$ and $B_e = B_s$.

L_T is the total column length.

In the limiting case, $\sigma = 0$, (batch) Eq. (4.47) becomes

$$\Delta_0 = \frac{H^{(0)} L_T}{4K^{(0)}} \quad (4.48)$$

Equation (4.48) is identical in the limit $\Delta_0 \rightarrow 0$ and for $C_1 C_2 = 1/4$, to Eq. (4.49), developed by FJO for the batch case.

$$q = e^{H^{(0)} L_T / K^{(0)}} \quad (4.49)$$

where q is the equilibrium separation factor,

$$\frac{C_e(1 - C_s)}{C_s(1 - C_e)}.$$

Other steady-state solutions of Eq. (4.42) which appear in the review article of Jones and Furry⁴⁷ are listed in the appendix of this thesis. These authors also treat the transient behavior of the column and the problem of multistage apparatus.

The "Forgotten Effect"

In the preceding development the effect of the separation on the density gradient was ignored, i.e., "forgotten". deGroot, Hoogenstraaten and Gorter^{118,120} and others,¹¹⁹ have been able to show both theoretically and experimentally that this second effect is of major importance in some cases. By using suitable approximations deGroot determined a mean value of $\frac{\partial c}{\partial x}$ to use in Eq. (4.34) for large plate spacings.

$$\frac{\partial c}{\partial x} = + 0.3 (\alpha/T)(\Delta T/2\omega). \quad (4.51)$$

This result may be used to improve the interpretation of column data.

It can be applied directly to Eqs. (4.47) and (4.38) by replacing $-\beta_T$ with $-\beta_T + 0.3(\alpha/T)(\partial \rho / \partial c_1)$ in Eq. (4.37) and substituting $\left[-\beta_T + 0.3 (\alpha/T)(\partial \rho / \partial c_1) \right]^2$ for β_T^2 in Eq. (4.38).

Summary

The assumptions that were made in the development of Eqs. (4.46), (4.47) and (4.48) are listed below. The number appearing to the right of each assumption refers to the equation that results most directly from that particular assumption. The equations used to compare theory and experiment are summarized following this list.

Assumptions.

- (1) $T = T(x)$ only (4.1)
- (2) Any variance in the direction normal to the x-y plane may be neglected. (4.2)(4.3)
- (3) The temperature and concentration dependence of D , α , β , can be ignored. (4.4)(4.29)(4.30)
- (4) The temperature level T can be replaced by its mean value, $\bar{T}$. (4.4)
- (5) $v = v(x)$ only. (4.4)
- (6) $\partial C_1 / \partial t = 0$ (steady state). (4.6)(4.7)(4.8)
- (7) The column width is constant in any one section.
- (8) The vertical diffusion term, $D \frac{\partial^2 C}{\partial y^2}$, is small compared to the convective velocity term, $v(x) \frac{\partial C_1}{\partial y}$. (4.8)
- (9) Laminar flow conditions exist between the plates. (4.8)(4.28)
- (10) $\partial C / \partial y$ does not depend on x (basis of development by FJO). (4.12)
- (11) $\partial C / \partial y = \psi(y)(1+\gamma x)$ (basis of this development). (4.15)
- (12) A mean value of ρ can be used to convert volumetric flows to mass flows. (Similarly average molecular weight values can be applied to mixtures to convert mol units to mass units.) (4.17)
- (13) Mean values of C_1 and C_2 can be used after their x dependence

has been described by H, K and E. (4.22)

(14) A solution for the y dependence at $x = 0$ is
satisfactory. (4.23)

(15) $\rho = f(T)$ only (4.36)

(16) $C_1 C_2 \approx 1/4$ (4.43)(4.44)

(17) $\sigma_e = \sigma_s = \sigma$ (4.47)

(18) $L_e = L_s = L_T/2$ (4.47)

(19) $B_e = B_s$ (4.47)

Equations Used to Compare Theory and Experiment

(All equations based on the assumption $C_1 C_2 \approx 1/4$)*

General Solution

$$\Delta = \frac{H}{4\sigma_e} \left(1 - \exp. \frac{-\sigma_e L_e}{K} \right) + \frac{H_s}{4\sigma_s} \left(1 - \exp. \frac{-\sigma_s L_s}{K_s} \right) \quad (4.46)$$

$$\underline{\sigma_e = \sigma_s = \sigma, L_e = L_s = L_T/2, B_e = B_s}$$

$$\Delta = \frac{H}{2\sigma} \left(1 - \exp. \frac{-\sigma L_T}{2K} \right) \quad (4.47)$$

$$\underline{\sigma = 0}$$

$$\Delta_o = \frac{H^{(o)} L_T}{4K^{(o)}} \quad (4.48)$$

*See appendix for other solutions.

Index of Equations Defining the Various Parameters

$$H_s = H^{(o)} h(\omega \gamma) \quad (4.37)$$

$$K = K_e + K_d + K_p \quad (4.52)$$

$$K_e = K_e^{(o)} k(\omega \gamma) \quad (4.38)$$

$$K_d = 2\omega DB\rho \quad (4.39)$$

$$\gamma = \frac{6\eta\sigma_e}{(2\omega)^4 \beta_T \rho g \cos \Theta \beta \Delta T} \quad (4.41)$$

(Values of H_s , K_s and γ_s are obtained by substituting flow rate, dimensions and properties relating to the stripping section in the above equations.)

V. INTERPRETATION OF EXPERIMENTAL RESULTS

In the preceding chapter the theoretical treatment of batch thermogravitational columns originally proposed by Furry, Jones and Onsager³¹ was extended to include continuous-flow thermogravitational columns. Data obtained using the equipment described in Chapter III provide a means of testing not only the modification of the theory proposed in Chapter IV but also the fundamental theory itself.

The equations developed in Chapter IV were shown to be similar to the more simple equations suggested by Jones and Furry.⁴⁷ Several investigators¹²¹⁻¹²³ have been successful in applying the equations of JF to predict the performance of continuous flow columns. Therefore it seemed desirable to attempt to define the limits of application of the less complicated equations of JF in addition to testing the modification proposed in Chapter IV. In the discussion that follows the term corrected equation refers to the developments of Chapter IV and the notation uncorrected equation indicates the use of the approximations of JF, i.e., equations excluding the terms $h(\omega \gamma)$ and $k(\omega \gamma)$.

The mixtures investigated in the continuous-flow thermogravitational columns were all concentrated (as opposed to dilute) binary liquid solutions. This type of mixture was chosen for several reasons: (1) There are relatively few data on such systems reported in the literature. (2) The maximum separation of any binary mixture should occur when the feed is composed of equal amounts of each component. (3) For the conditions $0.7 > C_1 > 0.3$, i.e., for $C_1 C_2 \approx 1/4$, the solution to the transport equation is of a simple form. The equations obtained for

the case $C_1 C_2 \approx 1/4$ have been summarized on Page 61. As Eq. (4.47) is considerably less complicated than Eq. (4.46), experimental conditions were generally adjusted to satisfy the assumptions under which Eq. (4.47) was obtained, i.e., $\sigma_e = \sigma_s \equiv \sigma$, $L_e = L_s = L_T/2$, and $B_e = B_s$:

$$\Delta = \frac{H}{2\sigma} \left(1 - \exp. \frac{-\sigma L_T}{2K} \right) \quad (4.47)$$

Qualitative Aspects of the Theory

The eighteen assumptions that were utilized in the development of Eq. (4.47) have been listed on Page 60. Many of these assumptions are reasonable when laminar flow conditions exist in the column and neither the temperature difference nor the concentration change is very large. Experimental conditions were chosen to satisfy these and other restrictions as much as possible. The validity of assumptions 8, 11, 12 and 13 on Page 60 can only be evaluated by comparing the theory with the results of experiments. In no case would a 1:1 correspondence be expected unless the effects of parasitic remixing, accounted for by the term K_p , are properly evaluated. In view of these inherent difficulties the data were first used to test the qualitative aspects of the theory. The quantitative correspondence of theory and experiment are considered later in this chapter.

Flow-Rate Dependence

Two of the first questions to be resolved were whether the flow-rate dependence predicted by Eq. (4.47) corresponded to the experimental results, and over what range the uncorrected equations of JF were applicable. Since the flow-rate dependence is here considered to be of prime importance, values of $H^{(0)}$ and $K^{(0)}$ in Eq. (4.47) were

determined empirically in such a manner that values calculated from Eq. (4.47) agreed with experimental data in the region $\sigma \rightarrow 0$. The following procedure was used to obtain empirical values of $H^{(o)}$ and $K^{(o)}$: If Eq. (4.47) is expanded in series, Eq. (5.1) results:

$$\Delta = \frac{HL}{4K} - \frac{HL^2}{8K^2} \sigma + \frac{HL^3}{16K^3} \sigma^2 - \dots \quad (5.1)$$

In the limit $\sigma \rightarrow 0$, the intercept Δ_0 and the initial slope $m_0 = (\partial \Delta / \partial \sigma)_{\sigma=0}$, are obtained from Eq. (5.1) by inspection.

$$\Delta_0 = \frac{H^{(o)}L}{4K^{(o)}} \quad (4.48)$$

$$m_0 = - \frac{H^{(o)}L^2}{8(K^{(o)})^2} \quad (5.2)$$

Eqs. (4.48) and (5.2) can thus be solved simultaneously for $H^{(o)}$ and $K^{(o)}$ values that will satisfy the experimental values of Δ_0 and m_0 .

Some typical data are presented in Figure 16. The complete solid lines represent values of the separation Δ calculated from uncorrected Eq. (4.47) with values of $H^{(o)}$ and $K^{(o)}$ determined in the manner described in the preceding paragraph. The solid lines ending in a dot represent separations calculated from the corrected Eq. (4.47) using these same $H^{(o)}$ and $K^{(o)}$ values. For relatively low flow rates, the corrected and uncorrected equations give almost identical results and agree very well with the data. At higher flow rates, the uncorrected equation deviates markedly from the data and predicts separations larger than those found experimentally. The corrected equation gives

Fig. 16. Separation in a Continuous-flow Thermogravitational Column as a Function of Flow Rate.

values that compare very well with the experimental data. However, for values of $\omega\gamma > 1$ (dots indicate $\omega\gamma = 1$) the series appearing in the corrections $h(\omega\gamma)$ and $k(\omega\gamma)$ (Eqs. (4.37b) and (4.38b)) diverge and lead to the indeterminate expression $\Delta = \infty \cdot 0$.

The dashed lines drawn as a continuation of the corrected curves represent the use of correction terms $h_1(\omega\gamma)$ and $k_5(\omega\gamma)$. Values of $h_1(\omega\gamma)$ are calculated by ignoring all terms but the first in the series appearing in Eq. (4.37b) and $k_5(\omega\gamma)$ values are calculated by considering only the first five terms of the series in Eq. (4.38b). These relations are given by Eqs. (5.3) and (5.4), and are represented graphically in Figures 17 and 18.

$$h_1(\omega\gamma) = 1 - 0.17143 (\omega\gamma)^2 \quad (5.3)$$

$$\begin{aligned} k_5(\omega\gamma) = & 1 - 0.39636(\omega\gamma)^2 + .033567(\omega\gamma)^4 + 2.2378 \\ & \times 10^{-3}(\omega\gamma)^6 + 3.949 \times 10^{-4}(\omega\gamma)^8 + 1.0392 \\ & \times 10^{-4}(\omega\gamma)^{10} + 3.464 \times 10^{-5}(\omega\gamma)^{12} \end{aligned} \quad (5.4)$$

Values of $h(\omega\gamma)$ and $k(\omega\gamma)$ for $|\omega\gamma| \leq 1$ are included in Figures 17 and 18 for comparison.

The term $h_1(\omega\gamma)$ becomes negative at large flow rates, and the separations predicted for $\omega\gamma > 2.43$ are opposite in sign to Δ_0 . The net result of the use of $k_5(\omega\gamma)$ is to limit the separations calculated for $\omega\gamma > 2.43$ to very small values. Negative separation values are shown in Figure 16. In other figures in the text the dotted line representing the corrected Eq. (4.47) is terminated at $\omega\gamma = 2.43$ because separations of opposite sign at higher flow rates have no physical significance. In most cases both calculated and measured separation values are equal to zero within experimental accuracy for $\omega\gamma > 2.43$. The agreement with experimental data for $2.43 > \omega\gamma > 1.0$

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Fig. 17. $h(\omega\gamma)$ and $h_1(\omega\gamma)$ as Functions of $|\omega\gamma|$.

Fig. 18. $k(\omega\gamma)$ and $k_5(\omega\gamma)$ as Functions of $|\omega\gamma|$.

that is obtained by using these approximations is remarkable, as there seems to be no justification for using only the first several terms in these divergent series.

Equations (4.48) and (5.2) were used to determine empirical values of $H^{(o)}$ and $K^{(o)}$ for most of the groups of experimental data listed in Tables I and II. The variation of the separation Δ with flow rate was properly accounted for by use of Eq. (4.47). In general the corrected equation with the terms $h_1(\omega\gamma)$ and $k_5(\omega\gamma)$ was superior to the uncorrected equation in representing the data.

The separation-flow rate data successfully represented by Eq. (4.47) were obtained for a variety of operating conditions. The theory predicts the effect of changes in the operating conditions and the empirical $H^{(o)}$ and $K^{(o)}$ values can be used to check these predictions. The functional dependence of the term $H^{(o)}$ is given by Eq. (4.37a). $K^{(o)}$ is composed of three additive terms: $K_c^{(o)}$ representing the remixing effects due to the convective flow; K_d , which accounts for vertical diffusion, and K_p , a term appended to the theory to account for parasitic remixing effects. Fortunately, for the range of variables investigated in connection with this research, both K_d and K_p appear to be negligibly small when compared to $K_c^{(o)}$. In this case, the functional dependence of $K^{(o)}$ is essentially given by Eq. (4.38a), i.e., that for $K_c^{(o)}$.

Temperature Difference (ΔT)

According to Eq. (4.37a) and Eq. (4.38a), both $H^{(o)}$ and $K^{(o)}$ are proportional to $(\Delta T)^2$. Values of $H^{(o)}$ and $K^{(o)}$ used in Eq. (4.47) were obtained from relations of the form $H^{(o)} = a(\Delta T)^2$ and $K^{(o)} = b(\Delta T)^2$. These relations seem to satisfy the data presented in Figures 16, 19 and 20 over a wide range of ΔT and for three different values of the plate spacing, 2ω . Experimental groups J and K substantiate these

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Fig. 19. Separation as a Function of Flow rate with Temperature Difference as Parameter.

Fig. 20. Separation as a Function of Flow Rate with Temperature Difference as Parameter.

conclusions. These data are included in Table I, but are not extensive enough to warrant graphical representation.

In Figures 19 and 20, and subsequent figures in which no curve (or curves) representing the corrected equation appears, the measurement of the plate spacing was too inaccurate to permit a proper evaluation of the correction.

Length (L_T)

The theory predicts that $H^{(o)}$ and $K^{(o)}$ are independent of the column length. From Eq. (4.48), Δ_o should be proportional to L_T and, according to Eq. (4.47), the separation should become independent of height at high flow rates. These theoretical predictions are definitely substantiated by the data presented in Figure 21. The difference between the values of $H^{(o)}$ and $K^{(o)}$ used to represent the two experimental groups and the deviation of the theoretical curves at high flow rates is due in part to slight differences in the plate spacing and ΔT .

Effective Gravitational Field ($g \cos \theta$)

The effective gravitational field was changed by tilting the column in the manner illustrated in Figure 6. This variation is accounted for in the theory by the product $g \cos \theta$. The results of experiments made with the hot plate on top (positive angles) are presented in Figure 22. The curves drawn on Figure 22 represent separations calculated using values of $H^{(o)}$ and $K^{(o)}$ obtained from relations of the form $H^{(o)} = a \cos \theta$ and $K^{(o)} = b \cos^2 \theta$ as predicted by theory.

Several experiments were made with the cold plate on the top (experimental groups P and T). Separations were obtained in this case and were generally smaller than values obtained at the corresponding positive angle (45°). Experiment No. 87-P was a notable exception. Experiment No. 116-T did not check this anomalous result. It is probable

Fig. 21. Separation as a Function of Flow Rate with Column Length as Parameter.

Fig. 22. Separation as a Function of Flow Rate with Column Inclined at Various Angles.

that Experiment No. 87-P is in error, but it would be of theoretical interest to investigate this question further, preferably in a batch column.

Plate Spacing (2ω)

According to the theory the separation should show a strong dependence on the plate spacing. From Eq. (4.37a) and (4.38a), $H^{(o)} = a(2\omega)^3$ and $K^{(o)} = b(2\omega)^7$. The magnitude of this effect is even more clearly emphasized by the fact that m_o , the initial slope, is inversely proportional to $(2\omega)^{11}$. The tremendous effect of the plate spacing is illustrated in Figure 23 by retaining the same relative scales on the four graphs. The curves on Figure 23 represent values calculated from Eq. (4.47) using values of $H^{(o)}$ and $K^{(o)}$ determined from the above relations. Values of a and b were determined from the data taken for $2\omega = 0.0908$ cm (Figure 23b), and slight corrections were made for variations in ΔT . The agreement appears to be quantitative largely because the scales are small.

Actually some discrepancies exist between the theoretical and experimental values for data taken at the larger plate spacings. Figure 24 represents other data taken to investigate the effect of plate spacing and will serve to illustrate the nature of these discrepancies. If the constants a and b in the relations $H^{(o)} = a(2\omega)^3$ and $K^{(o)} = b(2\omega)^7$ are evaluated from the data taken at the smaller plate spacing (larger Δ_o), values of $H^{(o)}$ and $K^{(o)}$ calculated from these relations fail to represent the data taken at the larger plate spacing (light line). The predicted value of Δ_o is somewhat smaller than that found experimentally, and experimental values of the separation at high flow rates are substantially smaller than the calculated values. On the other hand, values of $H^{(o)}$ and $K^{(o)}$

Fig. 23. Separation as a Function of Flow Rate for Four Different Plate Spacings.

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Fig. 24. Separation as a Function of Flow Rate with plate Spacing as Parameter.

obtained empirically from each individual set of data serve to represent the data very well (heavy lines).

A.L. Jones¹²⁵ has reported some qualitative conclusions based on an extensive investigation of the separation of liquids in continuous-flow thermogravitational columns. Although he does not indicate the nature of the dependence of the separation on the flow rate, his conclusions with regard to other variables are in general agreement with the theory and with the results of this investigation.

Quantitative Comparison

of Experimental and Theoretical Values of $K^{(o)}$ and $H^{(o)}$

The theoretical development given in detail in Chapter IV predicts not only the form of the equation that may be used to represent the data and the functional dependence of the terms $K^{(o)}$ and $H^{(o)}$, but the numerical values of these terms as well. Comparison of the experimental and theoretical values of $K^{(o)}$ and $H^{(o)}$ is a convenient method of investigating the quantitative nature of the theory.

Corrections on $K_c^{(o)}$ ($\phi_{K_c^{(o)}}$)

The factor $K^{(o)}$ is composed of three additive terms, $K_c^{(o)}$, K_d and K_p , as described previously. Values of $K_c^{(o)}$ and K_d can be calculated from Equations (4.38a) and (4.39) respectively and over the range of variables involved in this research $K_d \ll K_c^{(o)}$. K_p can only be evaluated empirically. For purposes of comparison, a factor $\phi_{K_c^{(o)}}$ is defined by Eq. (5.5).

$$\phi_{K_c^{(o)}} = \frac{[K_c^{(o)}]_{\text{expt.}}}{[K_c^{(o)}]_{\text{calc.}}} \quad (5.5)$$

Values of $[K_c^{(o)}]_{\text{expt.}}$, $[K_c^{(o)}]_{\text{calc.}}$ and $\phi_K^{(o)}$ are tabulated in Table IX and are discussed in detail in a later section of this chapter.

Corrections on $H^{(o)}$ ($\phi_H^{(o)}$)

In contrast to $K^{(o)}$, $H^{(o)}$ contains but one term, that given by Eq. (4.37a). It might therefore be expected that a comparison of the experimental and theoretical values of $H^{(o)}$ would prove a better criterion of the validity of the theory than the corresponding comparison of $K^{(o)}$ values. If anything, the inverse is true. This is because $H^{(o)}$ is proportional to the thermal diffusion "constant", α , and $K^{(o)}$ is independent of this term. Values of α for liquid systems reported in the literature are not only scarce but also very inconsistent. Determination of reliable values of α from separations made in thermogravitational columns is hampered by the fact that the theory is not quantitative. Because of the inadequacies of the theory two methods of determining α values from thermogravitational column data were developed.

One method is based on the fact that values of α calculated from the experimental data using the two independent Eqs. (4.37a) and (4.48) are generally not in agreement. The notation $\alpha_H^{(o)}$ is used to designate a value calculated from Eq. (4.37a) using an experimental value of $H^{(o)}$, and α_{Δ_o} will similarly identify the value as being obtained from the experimental value of the intercept Δ_o , using Eq. (4.48). It is assumed that the "correct" α value is obtained under the conditions $\alpha_H^{(o)} = \alpha_{\Delta_o}$. Figure 25a illustrates the manner in which the "correct" α value for the system n-heptane-benzene was determined from values of Δ_o and $H^{(o)}$ obtained from the data presented in Figure 24.

The other method used to determine "correct" α values is based on the assumption that the theoretical equations are quantitative

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Fig. 25. The Determination of the "Correct" α Value for the System n-heptane-benzene.

when $\phi_{K_c}(o) = 1.00$ (this is true only if $K_p \ll K_c$). In Figure 25b values of α_{Δ_o} are plotted as the ordinate with 2ω , the only parameter varied in the two investigations represented by circles, as the abscissa. These data were extrapolated to $2\omega = 0.067$ cm, the value of the plate spacing at which $\phi_{K_c}(o) = 1.00$. (This value of 2ω at $\phi_{K_c}(o) = 1.00$ was obtained from Figure 28b which is discussed later in this chapter.) A "correct" α value of 1.08 was obtained by the first method (Figure 25a), and the second method yielded $\alpha = 1.13$. An average of $\alpha = 1.1$ was used in the calculations.

A similar procedure was applied to the data taken with the 40 wt % ethyl alcohol-water system. The value of α for the 33 wt % ethyl alcohol-water system was determined from only one group of experimental data (Z), for which $\phi_{K_c}(o) = 1.00$ and $\alpha_{\Delta_o} = \alpha_H(o)$. The curve in Figure 26 represents values of the separation calculated from Eq. (4.47) using theoretical rather than empirical values of $K(o)$ and $H(o)$.

Results of investigations of both the n-heptane-benzene and ethyl alcohol-water systems have previously been reported in the literature. Trevo and Drickamer⁷¹ determined α_{Δ_o} values for the n-heptane-benzene system in a batch column 4 inches long operated at a ΔT of about 5°C. A value of α_{Δ_o} at 42°C taken from their data is represented by a triangle on Figure 25b. The agreement is remarkable when the differences in L_T and ΔT are considered.

Van Velden, van der Voort and Gorter¹⁶¹ determined values of α for the system ethyl alcohol-water over a considerable concentration range. They considered the concentration change at the two ends of a batch thermogravitational column 2-1/4 inches long as a function of time for $0.02 < 2\omega < 0.12$ cm. Values of α calculated from the

Fig. 26. Separation as a Function of Flow Rate. Values of $H^{(0)}$ and $K^{(0)}$ Calculated from Theory.

data of Van Velden et al., using the assumption $C_1 C_2 \approx 1/4$ are in excellent agreement with the "correct" α values determined from the data of this work. The nature of the agreement is illustrated in Figure 27.

It would appear, then, that the two methods of determining a "correct" α value are not only self-consistent but also yield values that are in agreement with the data of other observers. These "correct" α values were used to calculate theoretical values of $H^{(o)}$ and $\phi_H^{(o)}$ (defined by Eq. (5.6)). Table IX contains

$$\phi_H^{(o)} = \frac{H^{(o)}_{\text{Expt.}}}{H^{(o)}_{\text{Calc.}}} \quad (5.6)$$

a list of $H^{(o)}_{\text{Expt.}}$, $H^{(o)}_{\text{Calc.}}$ and $\phi_H^{(o)}$.

Unfortunately, accurate measurements of the plate spacing were not obtained for all the experiments, owing to the unexpected gasket behavior discussed in Chapter III. As a result only approximately 100 experiments were used to obtain the values of $\phi_H^{(o)}$ and $\phi_{K_c}^{(o)}$ listed in Table IX.

Correlation of $\phi_H^{(o)}$ and $\phi_{K_c}^{(o)}$

The majority of the experiments for which the plate spacing was accurately measured were devoted to the investigation of the effect of changes in the plate spacing. Three liquid systems (40 wt % EtOH-water, 33 wt % EtOH-water and 50 mol % n-heptane-benzene) and two columns (four and eight feet in length), were used during the course of these investigations. The effect of temperature difference was checked in runs W and X. Values of $\phi_H^{(o)}$ and $\phi_{K_c}^{(o)}$ are plotted as functions of $2w$ in Figure 28. The value of $\phi_{K_c}^{(o)}$ represented by the solid

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Fig. 27. The Thermal Diffusion "Constant" α for the System Ethyl Alcohol-Water as a Function of Concentration.

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Fig. 28. Correction Factors $\phi_{H(o)}$ and $\phi_{K_C(o)}$ as Functions of the Plate Spacing for Various Systems.

black triangle in Figure 28b was calculated (See appendix) from data on the approach to steady state in a batch thermogravitational column reported by Trevoy and Drickamer.⁷¹ The column used by Trevoy and Drickamer was 4 inches long and was operated at a ΔT of about 5°C . The results of their investigation are in remarkable agreement with the data obtained in the present research with a column 4 feet long operated with a ΔT of about 42°C .

Figure 28 is noteworthy in several respects:

(1) It would appear that the theory is quantitative at certain small values of the plate spacings.

(2) The theory is in good qualitative agreement with the experimental data over the entire range of variables investigated. Values of $\phi_H(o)$ and $\phi_{K_c}(o)$ for this investigation are in the range 0.10-1.00, with the large majority of the values between 0.4 and 1.00. In contrast $H^{(o)}$ values varied from 4.5×10^{-4} to 3×10^{-2} and $K^{(o)}$ from 5×10^{-2} to 228, a factor of over 4,000 in the latter case!

(3) The corrections $\phi_H(o)$ and $\phi_{K_c}(o)$ vary rapidly with changes in the plate spacing $2w$.

(4) $\phi_H(o)$ and $\phi_{K_c}(o)$ appear to be independent of the column length L_T , as might be anticipated.

(5) The corrections vary little with large changes in the temperature difference, ΔT , a result that is unexpected.

(6) Both $\phi_H(o)$ and $\phi_{K_c}(o)$ are functions of the physical properties of the system.

Other investigators have reported similar discrepancies between theory and experiment. Becker⁹⁵ was able to correlate thermogravitational column data taken with turbulence in the gas mixture by merely applying

a correction to the measured plate spacing. On this basis $\phi_{K_c}(o) = \phi_H(o)^{7/3}$ (assuming K_d and K_p are negligible). By calculating the initial transport, Becker further found that the ratio

$$\frac{K(o)}{(\phi_H(o))^2} = \frac{2\omega \bar{T}^2}{\alpha^2 \rho D} \frac{\phi_{K_c}(o)}{(\phi_H(o))^2}$$

was approximately constant over a wide pressure range. The group $\frac{2\omega \bar{T}^2}{\alpha^2 \rho D}$ is essentially independent of pressure and thus $\phi_{K_c}(o) = [\phi_H(o)]^2$. The values of the two exponents, 2.00 and 7/3, are in substantial agreement with each other and lend support to Becker's method of accounting for turbulence.

Values of $\phi_{K_c}(o)$ and $\phi_H(o)$ from Table IX plotted on Figure 29 indicate the relation between $\phi_{K_c}(o)$ and $\phi_H(o)$ given by Eq. (5.7):

$$\phi_{K_c}(o) = [\phi_H(o)]^a; \quad 3/2 > a > 1. \quad (5.7)$$

Equation (5.7) is in substantial disagreement with the results of Becker. This suggests that the need for correction might not depend on the existence of turbulence. According to Onsager and Watson⁹³ turbulence exists for Reynold's Nos. > 150.

$$Re_{\#} = \frac{(2\omega)^3}{36\sqrt{3}} \frac{\beta \rho g \cos \theta}{\eta^2} \quad (5.8)$$

For the systems investigated during the course of the present research, Reynold's Nos. calculated from Eq. (5.8) were all less than 40.

Drickamer and his co-workers⁹⁷⁻¹⁰³ have made an extensive investigation of the effect of pressure on the separation of gas mixtures in batch thermogravitational columns. They found that their experimental results were in accord with column theory only in the region of maximum

Fig. 29. $\phi_{K_c}(o)$ as a Function of $\phi_H(o)$.

separation. Drickamer, Mellow and Tung⁹⁹ proposed the following modification of Eq. (4.49) based on a quasi-theoretical development:

$$1 \text{ m } q = \frac{(\phi')^3 H^{(o)}_L}{\phi(\phi')^6 K_c^{(o)} + K_d^{(o)}} \quad (5.9)$$

In applying Eq. (5.9), Drickamer, Mellow and Tung utilized the factor ϕ' to correlate the data obtained at pressures less than optimum, and similarly the factor ϕ was used to bring theory and experiment into agreement at higher pressures. The relations used by Drickamer et al., are listed below:

$$\phi' = 1.00;$$

$$Gr\# > 1.2 \times 10^5 \quad (5.10a)$$

$$\phi' = 0.576 Gr\#^{0.0486};$$

$$1.2 \times 10^5 > Gr\# > 6 \times 10^3 \quad (5.10b)$$

$$\phi' = 0.866;$$

$$Gr\# < 6 \times 10^3 \quad (5.10c)$$

$$\phi = 1260 (\psi)^{1.2};$$

$$\psi < 1.35 \times 10^{-3} \quad (5.11a)$$

$$\phi = 13.6 (\psi)^{0.512};$$

$$6.3 \times 10^{-3} > \psi > 1.35 \times 10^{-3} \quad (5.11b)$$

$$\phi = 1.00;$$

$$\psi > 6.3 \times 10^{-3} \quad (5.11c)$$

$$Gr\# = \frac{(2\omega)^2 L_T \beta g \rho \Delta T}{4 \eta^2} \quad (5.12)$$

$$\psi = \frac{2D/2\omega}{(L \Delta T g \beta / \rho)^{1/2}} \quad (5.13)$$

Each correction suggested by Drickamer et al., applies to a specific region of column operation:

(1) Equations (5.10b) and (5.10c) are used when the convective velocity between the walls of the column is small and the term K_d is as important as $K_c^{(o)}$. The data of Nier,¹⁶² Taylor and Glockler,¹⁶³ and Whalley, Winter and Briscoe⁹² were all obtained under conditions that produced small convective velocities. These data were brought into agreement with the theory by evaluating the K_p term empirically as suggested by Jones and Furry⁴⁷ and making slight corrections on the calculated K_d term.

(2) The correction represented by Eq. (5.11a) is apparently necessary when there is turbulence in the fluid between the walls of the thermogravitational column, because this correction is in agreement with the results of Becker.⁹⁶

(3) Equation (5.11b) provides a correction at high convective flow rates in the laminar region. Under these conditions $K_d \ll K_c^{(o)}$, $\phi = 1.00$ and Eq. (5.9) reduces to

$$\ln q = \frac{H^{(o)}L}{\phi_{K_c^{(o)}}} \quad (5.14)$$

Equation (5.14) is comparable to Eq. (4.48), which when corrected by the terms $\phi_H^{(o)}$ and $\phi_{K_c^{(o)}}$ becomes

$$\ln \Delta_o = \frac{\phi_H^{(o)} H^{(o)}L}{\phi_{K_c^{(o)}} K_c^{(o)}} \quad (5.15)$$

The similarity of Eqs. (5.14) and (5.15) suggests the relation

$$\phi = \phi_{K_c^{(o)}} / \phi_H^{(o)} \quad (5.16)$$

Equation (5.16) is analogous in form to Eq. (5.7).

The relation between the terms ϕ , $\phi_H(o)$ and $\phi_{K_c}(o)$ can be clarified by considering their variation with respect to changes in the plate spacing. When Eq. (5.11b) and (5.13) are combined, ϕ is obtained as a function of 2ω in the region of high convective flow rates without turbulence:

$$\phi = a (2\omega)^{-0.512} \quad (5.17)$$

From Figure 28

$$\phi_H(o) = a^1 (2\omega)^{-1.5} \text{ and} \quad (5.18)$$

$$\phi_{K_c}(o) = a^{11} (2\omega)^{-2.0}. \quad (5.19)$$

The Eqs. (5.16)-(5.19) suggest that

$$\phi_H(o) = \phi^3 \text{ and} \quad (5.20)$$

$$\phi_{K_c}(o) = \phi^4. \quad (5.21)$$

These results are in good agreement with the relation given by Eq. (5.7).

The combination of Eq. (5.11b), (5.13), (5.20) and (5.21) yields

$$\phi_{K_c}(o) = b (L)^{-1.0} \text{ and} \quad (5.22)$$

$$\phi_{K_c}(o) = b^1 (\Delta T)^{-1.0}. \quad (5.23)$$

Both Eqs. (5.22) and (5.23) are in substantial disagreement with the conclusions drawn from Figure 28b.

The general agreement between Eq. (5.7) and (5.17)-(5.19) indicates that data on the separation of both liquids and gases in thermogravitational columns might be used to obtain a more general correlation than that proposed by Drickamer, Mellow and Tung.

Dimensional analysis may be used to arrange the variables of a system into convenient groups to aid in the correlation of data. As

the first step in this type of analysis, ϕ is considered as a general function of a number of important system variables in Eq. (5.24):

$$\phi = \phi \left[2\omega^a, L^b, B^c, \epsilon^d, \alpha^e, \beta^f, \rho^g, \eta^h, D^i, k_T^j, C_p^k, (g \cos \theta)^p, T^m, \Delta T^n \right]. \quad (5.24)$$

Variables included in Eq. (5.24) not previously defined are:

- ϵ , a length dimension - possibly a relative roughness;
- k_T , the thermal conductivity, and
- C_p , the heat capacity at constant pressure.

Equation (5.25) is obtained by applying the method of dimensional analysis to Eq. (5.24) and assuming that a solution in the form of a simple product of dimensionless groups is sufficient to represent the general function.

$$\phi = Z \left[\frac{L}{2\omega} \right]^b \left[\frac{B}{2\omega} \right]^c \left[\frac{\epsilon}{2\omega} \right]^d \alpha^e \left[\frac{\beta \Delta T}{\eta} \right]^f \left[\frac{\rho D}{\eta} \right]^g \left[\frac{k_T}{\eta C_p} \right]^j \left[\frac{g \cos \theta (2\omega)^3}{D^2} \right]^p \left[\frac{T}{\Delta T} \right]^m \quad (5.25)$$

Since both L and $B \gg 2\omega$ for all practical cases it seems reasonable to set $b = c = 0$ especially in light of the data presented in Fig. 28. Several other exponential unknowns can be eliminated by considering the theoretical equations developed in Chapter IV. The only manner in which either β or $g \cos \theta$ appears in the theory is in the equation describing the velocity distribution, Eq. (4.36). In this equation these variables appear as the product $\beta g \cos \theta$. It therefore seems reasonable to set $f = p$ in Eq. (5.25). Further, if Eq. (4.8) is made dimensionless, the term $\frac{\alpha \Delta T}{T}$ appears as a product and therefore it might be expected that $e = -m$ in Eq. (5.25). When these simplifications are applied to Eq. (5.25), Eq. (5.26) is obtained:

$$\phi = Z \left(\frac{T}{\alpha \Delta T} \right)^m \left(\frac{\epsilon}{2\omega} \right)^d \left(\frac{\beta g \cos \theta (2\omega)^3 \Delta T}{\eta D} \right)^f \left(\frac{\rho D}{\eta} \right)^g \left(\frac{k_T}{\eta C_p} \right)^j. \quad (5.26)$$

It might further be noted that

$$\frac{\beta g \cos \theta (2\omega)^3 \Delta T}{D} = 36\sqrt{3} \quad (\text{Re}\#)(\text{Sc}\#), \quad (5.27)$$

where $\text{Re}\#$ is the Reynold's number defined by Eq. (5.8) (actually a Grasshoff number) and $\text{Sc}\#$ is the Schmidt number defined by

$$\text{Sc}\# = \frac{\eta}{\rho D}. \quad (5.28)$$

By utilizing the definition of the Prandtl number,

$$\text{Pr}\# = \frac{\eta C_p}{k_T} \quad (5.29)$$

Eq. (5.28) can be written in the relatively simple form

$$\phi = Z \left(\frac{T}{\alpha \Delta T}\right)^m \left(\frac{\epsilon}{2\omega}\right)^d (\text{Re}\#)^f (\text{Sc}\#)^{f-g} (\text{Pr}\#)^{-j}. \quad (5.30)$$

The remaining exponents, m , d , f , g and j , must be evaluated empirically.

Some explanation of the correlating procedures is necessary before the results can be given:

(1) Instead of ϕ , ϕ^3 was treated as a function of the variables given in Eq. (5.30). Thus from Eqs. (5.20), (5.21) and (5.30),

$$\phi^3 = \phi_H(o) = (\phi_{K_c}(o))^{3/4} = Z^1 \left(\frac{T}{\alpha \Delta T}\right)^{a^1} \left(\frac{\epsilon}{2\omega}\right)^{b^1} (\text{Re}\#)^{c^1} (\text{Sc}\#)^{d^1} (\text{Pr}\#)^{e^1}. \quad (5.31)$$

(2) Values of $\phi_H(o)$ and $\phi_{K_c}(o)$ used in the correlation are those listed in Table IX.

(3) ϕ^3 values were obtained from data on the separation of gases in batch columns. Data reported by Drickamer and his co-workers^{99,102,103} were used. In order to eliminate as much as possible any corrections due to $K_d^{(o)}$, only data obtained at pressures greater than optimum were considered and ϕ values were calculated from Eq. (5.16). Calculation

details are given in the appendix.

When the pressure on a gas is increased, the Reynold's number (Eq. (5.8)) is effectively increased without changing any other variables.

From the data of Drickamer and his co-workers, $c' = -0.8$ or

$$\phi^3 = Z(\text{Re}\#)^{-0.8} \quad (5.32)$$

Equation (5.32) would predict that

$$\phi^3 = \phi_H(o) = (\phi_{K_c}(o))^{3/4} = a(2\omega)^{-2.4} \quad (5.33)$$

which is in substantial disagreement with Eq. (5.17)-(5.19). The modification of Eq. (5.33) proposed in Eq. (5.34) is in agreement with Eqs. (5.17)-(5.19) and thus seems applicable to both gas and liquid systems:

$$\phi_H(o) = Z\left(\frac{1}{2\omega}\right)^{-1} (\text{Re}\#)^{-0.8}. \quad (5.34)$$

(The term $\phi_H(o)$ is used in this and future equations to represent $\phi^3 = \phi_H(o) = \left[\phi_{K_c}(o)\right]^{3/4}$.) It is assumed that the necessary correction of the plate-spacing dependence is provided by the group $(\epsilon/2\omega)^{b'}$.

Since ϵ is an undefined length dimension it is assumed to be equal for all columns considered and is replaced by 1, making the final correlation dimensional.

The Schmidt and Prandtl numbers for two of the gas systems investigated by Drickamer and his co-workers (A-Ne and $\text{CO}_2\text{-C}_3\text{H}_8$) are essentially identical. ϕ^3 values for these two gas systems are correlated by setting $a' = -1.0$:

$$\phi_H(o) = Z\left(\frac{T}{\alpha\Delta T}\right)^{-1.0} \left(\frac{1}{2\omega}\right)^{-1.0} (\text{Re}\#)^{-0.8} \quad (5.35)$$

There remain but two exponents to be determined, d' and e' , and essentially 3 systems (two liquid and a combined gas system) to be correlated. It is possible to correlate these data approximately by using either of the following relations:

$$d' = -1/2; e' = 0 \quad (5.36)$$

$$d' = 0; e' = -3/2 \quad (5.37)$$

Because of these apparent discrepancies the Schmidt and Prandtl groups have been combined by applying the following reasoning: The Schmidt number is the ratio of the molecular momentum transfer to the molecular mass transfer. Similarly the Prandtl number is the ratio of molecular momentum transfer to molecular heat transfer. The ratio of these two groups ($Sc\#/Pr\#$) is the ratio of molecular heat transfer to molecular mass transfer. If the effects of the momentum transfer are properly accounted for in the Reynold's number then one might expect the ratio ($Sc\#/Pr\#$) to be the correlating group. By use of this ratio the following relation was obtained:

$$d' = -e = -0.8. \quad (5.38)$$

Equation (5.38) correlates the data better than either Eq. (5.36) or Eq. (5.37) and has been used in the final correlation:

$$\left[\phi_H(o)\right]^{-1} = 8.3 \times 10^{-5} \text{ cm } \left(\frac{T}{\alpha\Delta T}\right) \left(\frac{1}{2\omega}\right) (Re)^{0.8} (Sc\#/Pr\#)^{0.8} \quad (5.39)$$

A plot of ϕ^3 , $\phi_H(o)$ and $\left[\phi_K(o)\right]^{3/4}$ as a function of

$\left(\frac{T}{\alpha\Delta T}\right) \left(\frac{1}{2\omega}\right) (Re)^{0.8} (Sc\#/Pr\#)^{0.8}$ is presented in Figure 30 to illustrate the degree to which the data is correlated by Eq. (5.39). Equation (5.39) applies only for values of $\phi_H(o) < 1.00$ and should not be used beyond the range of data represented in Figure 30 without due regard for possible effects of turbulence.

The range of variables included in the correlation represented by Figure 30 are listed below:

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Fig. 30. General Correlation of the Correction Factors ϕ , $\phi_H(o)$ and $\phi_{K_C}(o)$.

L: 10 - 244 cm

α : 0.0117 - 1.1

ΔT : 4.9 - 180°C

$\bar{T}$: 295 - 380°K

2ω : 0.0508 - 0.308 cm

β : $3.7 \times 10^{-6} - 9.4 \times 10^{-4} \text{ gm cm}^{-3} \text{ } ^\circ\text{K}^{-1}$

ρ : 0.001 - 0.9 gm cm⁻³

$g \cos\theta$: 980 cm sec⁻²

η : 0.025 - 1.14 centipoise

Sc#: 0.696 - 1,200

Pr#: 0.663 - 11.5

Re#: 0.64 - 185

Although the vast majority of the data seem to be correlated well by Eq. (5.39), there are several notable exceptions:

(1) The open circles and open squares that deviate from the rest of the data represent experimental groups subject to large experimental error. The data of these experimental groups are correlated by Eq. (5.39) within the limits of experimental accuracy.

(2) The deviation of the black diamond from the general correlation is primarily due to the fact that α for the system EtOH-water varies rapidly with concentration whereas other physical properties do not. No explanation is offered for this discrepancy other than that the measured α value may be in error or that α should not appear in the correlation.

Comparison of α Values Measured by the
Static and Thermogravitational Methods

The comparison of α values determined from thermogravitational column data with α values measured by the static method should provide a severe test of the column theory. The nature of the agreement and disagreement between the α values thus measured is indicated in Table X.

Table X

Comparison of α Values Measured by the
Static and Thermogravitational Methods

System	α^a			
	Thermogravitational Method	Static Method	Calculated from Theory	Used in Correlation 5.41
43.55% Ne 56.45% A	0.186 ^{99,b}	0.15-0.23 ⁵⁹	0.186 ⁵⁹	0.186
55% CO ₂ 45% C ₃ H ₈	0.0117 ^{99,b}	-	0.0117 ⁹⁹	0.0117
40 wt. % EtOH 60 wt. % water	0.522 ^{161,c}	.079 ^c	-	0.522
33 wt. % EtOH 67 wt. % water	0.213 ^{161,c}	-	-	0.213
50 mole % nC ₇ 50 mole % benzene	1.1 ^{71,c}	0.35 ⁷⁵	-	1.1

(a) First-named component concentrates at the hot side in the static method and at the top of a thermogravitational column.

(b) Calculated from data given in reference cited.

(c) This work.

From Table X it is apparent that α values calculated from separations of gases in thermogravitational columns are in good agreement with values measured by the static method or calculated from theory. These conclusions are supported by the data of Nier,¹⁶² Taylor and Glockler,¹⁶³ and Whalley, Winter and Briscoe.⁹²

In the case of the liquid systems included in Table X the α values obtained by the two methods of measurement agree as to sign and order of magnitude only. Similar discrepancies have previously been reported for both organic⁸⁵ and inorganic⁸⁰ liquid systems. Only deGroot, Gorter and Hoogenstraaten¹¹⁸ have reported results of measurements made with liquids in thermogravitational columns that are in good agreement with data obtained by the static method.

In some cases the separation brought about in the column is large enough to influence the convective velocity and invalidate the theory as originally proposed by FJO. This effect can be approximately accounted for by applying Eq. (4.51) in the manner suggested in the latter part of Chapter IV. For both the ethyl alcohol-water and n-heptane-benzene systems this effect acts to increase the separation slightly, and α values calculated by using Eq. (4.51) are reduced by less than 10% of the values listed in Table X.

The discrepancy between the two α values for the 40 wt % ethyl alcohol-water system reported in Table X is somewhat greater than for other systems. It is unfortunate that only two measurements could be made before the ethyl alcohol solution ruined the interferometer cell used in the analysis. From the measurements made by Huse, Trevoy and Drickamer in a similar glass-diaphragm cell it can be concluded that equilibrium was attained in the 96-hour period of the experiment and

and that no significant error was introduced by the method used to measure the temperature drop across the diaphragm. The fact that the diaphragm itself may influence the degree of separation has been investigated by Alexander.⁷⁴ It should be noted, however, that the small separation obtained in the glass-diaphragm cell is in substantial agreement with other measurements made with ethyl alcohol-water solutions by Wirtz¹⁶⁴ and Wereide.¹¹ Neither of these investigators used diaphragms of any kind.

Several measurements of α for 0.1 N HCl were made in the glass diaphragm for comparison with the data of other observers. The nature of this "agreement" is indicated in Figure 31.

No further attempt will be made at present to explain the large discrepancies between the two methods of measuring values of α for liquid systems. Such comparison will be meaningful only when a reliable method of measuring α by the static method is developed (See Tanner¹⁰ or Thomas⁸⁵).

Miscellaneous Experimental Data

Column Operation with Unequal Flow Rates in the Two Column Sections.

$(\sigma_e \neq \sigma_s)$.

Equation (4.47) has been used to correlate all the column data discussed so far. Equation (4.47) was developed from a more complicated form, Eq. (4.46), by setting $\sigma_e = \sigma_s$. Investigation of Eq. (4.46) reveals that the equality of the two flow rates is not critical, and for $3 > \sigma_e/\sigma_s > 0.3$ leads to no appreciable error. This fact is illustrated by the dashed curve on Figure 32. In Figure 32, values of Δ calculated from Eq. (4.46) are plotted as a function of the ratios σ_e/σ_s and σ_s/σ_e for a constant average flow rate of 0.904g/min.

Fig. 31. Values of α for 0.1 N HCl.

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Fig. 32. Separation as a Function of the Ratio of the Flow Rates in the Two Sections of the Thermogravitational Column.

Physical properties for the system were evaluated for the average column concentration rather than for the feed concentration. The asymmetry of the curve is due to the fact that α for the system investigated (ethyl alcohol-water) varies rapidly with concentration.

One group of experiments (Y) was carried out to check the validity of Eq. (4.46). These data are represented on Figure 32 by dots and show a marked deviation from the predicted values indicated by the dashed line. It is possible to account for these discrepancies by making use of the following reasoning: If the internal convective circulation is large compared to the superimposed flow, the separation should be independent of the exact feed location, a view substantiated by A. L. Jones.¹²⁵ Under these conditions, it might be assumed that the effective feed location adjusts itself in such a way that a maximum separation is obtained, i.e., $C_F = C_i$. Equation (5.40) represents a material balance around the column with C_i substituted for C_F .

$$\sigma_e (C_e - C_i) = \sigma_s (C_i - C_s) \quad (5.40)$$

The differences within the parenthesis in Eq. (5.40) represent the separation occurring in each section of the column and can be considered to be proportional to the effective length of the respective sections. Eq. (5.41) results from this assumption.

$$\sigma_e L_e = \sigma_s L_s \quad (5.41)$$

Combining Eqs. (5.41) and (4.46) and noting that $L_e + L_s = L_T$ yields

$$\Delta = \frac{H}{2} \frac{\sigma}{\sigma_s \sigma_e} \left(1 - \exp. \frac{-\sigma_e \sigma_s}{\sigma} \frac{L_T}{2K} \right) \quad (5.42)$$

In Eq. (5.42) $\bar{\sigma}$ is the average flow rate, $(\sigma_e + \sigma_s)/2$, as previously defined. The solid curve drawn on Figure 32 represents values of Δ calculated from Eq. (5.42). It can be seen that no serious error is introduced by using Eq. (4.47) rather than Eq. (5.42) for $2 > \sigma_e / \sigma_s > 0.5$.

Heat Load

Part of the large expense involved in the separation of mixtures by thermal diffusion is attributable to the cost of maintaining a temperature gradient through the solution being separated. It is therefore imperative that the heat load be estimated accurately in any economic evaluation of such a process. Throughout the theoretical treatment of Chapter IV it was assumed that the temperature gradient was linear, i.e., that heat transfer was due to conduction alone. This assumption is valid within the accuracy of the experiments made during the course of the present investigation, as illustrated in Figure 33. The experimental errors involved in these measurements were very large because the temperature change in the cooling and heating water was limited to less than 1°C, and the heat losses were equal in magnitude to the heat transferred through the fluid.

Approach to Steady State in Continuous-Flow Thermogravitational Columns

No theoretical equations representing the rate of approach to steady state in a continuous-flow thermogravitational column were included in the review article of Jones and Furry⁴⁷ and no such equations have been developed in connection with the present work. However, it was found empirically that the data reported in Table V on the approach to steady state in a continuous-flow thermogravitational column could be well represented by

$$\Delta(t) = \Delta(0) + [\Delta(\infty) - \Delta(0)] (1 - e^{-t/t_r}), \quad (5.43)$$

Fig. 33. Values of k_T , the Thermal Conductivity Computed from the Measured Column Heat Load.

where $\Delta(0)$ and $\Delta(\infty)$ are the differences in concentration of the product streams at $t = 0$ (step change in flow rate) and $t = \infty$ (steady state).

The values of t_r which best represent the data are presented in Table V. The nature of the agreement between the data and Eq. (5.43) is indicated by Figure 34.

Summary

(1) The equations developed in Chapter IV properly account for the effects of continuous flow through a thermogravitational column. The relatively simple equations previously presented by Jones and Furry⁴⁷ to represent this case are excellent first approximations. The corrections represented by Eq. (4.37b), (4.38b), (5.3) and (5.4) reduce the deviations between experiment and theory at high flow rates.

(2) Equations (4.37a) and (4.38b) can be used to predict the qualitative effect of changes in operational variables on H and K terms evaluated empirically. Values of H and K can be determined either from data obtained with a continuous-flow thermogravitational column or from data on the approach to steady state in a batch thermogravitational column.

(3) Theory and experiment are generally not in quantitative agreement. Excellent agreement between theory and experiment can be attained under certain conditions by slightly modifying the theory. It is believed that Eq. (5.39) provides such a correction to the theory in the region of high laminar convective-flow rates when $K_p \ll K_c^{(0)}$.

Fig. 34. Approach to Steady State in a Continuous-Flow Thermogravitational Column.

(4) Measurements made by the static method can be used quantitatively to predict separations in thermogravitational columns only for gas mixtures.

(5) Use of the average-flow-rate equation, Eq. (4.47), is permissible in the range $2 > \sigma_e / \sigma_s > 0.5$. Outside this range Eq. (5.42) is preferable to Eq. (4.46).

(6) Heat transfer through the liquid between the walls of a thermogravitational column is conduction-controlled in the nonturbulent region.

(7) The rate of approach to equilibrium in a continuous-flow thermogravitational column can be represented by an equation of the simple exponential type given by Eq. (5.43).

VI. PROCESS DESIGN

If the thermal diffusion process is to be evaluated in comparison with other separation processes an accurate design procedure must be established. From the discussion presented in Chapter V, it would appear that the equations of Furry, Jones and Onsager³¹ (uncorrected Eq. (4.47) for example) are sufficiently accurate to form the basis of a reasonable design technique. Krasney-Ergen¹⁶⁵ has developed equations for estimating optimum dimensions in the design of thermal diffusion processes based on the equations of FJO. Krasney-Ergen was principally interested in the concentration of relatively rare isotopes and treated the case in which the relative amount of the substance being concentrated, C_1 , is very small throughout the apparatus ($C_1 \ll 1$). The equations "tested" in Chapter V, on the other hand, were based on the assumption that the materials being separated are present in almost equal amounts ($C_1 C_2 \approx 1/4$). In the next section the method of Krasney-Ergen will be applied to develop a design procedure for the case $C_1 C_2 \approx 1/4$.

Development of Equations for Determining the Optimum Dimensions

of a Thermal Diffusion Apparatus ($C_1 C_2 \approx 1/4$)

The optimum dimensions are considered as those which yield minimum costs. The costs are considered in two categories only: (1) fixed charges, mainly depreciation of the capital investment, and (2) power costs which are defined so as to include both the cost of fuel and the cost of cooling water. The notation "\$" is used to denote the amount of fixed charges per unit area (cm^2) per unit time (day). The amount of heat transferred is inversely proportional to the plate spacing (see Figure 3B) and therefore the power cost per cm^2 per day

is designated by $p_c/2\omega$. The total cost is given by

$$\pi = \left[S + p_c/2\omega \right] \int_A dA = \left[S + p_c/2\omega \right] BL_T. \quad (6.1)$$

From Eq. (4.47),

$$L_T = \frac{2K}{\sigma} \left[-\ln \left(1 - \frac{2\sigma\Delta}{H} \right) \right]. \quad (6.2)$$

If the angle of the plates from the vertical ($\cos \theta$) is set arbitrarily and the temperature difference (ΔT) and temperature level ($\bar{T}$) are dictated by the available heating and cooling media, for any particular system the terms $H^{(o)}$ and $K^{(o)}$ can be considered to be functions of the column width B and the plate spacing 2ω . (The terms $h(\omega, \gamma)$ and $k(\omega, \gamma)$ are ignored in this development):

$$H^{(o)} = aB(2\omega)^3, \quad (6.3)$$

$$K^{(o)} = a'B(2\omega)^7 + b'B(2\omega). \quad (6.4)$$

Eq. (6.5) is obtained by combining Eqs. (6.1) through (6.4).

$$\pi = \frac{2B^2}{\sigma} \left[a'S(2\omega)^7 + a'p_c(2\omega)^6 + b'S(2\omega) + b'p_c \right] \left[-\ln \left(1 - \frac{2\sigma\Delta}{aB(2\omega)^3} \right) \right] \quad (6.5)$$

In general, the required separation Δ and the average flow rate σ are designated. The total cost, π , is then a function of 2ω and B only. From Eq. (6.5) it can be shown that the costs are infinite in both of the limits $B \rightarrow \infty$ and $\frac{2\omega\Delta}{aB(2\omega)^3} \rightarrow 1.0$. Clearly then at least one minimum must exist between the limits defined by

$$0 > \frac{2\sigma\Delta}{aB(2\omega)^3} > 1.00. \quad (6.7)$$

In order for the total cost to be minimized these conditions must be satisfied:

$$\frac{\partial \pi}{\partial B} = 0 = \frac{\partial \pi}{\partial (2\omega)} \quad (6.8)$$

By differentiating Eq. (6.5) with respect to B and combining with Eq. (6.8), we obtain

$$-2 \ln \left(1 - \frac{2 \sigma \Delta}{a B^* (2\omega)^3} \right) = \frac{1}{\frac{a B^* (2\omega)^3}{2 \sigma \Delta} - 1} \quad (6.9)$$

B* refers to the optimum value of the column width for any plate spacing.

The optimum plate spacing as a function of the various parameters is obtained by differentiating Eq. (6.5) with respect to 2ω and combining the resulting equation with Eqs. (6.8) and (6.9):

$$(2^* \omega)^7 - 5 \frac{b^*}{a^*} (2^* \omega) - 6 \frac{b^*}{a^*} \frac{p^* c}{S} = 0. \quad (6.10)$$

Eq. (6.10) is identical to the relation developed by Krasney-Ergen for the case $C_1 \ll 1$.

If Γ is defined by

$$\Gamma = \frac{2 \sigma \Delta}{a (2\omega)^3} \quad (6.11)$$

Eq. (6.9) can be reduced to

$$-2 \ln (1 - \Gamma/B) = \frac{1}{B/\Gamma - 1} \quad (6.12)$$

The solution to Eq. (6.12) is

$$B^* = 1.39 \Gamma \quad (6.13)$$

which is considerably more simple than the analogous relation developed by Krasney-Ergen. (Krasney-Ergen's results are listed in the appendix.)

Design Illustration

Both Krasney-Ergen¹⁶⁵ and Jones and Furry⁴⁷ have included numerical examples of the design of processes for concentrating dilute mixtures of isotopic gases. It is interesting to apply the equations developed in the preceding section to the design of a single-state apparatus for the separation of a concentrated liquid mixture.

For purposes of illustration a thermal diffusion plant to process 1,000 barrels per day of a 50 mol % n-heptane-benzene mixture will be designed. This particular design would have no commercial significance, as n-heptane-benzene is easily separated by distillation. Consider, however, that the process is indicative of separations of aromatics and aliphatics, a difficult separation when applied to lubricating oils.

Equation (4.47) used in the above development was restricted to the range $0.7 > C_1 > 0.3$ and to equal flow rates in each section. With these restrictions in mind the following product specifications were arbitrarily designated:

Top product = 500 bbl/day 70 mol % n-heptane

Bottom product = 500 bbl/day 30 mol % n-heptane

From these specifications it follows that $\Delta = 0.40$. The problem is further defined by setting $\cos \Theta = 1.00$, $\Delta T = 100^\circ\text{C}$ and $\bar{T} = 315^\circ\text{K}$. (This value of $\bar{T}$ was chosen so that the physical properties listed in Table VIII could be used.)

The power costs p_c were approximated by considering the cost of heating and cooling media to be twice the cost of fuel at \$0.30 per million BTU. A value of $\$7.32 \times 10^{-6}/\text{day-cm}^2/\text{cm}$ was obtained for p_c .

The equipment costs were assumed to be independent of 2ω and the cost per square foot of area of one plate was estimated to be \$60.00 per square foot. This is ten times the value obtained from Chilton's¹⁶⁶

cost curves for heat exchange surface and is intended to include cost of auxiliary equipment, design, etc. On this basis a value of $\$3.91 \times 10^{-5}/\text{day-cm}^2$ was obtained for S.

These cost data and values of the other system parameters were used in Eqs. (6.2a), (6.10) and (6.13a) through (6.15) to obtain the dimensions for the "optimum" design listed in Table XI. Estimates of the total heat load, capital investment, and operating costs are included.

Even though a column 1.43 cm long and 82.7 miles wide with a plate spacing of 0.182 mm may be "optimum" it would hardly seem practical. An increase in the plate spacing would decrease the column width and increase the column length. The cost would also be increased by any increase in plate spacing. (Actually a decrease in fabrication cost with an increase in 2ω would probably offset the predicted increase in cost.) A plate spacing of 0.793 mm (1/32 inch) was arbitrarily chosen as a minimum practical plate spacing, and values of B and L_T were calculated from Eqs. (6.2a) and (6.13a) through (6.16). The results of these calculations are listed under "Practical" Design in Table XI for comparison with the "Optimum" design. The values of the column length (17 ft) for this arbitrary plate spacing represent a practical construction and thus no other designs were considered.

The cost data used in the above estimates are certainly only approximate, and yet the results should indicate the order of magnitude of the costs. As pointed out previously, thermal diffusion is an expensive process. However, with motor oil selling for \$0.60 per quart the process may become economically feasible in the near future.

Table XI

Summary of Design Estimates

Plant to process 1,000 bbl per day of 50 mol % n-heptane-benzene

	"Optimum"	"Practical"
	<u>Design</u>	<u>Design</u>
2 ω - cm	0.0182	0.0793
(in)	(0.0072)	(1/32)
B - cm	$1.33 \times 10^{+7}$	$1.60 \times 10^{+5}$
(ft)	$(4.36 \times 10^{+5})$	$(5.25 \times 10^{+3})$
(miles)	(82.7)	(1.0)
L - cm	1.43	514
(ft)	(0.0468)	(16.9)
<u>Total Area</u>		
(B x L) cm ²	$1.90 \times 10^{+7}$	$8.23 \times 10^{+7}$
(ft ²)	$(2.05 \times 10^{+4})$	$(8.88 \times 10^{+4})$
Heat Load - BTU/hr	$5.27 \times 10^{+8}$	$5.27 \times 10^{+8}$
Capital Investment	\$1,230,000	\$5,320,000
<u>Operating Costs</u>		
Fuel and Cooling Water	\$7,670	\$7,670
Fixed Charges	<u>743</u>	<u>3,230</u>
Total	\$8,413	\$10,900
Cost per barrel of feed processed	\$8.41	\$10.90
Cost per gallon of feed processed	\$0.20	\$0.26

Summary of Design Procedures

Equations

Although there is some doubt as to the usefulness of the equations developed above in their application to liquids they are summarized here for convenient reference:

Optimum Plate Spacing (2ω)

$$(2\omega)^7 - 5 \frac{b^{\dagger}}{a^{\dagger}} (2\omega) - 6 \frac{b^{\dagger}}{a^{\dagger}} \frac{P_c}{S} = 0 \quad (6.10)$$

$$\frac{b^{\dagger}}{a^{\dagger}} = 9 \left(\frac{D \eta}{\beta_T g \cos \Theta \Delta T} \right)^2 \quad (6.14)$$

Optimum Column Width (B^*)

$$B^* = 1.39 \Gamma = \frac{2.78 \sigma \Delta}{a(2\omega)^3} \quad (6.13a)$$

$$a = \frac{\alpha \beta_T \rho g \cos \Theta (\Delta T)^2}{6! \eta \bar{T}} \quad (6.15)$$

Column Length (L_T^*)

$$L_T^* = \frac{2K^{(o)}}{\sigma} \left[-\ln \left(1 - \frac{2\sigma \Delta}{H^{(o)}} \right) \right] = \frac{2.54 K^{(o)}}{\sigma} \quad (6.2a)$$

$$K^{(o)} = 2\omega D B^* \rho \left[\frac{a^{\dagger}}{b^{\dagger}} (2\omega)^6 + 1 \right] \quad (6.16)$$

Determination of Design Constants

The equations listed above are most useful when applied to the separation of binary mixtures for which all the required data on the physical properties including the ordinary and thermal diffusion coefficient are known. Under these conditions the application of the equations is straightforward as was shown in the design illustration.

In general, not many of the required physical data are available even for binary systems. This is especially true of thermal diffusion data. In this more general case the terms a , a' , b' and $K^{(o)}$ can be evaluated empirically from data taken with either the continuous-flow or the batch-type thermogravitational column.

In treating continuous-flow thermogravitational-column data, values of $H^{(o)}$ and $K^{(o)}$ would be obtained by using Eqs. (4.48) and (5.2) as described in Chapter V. Values of $H^{(o)}$ and $K^{(o)}$ for batch columns are obtained from data on the approach to steady state in the column by applying the transient-state equations summarized by JF.⁴⁷ (See appendix for one example - see also Nier.¹⁶²) In either case, these $H^{(o)}$ and $K^{(o)}$ values can be used to determine a , a' and b' by applying Eqs. (6.3) and (6.4). Constants a' and b' can be determined from Eq. (6.4) by making several determinations at two different plate spacings.

In light of the results presented in Chapter V it would appear that determination of $H^{(o)}$ and $K^{(o)}$ values to be used in any final design should be made in an apparatus with the same plate spacing (2ω) as that to be used in the plant. Further, when these constants are determined empirically, this design procedure can be applied also to the treatment of multicomponent mixtures.

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APPENDIX

Calculation of Empirical Values of

$K^{(o)}$ and $H^{(o)}$ for Batch Thermogravitational Columns

(Data of Trevoy and Drickamer⁷¹)

Empirical values of $K^{(o)}$ and $H^{(o)}$ can be obtained from data on the approach to steady state in batch thermogravitational columns by utilizing the equations of Furry, Jones and Onsager.³¹ For a batch column with reservoirs of equal volume V at both ends in which liquid solutions of approximately equal molal concentration ($C_1 C_2 \approx 1/4$)* are being separated the following equations apply:

Rate of approach to equilibrium

$$\Delta_o(t) = \Delta_o(\infty) \left[1 - e^{-t/t_r} \right] \quad (A.1)$$

Empirical value of $K^{(o)}$

$$K_{\text{Expt.}}^{(o)} = \frac{V L_T}{2 \left[t_r \right]_{\text{Expt.}}} \quad (A.2)$$

Empirical value of $H^{(o)}$

$$H_{\text{Expt.}}^{(o)} = \frac{4 \Delta_o K_{\text{Expt.}}^{(o)}}{L_T} \quad (A.3)$$

Thus by determining a value of $\left[t_r \right]_{\text{Expt.}}$ from data on the approach to steady state in a column, empirical $K^{(o)}$ and $H^{(o)}$ values can be obtained.

*See reference 47 for other cases.

Trevoy and Drickamer⁷¹ operated such a column and found $\left[t_r \right]_{\text{Expt.}} = 936$ seconds. Using a theoretical value of $K^{(o)}$ calculated from Eq. (4.38a) they obtained $\left[t_r \right]_{\text{calc.}} = 379$ seconds from Eq. (A.2). From Eq. (5.5) and Eq. (A.2)

$$\phi_K(o) = \frac{\left[t_r \right]_{\text{Calc.}}}{\left[t_r \right]_{\text{Expt.}}} \quad (\text{A.4})$$

from which a value of $\phi_K(o) = 0.40$ was calculated. This value is represented by a solid black triangle in Figures 28 and 30.

Calculation of ϕ Values

Used in the General Correlation

(Data of Drickamer, Mellow and Tung⁹⁹)

Data on the separation of gas mixtures in batch thermogravitational columns published by Drickamer, Mellow and Tung⁹⁹ have been used in obtaining the general correlation (Figure 30). As explained in Chapter V, only data obtained at pressures greater than that required for maximum separation were considered. Data listed by Drickamer, Mellow and Tung include values of $\bar{T}$, P , ρ , q , ΔT , α' and $\underline{\alpha}$ for each experiment. Values of α' were calculated by the authors by using the relation

$$\alpha' = \frac{K_{\text{Calc.}}^{(o)} \ln q}{(H^{(o)}/\alpha)_{\text{Calc.}} L_T} \quad (\text{A.5})$$

obtained from Eq. (4.49) and $\underline{\alpha}$ values were calculated by applying the corrections suggested by Drickamer, Mellow and Tung.⁹⁹ Values of ϕ that were used in the general correlation were calculated using Eq. (A.6) that was obtained by combining Eqs. (A.5) and (5.14):

$$\phi = \frac{\alpha_{\text{actual}}}{\alpha'} \quad (\text{A.6})$$

The α_{actual} values used in the correlation are listed in Table X and in general correspond to values calculated from gas theory or measured by the static method.

SUMMARY OF THE STEADY STATE SOLUTIONS OF THE TRANSPORT
EQUATION PREVIOUSLY PRESENTED BY R. C. JONES AND W. H. FURRY⁴⁷

Continuous Flow Operation

Transport Equation

$$\sigma_e (C_e - \bar{C}_1) = H\bar{C}_1\bar{C}_2 - K \frac{d\bar{C}_1}{dy} \quad (4.42)$$

Exact General Solution (One section only)*

$$\tanh \frac{1}{2} b^1 \varepsilon = \frac{b^1 (C_e - C_i)}{C_e + C_i - 2C_e C_i - n(C_e - C_i)} \quad (A.7)$$

where

$$b^1 = \left[(1+n)^2 - 4nC_e \right]^{1/2}, \quad (A.8)$$

$$\varepsilon = \frac{HL}{K}, \text{ and}$$

$$n = \frac{\sigma_e}{H}$$

Solution for $C_1 C_2 \approx \frac{1}{4}$ (One section only)*

$$C_e - \bar{C}_i = (1 - e^{-n\varepsilon})/4n \quad (A.9)$$

Solution for $C_1 \ll 1$ (One section only)*

$$\bar{C}_i/C_e = (e^{-\varepsilon(1+n)} + n)/(1+n) \quad (A.10)$$

Solution for $C_1 \approx 1$ (One section only)*

$$\frac{(1 - \bar{C}_i)}{(1 - \bar{C}_e)} = (e^{\varepsilon(1-n)} - n)/(1-n) \quad (A.11)$$

*In order that these formula apply to the other section (the stripper or scrubber) it is necessary only to substitute $1-C_i$ for C_i , C_s for $1-C_e$ and σ_s for σ_e .

The General Linear Approximation (One section only)*

$$C_e = \frac{(1 - r - s + n) \bar{C}_i + rs \left\{ 1 - \exp. [-y(1 - r - s + n)] \right\}}{n + (1 - r - s) \exp. [-y(1 - r - s + n)]} \quad (A.12)$$

r and s are values of C_1 differing in value by no more than 0.2 and defining the range of C_1 encountered in the column.

The case of multistage apparatus has been extensively reviewed by JF and the reader is referred to their excellent review article⁴⁷ for further details.

*In order that these formula apply to the other section (the stripper or scrubber) it is necessary only to substitute $1 - C_i$ for C_i , C_s for $1 - C_e$ and σ_s for σ .

OPTIMUM DESIGN EQUATIONS

(Results of Krasny-Ergen¹⁶⁵)

Case of $C_1 \ll 1$ (One section only)

Optimum Plate Spacing ($2^*\omega$)

$$(2^*\omega)^7 - 5 \frac{b^i}{a^i} (2^*\omega) - 6 \frac{b^i}{a^i} \frac{p_c}{s} = 0 \quad (6.10)$$

where

$$\frac{b^i}{a^i} = 9 \left(\frac{D\eta}{\beta_T g \cos \Theta \Delta T} \right)^2 \quad (6.14)$$

Optimum Column Width (β^*)

$$\beta^* = \frac{\sigma}{n^* a (2\omega)^3} \quad (A.13)$$

where

$$a = \frac{\alpha \beta_T \rho g \cos \Theta (\Delta T)^2}{6 \eta \bar{T}} \quad \text{and} \quad (6.15)$$

n^* is the root of the equation

$$\left(\frac{C_i}{C_e} - 1 \right) n^* (1+n^*) = (1+2n^*) \left[(1+n^*) \frac{C_i}{C_e} - n^* \right] \ln \left[(1+n^*) \frac{C_i}{C_e} - n^* \right].$$

Column Length (L_e)

$$L_e = \frac{2K}{H} \left(1 + \frac{b^i}{a^i (2\omega)^6} \right) X^i \quad (A.14)$$

$$\text{where } X^i = \left\{ - \ln \left[(1+n^*) \frac{C_i}{C_e} - n^* \right] \right\} / 2 (1+n^*) \quad (A.15)$$

The terms n^* and X' are listed below as functions of C_e^*/C_i :

C_e/C_i	n^*	X'	C_e/C_i	n^*	X'	C_e/C_i	n^*	X'
2	0.745	0.59	7	0.133	1.56	12	0.074	1.92
3	0.381	0.91	8	0.115	1.67	13	0.068	1.97
4	0.259	1.14	9	0.101	1.74	14	0.063	2.06
5	0.197	1.37	10	0.090	1.80	15	0.060	2.16
6	0.159	1.46	11	0.081	1.86			

TABLE I

SEPARATION AND FLOW RATE MEASUREMENTS FOR THE SYSTEM ETHYL ALCOHOL-WATER

Exp. No. and Grp.	σ_e Top Product Flow Rate	σ_s Bottom Product Flow Rate	σ $\frac{\sigma_e + \sigma_s}{2}$	C_e Top Product Comp.	C_s Bottom Product Comp.	Δ $C_e - C_s$	ΔT Temp. Diff.
-	<u>Grams</u> min.	<u>Grams</u> min.	<u>Grams</u> min.	Weight Frac. EtOH	Weight Frac. EtOH	Weight Frac. EtOH	°C
3-B	0.159	0.123	0.141	.4109	.3873	.0236	32.6
4-B	0.290	0.285	0.2875	.4088	.3845	.0243	32.3
5-B	0.97	1.37	1.17	.4141	.3903	.0238	32.3
6-B	1.99	2.55	2.27	.4110	.3903	.0207	32.4
7-B	0.99	0.81	0.90	.4074	.3845	.0229	32.3
8-B	3.11	2.94	3.02	.4061	.3875	.0186	32.3
9-C	0.93	1.19	1.06	.4071	.3872	.0199	20.2
10-D	0.80	0.85	0.825	.4033	.3907	.0126	8.45
11-E	1.10	1.00	1.05	.4000	.3952	.0048	4.03
14-B	8.50	8.95	8.725	.4034	.3907	.0127	32.3
15-B	27.80	29.50	28.65	.3982	.3961	.0021	32.3
16-D	2.38	2.80	2.59	.3990	.3944	.0046	8.05
17-D	0.15	0.42	0.285	.4046	.3879	.0167	8.05
18-E	0.44	0.45	0.445	.4005	.3903	.0102	4.03
19-D	0.39	0.40	0.395	.4037	.3878	.0159	8.05
20-C	0.45	0.45	0.45	.4074	.3849	.0225	20.2
21-A	0.47	0.51	0.49	.4087	.3829	.0258	44.3
22-A	3.05	2.99	3.02	.4078	.3841	.0237	44.3
23-A	8.9	8.1	8.5	.4047	.3877	.0170	44.3
24-A	34.2	34.5	34.35	.3983	.3957	.0026	44.3
25-C	8.3	8.1	8.2	.4008	.3936	.0072	20.2
26-E	0.11	0.061	0.0855	.4051	.3898	.0153	4.03
27-C	0.113	0.12	0.1165	.4084	.3833	.0251	20.2
28-A	0.113	0.123	0.118	.4080	.3804	.0276	44.3
29-B	0.113	0.114	0.1135	.4091	.3833	.0258	32.3
30-B	2.76	2.55	2.65	.4064	.3865	.0199	32.3
31-D	2.64	2.62	2.63	.3993	.3946	.0047	8.05
32-C	2.32	2.53	2.42	.4050	.3897	.0153	20.2
33-A	2.23	1.98	2.10	.4090	.3848	.0242	44.3
34-B	1.144	1.069	1.106	.4164	.3717	.0447	34.85
35-G	1.114	1.044	1.079	.4050	.3816	.0234	21.05
36-I	1.128	0.592	0.860	.3943	.3920	.0023	7.55
37-G	2.941	2.66	2.801	.3954	.3921	.0033	20.60
39-I	0.419	0.341	0.380	.3977	.3900	.0077	7.55
40-G	0.419	0.341	0.380	.4125	.3755	.0370	20.5
41-F	0.410	0.340	0.375	.4279	.3592	.0687	31.9
42-F	5.692	7.608	6.650	.3940	.3926	.0014	31.55
43-F	0.0467	0.0253	0.0360	.4832	.3322	.1510	31.50

TABLE I

(-2-)

Exp. No. and Grp.	σ_e	σ_s	σ	C_e	C_s	Δ	ΔT *
44-G	0.0319	0.0241	0.0280	.4730	.3348	.1382	20.55
45-I	0.180	0.0145	0.0163	.4334	.3417	.0917	7.55
46-I	0.1067	0.0637	0.0852	.4022	.3791	.0231	7.5
47-G	0.120	0.117	0.118	.4354	.3517	.0837	20.96
48-F	0.120	0.125	0.122	.4571	.3363	.1208	31.5
49-F	0.363	0.333	0.348	.4243	.3512	.0731	31.35
50-G	0.343	0.354	0.349	.4095	.3686	.0409	20.77
51-H	0.321	0.325	3.23	.4019	.3767	.0252	14.7
52-H	0.086	0.111	0.0985	.4191	.3623	.0568	14.7
53-H	1.165	1.095	1.13	.3957	.3858	.0099	14.65
54-G	0.95	0.893	0.922	.3990	.3791	.0199	20.7
55-F	0.835	0.875	0.855	.4075	.3719	.0356	31.0
56-H	0.86	0.96	0.91	.3963	.3836	.0127	14.8
57-F	2.546	2.87	2.708	.3928	.3867	.0061	30.8
58-F	0.025	0.014	0.0195	.5056	.3227	.1829	31.2
61-J	2.94	2.70	2.82	.4141	.3914	.0227	36.8
62-K	0.343	0.27	0.307	.4136	.3888	.0248	17.5
63-J	9.475	8.65	10.45	.4038	.3920	.0118	35.85
			8.45	.4060	.3934	.0126	
64-J	27.23	26.9	27.065	.4004	.3991	.0013	34.6
65-J	0.892	1.01	0.951	.4149	.3860	.0289	35.3
66-J	0.375	0.385	0.38	.4159	.3854	.0305	36.5
67-J	2.74	2.70	2.72	.4093	.3862	.0231	36.1
68-K	2.68	3.04	2.86	.4064	.3947	.0117	18.2
69-L	1.67	1.69	1.68	.4108	.3828	.0280	36.0
70-M	0.363	0.355	0.359	.4208	.3758	.0450	35.8
71-M	0.94	0.935	0.9375	.4180	.3796	.0384	34.85
72-M	2.765	2.74	2.75	.4131	.3868	.0263	34.85
73-M	10.066	0.077	9.572	.4041	.3957	.0084	35.4
74-M	18.867	20.8	19.83	.4009	.3992	.0017	35.5
75-M	0.121	0.1175	0.1193	.4262	.3749	.0513	35.5
76-M	2.525	2.46	2.493	.4144	.3858	.0286	35.6
77-N	0.116	0.1045	0.110	.4356	.3670	.0686	35.8
78-N	2.68	2.66	2.67	.4115	.3863	.0252	35.8
79-N	0.963	1.093	1.03	.4204	.3792	.0412	35.8
80-N	10.7	10.7	10.7	.4008	.3973	.0035	35.8
81-N	0.038	0.043	0.0405	.4442	.3654	.0788	35.0
82-L	0.0425	0.045	0.0435	.4208	.3824	.0384	35.2
83-O	2.725	2.35	2.54	.4083	.3892	.0191	35.4
84-O	0.042	0.031	0.037	.4605	.3542	.1063	35.5
85-O	0.306	0.30	0.303	.4380	.3627	.0753	35.6

*See first page of Table I for definitions and units.

TABLE I

(-3-)

Exp. No. and Grp.	σ_e	σ_s	σ_c	C_e	C_s	Δ	ΔT^*
86-O	0.020	0.020	0.020	.4609	.3479	.1130	35.4
87-P	0.0185	0.0135	0.016	.4426	.3536	.0890	32.8
88-P	2.52	2.46	2.49	.3986	.3976	.0010	32.8
89-P	0.220	0.220	0.220	.4009	.3922	.0087	32.7
90-P	0.0415	0.030	0.0358	.4110	.3753	.0357	32.7
91-L	0.415	0.390	0.402	.4143	.3768	.0375	35.4
92-L	10.0	9.40	9.7	.4014	.3908	.0106	35.3
93-L	24.7	23.9	24.3	.3976	.3958	.0018	35.0
94-Q	10.55	9.5	10.025	.3982	.3913	.0069	35.4
95-Q	0.79	0.773	0.782	.4001	.3892	.0109	35.3
96-Q	0.125	0.0895	0.107	.3992	.3874	.0118	35.1
97-Q	2.26	2.12	2.19	.4009	.3904	.0105	35.3
98-Q	0.2815	0.2175	2.495	.4002	.3886	.0116	35.2
99-Q	5.4	4.3	4.85	.4005	.3916	.0089	34.8
100-Q	24.0	24.85	24.42	.3976	.3948	.0028	35.0
101-Q	1.28	1.90	1.59	.4001	.3896	.0105	35.0
102-R	9.95	9.9	9.9	.4026	.3910	.0116	36.4
103-R	0.915	0.85	0.88	.4074	.3870	.0204	36.6
104-R	24.37	25.47	24.92	.3998	.3959	.0039	36.6
105-R	0.280	0.2805	0.280	.4100	.3860	.0240	37.5
106-R	2.85	2.795	2.82	.4074	.3882	.0192	37.3
107-R	46.6	47.3	47.0	.3977	.3974	.0003	36.8
108-R	9.8	8.5	9.2	.4036	.3917	.0119	37.3
109-R	0.84	0.83	0.835	.4098	.3859	.0239	37.5
110-R	0.12	0.10	0.11	.4109	.3857	.0252	37.5
111-S	1.71	1.47	1.59	.4090	.3851	.0239	35.7
112-S	16.63	15.27	15.95	.4019	.3954	.0065	35.7
113-S	33.30	34.81	34.06	.3991	.3982	.0009	36.2
114-S	43.02	45.23	44.13	.3990	.3984	.0006	35.7
115-S	6.73	6.200	6.47	.4053	.3910	.0143	35.7
116-T	0.027	0.038	0.032	.3977	.3948	.0029	31.5
117-T	0.50	0.65	0.58	.3991	.3965	.0026	31.2
118-U	2.76	2.85	2.80	.3992	.3980	.0012	31.2
119-U	0.0225	0.0255	0.0240	.4982	.3260	.1722	29.4
120-U	0.327	0.255	0.291	.4205	.3668	.0537	29.4
121-U	2.930	3.033	2.98	.3988	.3982	.0006	29.2
122-U	0.85	0.940	0.90	.4031	.3912	.0119	29.3
125-V	0.2205	0.258	0.239	.4022	.3960	.0062	35.5
126-V	9.7	7.2	8.45	.4013	.3978	.0035	35.8
127-V	0.814	0.964	0.889	.4014	.3969	.0045	35.5
128-V	16.6	15.9	16.25	.4006	.3983	.0023	35.6
129-V	42.8	44.2	43.5	.4000	.3988	.0012	35.6
130-V	22.3	25.9	24.1	.4002	.3988	.0014	35.6
131-V	0.219	0.2245	0.222	.4011	.3962	.0049	35.8
132-V	48.35	51.0	49.7	.4000	.3982	.0018	35.4
133-V	4.68	5.39	5.04	.4012	.3973	.0039	35.6
134-W	13.55	14.3	13.9	.3986	.3982	.0004	36.2
135-W	6.9	6.6	6.75	.4011	.3955	.0056	36.0

*See first page of Table I for definitions and units.

TABLE I

(-4-)

Exp. No. and Grp.	σ_e	σ_s	σ	C_e	C_s	Δ	ΔT *
136-W	0.52	0.67	0.595	.4206	.3798	.0408	36.0
137-W	2.175	2.29	2.233	.4121	.3878	.0243	36.0
138-W	0.0275	0.0145	0.021	.4221	.3706	.0515	35.9
139-W	0.853	0.814	0.834	.4087	.3893	.0194	18.0
140-X	2.90	2.63	2.76	.4019	.3973	.0046	18.15
141-X	6.09	5.55	5.82	.4000	.3992	.0008	18.03
142-X	0.042	0.035	0.038	.4203	.3746	.0457	18.12
144-Y	0.271	1.545	0.908	.4394	.3914	.0480	35.9
145-W	0.845	0.935	0.89	.4189	.3828	.0361	36.0
146-Y	0.615	1.225	0.920	.4250	.3856	.0394	36.0
147-Y	0.040	1.45	0.75	.4557	.3981	.0576	36.0
148-Y	1.475	0.294	0.885	.4075	.3744	.0331	35.7
149-W	9.75	8.95	9.35	.4000	.3981	.0019	35.8
150-W	3.55	3.875	3.71	.4060	.3914	.0146	35.9
151-W	6.3	6.5	6.4	.4012	.3965	.0047	36.2
152-W	12.55	12.4	12.48	.3988	.3996	.0008	35.8
164-W	0.018	0.034	0.026	.4210	.3693	.0517	35.15
168-Z	0.890	0.747	0.823	.3414	.3226	.0188	35.3
169-Z	2.27	1.80	2.03	.3378	.3272	.0106	35.4
170-Z	0.0413	0.0133	0.027	.3515	.3194	.0321	35.55
171-Z	0.2406	0.1183	0.179	.3506	.3200	.0306	35.4
172-Z	0.234	0.257	0.245	.3464	.3190	.0274	35.35
173-Z	5.55	5.375	5.46	.3346	.3320	.0026	35.65
174-Z	1.70	3.0	2.35	.3391	.3306	.0085	35.65
175-Z	6.465	7.09	6.78	.3339	.3330	.0009	35.05

*See first page of Table I for definitions and units.

TABLE II

SEPARATION AND FLOW RATE MEASUREMENTS FOR THE SYSTEM n-HEPTANE-BENZENE

Exp. No. and Grp.	σ_e Top Product Flow Rate	σ_s Bottom Product Flow Rate	σ $\frac{\sigma_e + \sigma_s}{2}$	C_e Top Product Comp. Mol Frac. nC ₇	C_s Bottom Product Comp. Mol Frac. nC ₇	ΔC_{es} Mol Frac. nC ₇	ΔT Temp. Diff. °C
177-BA	2.03	1.90	1.96	.528	.461	.067	38.9
178-BA	1.37	1.04	1.20	.529	.456	.073	38.9
179-BA	5.4	5.2	5.3	.516	.465 ₅	.050 ₅	38.9
180-BA	10.4	9.35	9.97	.511	.477 ₅	.034 ₅	38.4
181-BA	0.46	0.51	0.485	.543	.458	.085	38.4
182-BA	2.6	2.6	2.6	.528	.463	.065	38.2
183-BA	8.2	7.4	7.8	.511	.472	.039	38.3
184-BA	18.2	22.8	20.5	.501 ₃	.486 ₇	.014 ₆	38.3
186-BB	1.45	1.90	1.67	.531	.482	.049	42.2
187-BB	8.7	9.2	8.95	.522	.487	.035	42.2
188-BB	0.37	0.52	0.44	.533	.478 ₅	.054 ₅	42.2
189-BB	24.5	22.0	23.2	.511 ₅	.495 ₃	.016 ₂	42.2
190-BB	36.2	37.2	36.7	.506 ₅	.499 ₅	.006 ₅	42.2
191-BB	14.7	14.9	14.8	.516	.490 ₅	.025 ₅	42.2
192-BB	50.0	50.5	50.2	.503	.501 ₅	.002 ₅	42.2
193-BC	9.5	9.9	9.7	.511	.490	.021	43.7
194-BC	1.9	1.8	1.85	.549	.452	.097	43.2
195-BC	14.7	14.2	14.4	.503 ₅	.493 ₅	.010	43.4
196-BC	0.21	0.41	0.31	.584	.437	.147	43.2
197-BC	0.73	6.2	6.75	.522	.476	.046	42.9
198-BC	3.65	3.75	3.76	.534	.465	.069	42.6
199-BC	20.1	19.7	19.9	.501	.496	.005	42.8
200-BC	0.86	0.90	0.88	.563	.435	.128	42.2

TABLE III

MEASURED VALUES OF COLUMN PARAMETERS

Grp.	Included Runs	Plate Spacing From Direct Measure 2 ω	Mean Temp. Diff. ΔT_m	Angle** From Vertical Θ	Total Column Height L_T	Column Width B	Feed Conc. C_F
		cm	°C	°	cm	cm	
A	21-24, 28, 33	-	44.3	+1.0	237.8	15.30	.3964-.3999
B	3-8, 14, 15, 29, 30, 34	-	32.4	"	"	"	"
C	9, 20, 25, 27, 32	-	20.2	"	"	"	"
D	10, 16, 17, 19, 31	-	8.13	"	"	"	"
E	11, 18, 26	-	4.0	"	"	"	"
F	41-43, 48, 49, 55, 57, 58	0.1022-0.0617*	31.3	"	"	"	.3913
G	35, 37, 40, 44, 47, 50, 54	"	20.8	"	"	"	"
H	51-53, 56	"	14.7	"	"	"	"
I	36, 39, 45, 46	"	7.54	"	"	"	"
J	61, 63-67	0.1484-0.1283*	35.8	"	"	"	.3960-.3989
K	62, 68	"	17.9	"	"	"	"
L	69, 82, 91-93	0.1283-0.1140*	35.4	+1.0	"	"	"
M	70-76	"	35.3	+45.0	"	"	"
N	77-81	"	35.4	+60.0	"	"	"
O	83-86	"	35.3	+70.0	"	"	"
P	87-90	"	32.7	-45.0	"	"	"
Q	94-101	0.1356-0.1344*	35.2	+1.0	115.8	15.32	.3933-.3962
R	102-110	0.1454-0.1378*	37.0	"	237.8	15.30	.3977
S	111-115	0.1344†	35.9	"	"	"	.3982
T	116-118	0.1320†	31.3	-45.0	"	"	.3982
U	119-122	0.0634-0.0622*	29.3	+1.0	115.8	15.16	.3982
V	125-133	0.1928†	35.6	"	"	15.24	.3986
W	134-138, 145, 149-152, 164	0.0908†	36.0	"	"	15.17	.3986
X	139-142	0.0908†	18.1	+1.0	115.8	15.17	.3986
Y	144, 146-148	0.0908†	35.9	"	"	"	.3986
Z	168-175	0.0850†	35.4	"	"	"	.3322
BA	177-184	0.0813	41.1	"	"	"	.492
BB	186-192	0.1078†	42.1	"	"	15.59	.502
BC	193-200	0.0805†	43.0	"	"	15.66	.500

*Extremes of measured values

†Average value (Data self-consistent)

**Positive angles indicate hot plate on top.

TABLE IV

COLUMN HEAT LOAD

Expt. Nos. Incl.	Water Stream	ΔT Water Temp. Drop Thru Column	W Water Flow Rate	Q Heat Trans. From (to) Water	Q_L Heat Losses	Q_{WS} Heat Trans. Thru Work'g Space	$\frac{2W}{A\Delta T}$ Column Dimen- sions	k_T	$(k_T)_{ave}$ Measured Thermal Conductivity
		$^{\circ}C$	$\frac{\#}{sec}$	$\frac{BTU}{sec}$	$\frac{BTU}{sec}$	$\frac{BTU}{sec}$	$\frac{1}{ft^{\circ}F}$	$\frac{BTU}{hr ft^{\circ}F}$	$\frac{BTU}{hr ft^{\circ}F}$
119-122	H	0.89	3.32	5.32	1.84	3.48	2.02×10^{-5}	0.253	
									0.280
	C	0.91	3.35	5.49	1.27	4.22	2.02×10^{-5}	0.307	
125-133	H	0.42	3.32	2.51	1.84	0.67	5.05×10^{-5}	0.122	
									0.158
	C	0.39	3.32	2.33	1.27	1.06	5.05×10^{-5}	0.193	
134-138	H	0.79	3.36	4.78	1.84	2.94	2.39×10^{-5}	0.253	
									0.254
	C	0.71	3.32	4.24	1.27	2.97	2.39×10^{-5}	0.256	
139-142	H	0.39	3.36	2.36	1.84	0.52	4.74×10^{-5}	0.089	
									0.120
	C	0.36	3.32	2.15	1.27	0.88	4.74×10^{-5}	0.150	
143-151	H	0.86	3.36	5.20	1.84	3.36	2.39×10^{-5}	0.289	
									0.280
	C	0.78	3.32	4.42	1.27	3.15	2.39×10^{-5}	0.271	

TABLE V

APPROACH TO STEADY STATE IN THE COLUMNS

Exp. No. and Group	t Time	C _e Top Product Composition	C _s Bottom Product Composition	Δ C _e -C _s	t _r Relaxation Time
	Hours	(Weight Fraction Ethyl Alcohol)			Hours
49-F	0	.4615	.3420	.1195	0.28
	0.43	.4525	.3400	.1125	
	0.62	.4555	.3420	.1135	
	0.90	.4496	.3440	.1056	
	1.15	.4496	.3460	.1036	
	1.37	.4496	.3480	.1016	
	1.67	.4466	.3480	.0986	
	4.16	.4320	.3520	.0800	
	12.33	.4295	.3560	.0735	
	12.49	.4277	.3543	.0734	
	23.5	.4295	.3540	.0755	
	23.8	.4258	.3516	.0742	
	24.5	.4228	.3510	.0718	
	25.3	.4265	.3560	.0705	
	∞			.0715	
50-G	0			.0715	3.15
	0.66	.4212	.3645	.0567	
	1.42	.4238	.3603	.0635	
	1.84	.4212	.3625	.0587	
	2.55	.4185	.3645	.0540	
	3.10	.4075	.3561	.0514	
	3.53	.4157	.3657	.0500	
	4.12	.4157	.3690	.0467	
	4.85	.4130	.3712	.0418	
	11.11	.4185	.3755	.0430	
	11.50	.4185	.3755	.0430	
	12.0	.4100	.3685	.0415	
	12.6	.4155	.3755	.0400	
	21.6	.4155	.3735	.0420	
	21.8	.4107	.3681	.0426	
	22.6	.408	.3692	.0388	
	∞			.0400	
51-H	0			.0400	1.4
	0.167	.4157	.3755	.0402	
	0.667	.4100	.3755	.0345	
	1.167	.4075	.3755	.0320	
	1.667	.4050	.3755	.0295	
	2.16	.4050	.3755	.0295	
	3.16	.3995	.3755	.0240	
	3.70	.4025	.3755	.0270	
	4.30	.3995	.3755	.0240	
	4.80	.4025	.3755	.0270	

TABLE V
(2)

Exp. No. and Group	t	C _e	C _s	Δ	t _r *
51-H	7.42	.4075	.3800	.0275	1.4
	7.75	.4027	.3767	.0260	
	8.8	.4018	.3774	.0244	
	9.3	.4012	.3767	.0245	
	∞			.0250	
53-H	0	.4267	.3667	.0600	0.83
	.28	.4210	.3712	.0498	
	.52	.4130	.3755	.0375	
	.75	.4075	.3778	.0297	
	1.07	.4050	.3825	.0225	
	1.49	.4025	.3850	.0175	
	2.02	.4025	.3900	.0125	
	2.48	.4025	.3945	.0080	
	3.28	.4025	.3954	.0071	
	3.5	.3964	.3863	.0101	
	4.0	.3955	.3858	.0097	
	4.3	.3962	.3863	.0101	
	∞			.0080	
58-F	0	.3927	.3867	.0060	10.05
	3.0	.4266	.3734	.0532	
	6.0	.4322	.3604	.0718	
	18.75	.4878	.3342	.1536	
	20.0	.4910	.3342	.1568	
	21.4	.4970	.3342	.1628	
	22.6	.5000	.3302	.1698	
	30.8	.5030	.3283	.1747	
	31.00	.5083	.3265	.1818	
	31.16	.5056	.3265	.1791	
	51.33	.5056	.3227	.1829	
	51.35	.5056	.3227	.1829	
	∞	.5056	.3227	.1829	
78-N	0	.4361	.3670	.0691	0.90
	1	.4190	.3784	.0406	
	1.78	.4139	.3837	.0302	
	2.48	.4120	.3850	.0270	
	3.52	.4114	.3863	.0251	
	∞	.4115	.3863	.0252	
85-O	0	.4615	.3536	.1079	2.3
	1.05	.4548	.3555	.0993	
	2.00	.4468	.3577	.0891	
	2.97	.4401	.3601	.0800	
	3.85	.4401	.3607	.0794	
	4.84	.4388	.3622	.0766	
	7.30	.4380	.3627	.0753	
	∞	.4380	.3627	.0753	

*See first page of Table V for definitions and units.

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TABLE V
(3)

Exp. No. and Group	t	C _e	C _s	Δ	t _r *
88-P	0	.4442	.3535	.0907	0.47
	.59	.4016	.3713	.0303	
	1.59	.3997	.3960	.0037	
	2.68	.3991	.3971	.0020	
	3.73	.3986	.3977	.0009	
	∞	.3986	.3976	.0009	
119-U	0	.3981	.3981	0	7.8
	1.1	.4185	.397	.0215	
	3.2	.4275	.3775	.0500	
	5.8	.4585	.3605	.0980	
	11.5	.4765	.3425	.1340	
	21.0	.4495	.3340	.1155	
	22.2	.4495	.3340	.1155	
	26.2	.4875	.3340	.1535	
	29.2	.4795	.3340	.1455	
	30.3	.4910	.3325	.1585	
	30.5	.4990	.3254	.1736	
	35.3	.4970	.3340	.1630	
	35.4	.4975	.3267	.1708	
	∞	.4982	.3260	.1722	

*See first page of Table V for definitions and units.

TABLE V
(4)

APPROACH TO STEADY STATE IN THE COLUMNS

Exp. No. and Group	t Time	C _e Top Product Composition	C _s Bottom Product Composition	Δ C _e - C _s	t _r Relaxation Time
	Hours	(Mol Fraction n-Heptane)			Hours
181-BA	0	.511	.477	.034	.07
	0.2	.554	.473	.0810	
	0.5	.553	.471	.0820	
	0.8	.55	.467	.0830	
	1.4	.543	.464	.0790	
	2.6	.545	.4615	.0835	
	2.9	.543	.463	.0800	
	3.2	.543	.4585	.0845	
	3.7	.545	.458	.0870	
	∞	.543	.458	.085	
196-BC	0	.5035	.4935	.010	.26
	0.2	.532	.457	.0750	
	0.3	.5525	.448	.1045	
	0.6	.574	.4365	.1375	
	0.8	.5825	.436	.1465	
	1.1	.584	.4365	.1475	
	1.57	.583	.4365	.1465	
	∞	.584	.437	.1470	

TABLE VI

Measurements Made with 0.1 N HCl in the Glass Diaphragm Cell

T_h	T_c	Time Hour	C_h Normality	C_c	α^+
315.1	305.1	31	.0983	.1007	-.747
315.5	305.6	67	.0990	.1013	-.727
315.2	306.1	70	.0988	.1005	-.587
$+ \quad \alpha = \frac{\ln (C_h/C_c)}{\ln (T_h/T_c)}$					

TABLE VII

Measurements Made with 40 wt % Ethyl Alcohol - Water
in the Glass Diaphragm Cell

T_h	T_c	Time Hour	Interferometer Reading	$C_h - C_c$ Weight Fraction	α^*
326.7	317.2	23	50	.00035	.047
327.1	317.4	96	74	.00060	.079
<p>* $\alpha = 4T \Delta C / \Delta T$</p>					

TABLE VIII

Values of Physical Properties Used in the Calculations

System		Fraction	Aver. Temp.	Density	$-\frac{\partial \rho}{\partial T}$	Diff. Coef.	Coef. of Viscosity		
A	B	A	$\bar{T}$	ρ	$\beta \times 10^4$	$D \times 10^5$	η	k_T	C_P
-	-	-	°K	$\frac{\text{gm}}{\text{cm}^3}$	$\frac{\text{gm}}{\text{cm}^3 \cdot ^\circ\text{C}}$	$\frac{\text{cm}^2}{\text{sec}}$	centi- poise	$\frac{\text{BTU}}{\text{hr. ft. } ^\circ\text{F}}$	$\frac{\text{BTU}}{\text{lb. } ^\circ\text{F}}$
EtOH	H ₂ O	.3986 ^a	322.1	.9133 ^c	8.11	1.04 ^e	1.14 ^d	0.229 ^h	0.953 ^d
EtOH	H ₂ O	.3913 ^a	322.1	.9150 ^c	8.08	1.06 ^e	1.12 ^d		
EtOH	H ₂ O	.3322 ^a	322.1	.9273 ^c	7.80	1.262 ^e	1.09 ^d	0.252 ^h	0.988 ^d
n- Heptane	Benzene	.500 ^b	315.4	.7363 ^d	9.44	3.21 ^f	0.351 ^g	0.086 ⁱ	0.48 ⁱ

a Weight Fraction

b Mole Fraction

c References 154 and 155

d Reference 154

e References 156, 157 and 158

f Reference 160

g Reference 159

h Reference 168

i Reference 153

TABLE IX

Values of $K^{(o)}$, $H^{(o)}$, $\phi_{K_c}^{(o)}$ and $\phi_H^{(o)}$

Exp. Grp(s)	$K^{(o)}$ Expt.	$K^{(o)}$ Calc.	$\phi_{K_c}^{(o)}$	$H^{(o)}$ Expt.	$H^{(o)}$ Calc.	$\phi_H^{(o)}$
	$\frac{gm}{cm}$ sec	$\frac{gm}{cm}$ sec	-	$\frac{gm}{sec}$	$\frac{gm}{sec}$	-
A-E	$1.08 \times 10^{-2} (\Delta T)^2$	-	-	$4.72 \times 10^{-6} (\Delta T)^2$	-	-
F-I	$3.31 \times 10^{-4} (\Delta T)^2$	-	-	$1.072 \times 10^{-6} (\Delta T)^2$	-	-
J-K	$7.82 \times 10^{-3} (\Delta T)^2$	-	-	$4.12 \times 10^{-6} (\Delta T)^2$	-	-
L-O	$6.70 \cos^2 \theta$			$4.20 \times 10^{-3} \cos \theta$		
P	-	-	-	-	-	-
Q	7.49	18.10	0.413	3.16×10^{-3}	6.70×10^{-3}	0.472
R	9.90	24.50	0.404	4.27×10^{-3}	7.94×10^{-3}	0.538
S	8.12	19.1	0.425	3.82×10^{-3}	7.14×10^{-3}	0.535
T	-	-	-	-	-	-
U	6.66×10^{-2}	5.66×10^{-2}	1.18	5.07×10^{-4}	4.53×10^{-4}	1.12
V	21.0	228.5	0.092	2.91×10^{-3}	19.78×10^{-3}	0.147
W	1.04	1.17	0.890	1.88×10^{-3}	2.10×10^{-3}	0.895
Y	-	1.17	-	-	2.10×10^{-3}	0.895
Z	0.606	0.606	1.00	6.94×10^{-4}	6.94×10^{-4}	1.00
BB	8.16	18.2	0.448	1.55×10^{-2}	3.08×10^{-2}	0.504
BC	1.736	2.77	0.627	0.955×10^{-2}	1.42×10^{-2}	0.673

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NOTATION

a, a', a'' = general constants.

A = area of the working space in a thermogravitational column ($B \times L_T$).

B = column width when $B_e = B_s$.

B^* = optimum value of the column width, obtained from Eq. (6.13).

B_e, B_s = column width in the enriching section, stripping section.

b, b' = general constants.

C_1, C_2 = fraction of component 1, 2 in a binary solution.

$\bar{C}_1, \bar{C}_2$ = mean values of the fraction of component 1, 2 that are independent of x .

C_e, C_s = fraction of component 1 in the product stream exiting from the enriching section, stripping section.

C_F = fraction of component 1 in the feed stream.

$\bar{C}_1$ = mean value of fraction of component 1 in column at the feed point.

C_p = heat capacity at constant pressure.

Calc. = subscript used to indicate a value calculated from equations developed from theory.

D = ordinary diffusion coefficient.

E = parameter defined by Eq. (4.27) ($E = -\sigma$).

Expt. = subscript used to indicate a value obtained from experimental data.

e = subscript used to identify variables in enriching section ($y > 0$).

F = subscript used to identify feed properties.

FJO = Reference 31.

f = general functional notation.

$G(x)$ = relation defined by Eq. (4.11).

$G^*(x)$ = relation defined by Eq. (4.14).

$Gr\#$ = Grasshoff number defined by Eq. (5.12).

g = acceleration due to gravity.

H = parameter defined by Eq. (4.24) and evaluated by Eq. (4.37).

H_s = value of H that applies to the stripping section.

$H^{(o)}$ = H for a column with no net flow of material through the working space.

$h(\omega \gamma)$ = series appearing in Eq. (4.37).

$h_1(\omega \gamma)$ = use of the first term in the series defined by Eq. (4.37b).

I_1, I_2, I_3 = constants of integration.

i = subscript used to identify variables at the feed point ($y=0$).

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

J_{x-OD}, J_{y-OD} = flux of component 1 in the x, y direction due to ordinary diffusion.

JF = Reference 47.

$K = K_c + K_d + K_p$.

K_c = parameter defined by Eq. (4.25) and evaluated by Eq. (4.38).

$K_c^{(o)}$ = K_c for a column with no net flow of material through the working space.

K_d = parameter defined and evaluated by Eq. (4.26) or Eq. (4.39).

K_p = a term appended to the mathematical treatment to account for the effects of parasitic remixing.

K_s = value of K that applies to the stripping section.

$k(\omega \gamma)$ = series appearing in Eq. (4.38).

$k_5(\omega \gamma)$ = use of the first five terms in the series defined by Eq. (4.38b).

k_T = thermal conductivity.

L_e, L_s = length of the enriching, stripping section.

L_T = total column length.

$\ln$ = natural logarithm.

$m_o = (2 \Delta / 20) \sigma = 0$.

n = index number used in equation (4.38b).

P = pressure.

$$Pr\# = (\eta C_p / k_T).$$

p = a constant empirical term used in Eqs. (2.1) and (2.2) to account for the effects of parasitic remixing.

p_c = power costs per unit area (cm^2) per unit time (day) for an apparatus with transfer plates at unit distance (cm).

$$q = \text{equilibrium separation factor for a thermogravitational column, } \frac{C_e(1-C_s)}{C_s(1-C_e)}.$$

Re# = Reynold's number defined by Eq. (5.8).

S = amount of fixed charges per unit area (cm^2) per unit time (day).

$$Sc\# = (\eta / \rho D).$$

s = subscript used to identify variables in the stripping section ($y < 0$).

T = absolute temperature.

$\bar{T}$ = arithmetic average of the hot and cold plate temperatures.

t = time

t_r = relaxation time in a thermogravitational column.

V = volume of one reservoir in a batch thermogravitational column having reservoirs of equal volumes.

$v(x)$ = general velocity distribution function.

x = axis normal to the plates.

y = axis parallel to the plates in the direction of normal convective flow.

α = thermal diffusion "constant".

$\alpha_H(o)$ = value of α calculated from Eq. (4.37a).

$\alpha_{\Delta o}$ = value of α calculated from Eq. (4.48).

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

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

γ = parameter defined by Eq. (4.13) and evaluated by Eq. (4.41).

γ_s = parameter defined by Eq. (4.14) and evaluated by Eq. (4.45).

Δ = difference of concentrations at the ends of a thermogravitational column at steady state.

Δ_o = difference of concentrations at the ends of a thermogravitational column at steady state with no net flow of material through the working space.

$\Delta(t)$ = difference of concentrations at the ends of a thermogravitational column as a function of time.

ΔT = difference in temperature of the hot and cold plate.

ϵ = undefined length dimension.

η = coefficient of viscosity.

θ = angle of the plates of a thermogravitational column from the vertical.

λ = index number used in Eqs. (4.37b) and (4.38b).

π = total cost of operating a thermal diffusion plant per unit time (day).

ρ = density.

$$\bar{\sigma} = \frac{\sigma_e + \sigma_s}{2}$$

σ_e, σ_s = mass flow rate out the enriching, stripping section.

σ_F = mass flow rate of the feed stream.

ϕ = correction utilized by Drickamer et al (See Eq. (5.11a-c)).

ϕ' = correction utilized by Drickamer et al (See Eqs. (5.10a-c)).

$$\phi_H(o) = H_{\text{Expt.}}^{(o)} / H_{\text{Calc.}}^{(o)}$$

$$\phi_{K_c}(o) = [K_c^{(o)}]_{\text{Expt.}} / [K_c^{(o)}]_{\text{Calc.}}$$

ψ = dimensionless group defined by Eq. (5.13).

$\psi(y)$ = relation defined by Eq. (4.13).

ω = one-half of the distance between the plates of a thermogravitational column.

$2^*\omega$ = optimum value of the plate spacing obtained from Eq. (6.10).

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