A NEW COLUMN
FOR LIQUID THERMAL DIFFUSION

By

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ABSTRACT

A New Column for
Liquid Thermal Diffusion

The purpose of this thesis is to try a new idea for a liquid thermal diffusion column which would be of a larger capacity than that of any previous, and that perhaps would satisfy the demand for the application of this novel separation process on an industrial scale.

Since one of the most limiting factors in liquid thermal diffusion is its very small path, an attempt was made to increase the path thus increasing the corresponding capacity of the unit and facilitating the construction of industrial-size equipment.

The results of the experimental work justify the following conclusions:

1) The path of liquid thermal diffusion can be increased to at least four times that established by previous investigators limit.

2) The ratio of capacity to size of equipment can be increased by a factor of at least four.

3) This factor if compared with the Jones and Milberger column is increased by a factor of twenty or more.

4) The energy consumption is reduced to 13 times less than that of the Jones and Milberger column.

5) The position of the column affects the degree of separation and the order of arrangement of the various components.

6) The control of the column is very simple and does not require any skill or special attention during the operation.

INTRODUCTION

The thermal diffusion process refers to a transport phenomenon in which a concentration gradient is found in a homogeneous mixture when a gradient of temperature is maintained. This phenomenon was first observed one hundred years ago in liquids, but since then has been detected in solids and gases as well. In liquids it is often referred to as the Soret effect, in honor of one of its discoverers.

The thermal diffusion phenomenon results from the coupling of diffusion and heat conduction in much the same manner as the Peltier and Thomson effects are cross-phenomena involving heat and electrical conduction.

In general, whenever two or more irreversible processes (such as heat flow, diffusion, electric current, or shearing forces) occur simultaneously, they interact and give rise to new effects.

The inverse of thermal diffusion, - temperature difference arising when a concentration gradient exists -

usually called the Dufour effect, has also been observed.

In thermal diffusion no change of phase is involved. The principles which govern and limit thermal diffusion separations are completely different from those of distillation, solvent extraction, adsorption, or fractional crystallization. (Jones, 1953, p. 2689)

As a result of this difference, it is now possible to accomplish separations by means of this newly developed tool that have previously been considered either impossible or so difficult as to be impractical.

However the best equipment available up to now, has a very small capacity and thus the industrial application of thermal diffusion has not yet been achieved.

The research of this thesis is directed towards the development of a column which promises to provide a practical means for the industrial utilization of this highly important new process.

The first experimental evidence of thermal diffusion was that of Ludwig, in 1856, who used an inverted U-tube cooled by ice on one side and heated by boiling water on the other. Sodium sulfate crystallized from the solution at the cold end after several hours indicating an increased concentration of the salt on the cold side.

In 1879, Soret unaware of the previous work, found that salts in aqueous solutions tend to concentrate at the cold end of a vertical tube when the solution is subjected to a temperature gradient.

In 1890 Van Berchem and Arrhenius in 1898 reported studies on thermal diffusion of aqueous solutions of salts and dissolved gases.

Abeeg, in 1898, and Scarpa, in 1908, reported similar work a few years later, but their results, as well as the results of earlier investigators, are only qualitatively accurate because the duration of the runs was too short, convection was not always eliminated, and the temperatures were not accurately maintained.

Other investigations were made on a variety of organic and inorganic solutions by Eibert in 1914, Bruins in 1927, Chipman (Chipman, 1926m p. 2577), and Tunner (Tunner, 1927, p. 75).

Thermal diffusion in gases and solids has also received considerable attention. Balay in 1928 and Reinhold in 1929 have published data on thermal diffusion in metals and metallic salts. Chapman (Chapman, 1917, p. 248), Elliot and Masson (Elliot, 1925, p. 378), Lugg (Lugg, 1929, p. 1019), Blueh in 1934, Becker in 1947, and Drickamer et al (Drickamer, 1949, p. 408) have measured thermal diffusion in gases.

A theoretical derivation by Ensuog and Chapman in 1911 had predicted thermal diffusion in cases and preceded its verification experimentally.

All the thermal diffusion work thus far mentioned was accomplished in the so-called "convection-free cells" in which the separation occurs entirely by a diffusional process. In 1938 Clusius and Dickel discovered that by an appropriate combination of convection and thermal diffusion a tremendous improvement in separation was obtained. Their apparatus consisted of a vertical glass tube with electrically heated wire along its axis. A temperature gradient was thereby maintained between the hot wire and the cooled wall, with the light molecules diffusing towards the wire. In addition, a convection pattern is set up; the hot gas at the wire flows upward and the colder gas at the wall flows downward. With this ingenious method the effect of thermal diffusion sets up a horizontal concentration gradient with convection causing a gradient of concentration in the vertical direction.

Several modifications to improve column efficiency have been proposed by various investigators, but almost all of these can be placed into two general categories: vertical concentric tubes or vertical parallel flat plates.

This thesis then proposes a different column which is a multistage unit in the same sense that a fractionating tower is a combination of many batchwise distillations. It is intended primarily for liquids, though there is no reason why its use for gases is precluded.

In the development of this study, the technical discussion is organized in terms of the following:

Theory

Experimental Work

Discussion

Applications

THEORY

The most important theories advanced for the explanation and description of liquid thermal diffusion are four:

a) The Thermodynamics of Irreversible Processes

b) The Kinetic Theory

c) The Phenomenological Theory

d) Theory of Rate Processes

Since the subject of this thesis has nothing to do with the theoretical part of termal diffusion; we will here describe briefly only one of these theories, the Thermodynamics of Irreversible Processes, which happens to be the most widely accepted.

This theory, developed by E. L. Dougherty, Jr., and H. G. Drickamer (Dougherty, 1955, p. 295) is as follows:

Q_i is the heat of transport, i.e. the amount of energy transported across a given reference plane per mole of the ith component when no temperature gradient exists.

And Q_i^o is the net heat of transport equal to $Q_i - \bar{H}_i$; $\bar{H}_i$ is the partial molal enthalpy of the ith component in the solution.

The flux of component i in a multicomponent constant pressure system is

$$Ji = - \sum_{k=I}^{n} Lik \left[(Qk - \bar{H}k) \frac{\text{grad } T}{T} + \sum_{i=I}^{n-I} \frac{\partial \mu_k}{\partial x_i} \text{ grad } Xi \right] \qquad (I)$$

where

Ji = flux of component i, moles/cm^2 - hr

μk = chemical potential of component k

T = absolute temperature, ^{o}K

Xi = mole fraction of component i

Lik = phenomenological coefficient

In a steady-state concentration gradient resulting from a temperature gradient ($Ji=0 \quad i = I,2,\ldots$) in a binary system:

$$\frac{1}{Xi} \text{ grad } Xi = - \frac{Qi - Hi}{Xi(\partial \mu_1/\partial x_i)} \frac{\text{grad } T}{T} = \frac{- Q_i^{o}}{Xi(\frac{\partial \mu_i}{\partial x_i})} \frac{\text{grad } T}{T} \qquad (2)$$

and for component 2:

$$\frac{1}{X2} \text{ grad } Xi = \frac{- Q_2^{o}}{X_2 \left(\frac{\partial \mu_2}{\partial x_i}\right)} \frac{\text{grad } T}{T} \qquad (3)$$

Combining (2) and (3) and making use of the Gibbs-Duhem equation in the form

$$Xi \left(\frac{\partial \mu_i}{\partial x_i}\right) + X_2 \left(\frac{\partial \mu_2}{\partial x_i}\right) = 0 \qquad (4)$$

gives for the steady-state concentration gradient

$$\frac{1}{X_i X_2} \text{ grad } X_i = \frac{Q_2^o - Q_i^o}{X_i \left(\frac{\partial \mu_i}{\partial X_i}\right)} \; \frac{\text{grad } T}{T} \qquad (5)$$

The convention flux equation for a binary system is

$$J_i = -\rho D \left[\text{grad } X_i - \frac{\alpha X_i X_2}{T} \text{ grad } T \right] \qquad (6)$$

where

ρ = density

D = diffusion coefficient

α = thermal diffusion ratio, sT (s = Soret coefficient)

For the steady-state separation (6) gives

$$\frac{1}{X_i X_2} \text{ grad } X_i = \frac{\alpha \text{ grad } T}{T} \qquad (7)$$

Comparison with (5) gives the desired expression for α:

$$\alpha = \frac{Q_2^o - Q_i^o}{X_i \left(\frac{\partial \mu_i}{\partial X_i}\right)} \qquad (8)$$

When (7) is interpreted for a two-chamber cell, the following expression for α in terms of the steady-state separation is obtained

$$\ln \left(\frac{X_i}{X_2}\right)_{Hot} \left(\frac{X_2}{X_i}\right)_{Cold} = \alpha \ln \frac{T_{Hot}}{T_{Cold}}$$

Equation (4) yields the following relationship which the net heats of transport must satisfy:

$$X_i Q_i^o + X_2 Q_2^o = 0$$

EXPERIMENTAL WORK

Apparatus

The apparatus (Fig. 1) is a composite cell of total gap of 1 cm with partitions of dense filter paper in 2-mm spacings and containing packing of glass cloth (Glass Fabric Tape, Trevarno, Boat "A") for the elimination of the convection currents.

The packing is confined by brass or plastic rings of 14-cm ID, 15-cm OD, 2-mm height and having appropriate grooves where the filter paper is sealed into place thus making one closed compartment for every ring.

Inside the packing a spiral from 22-gage Nichrome wire is placed (Fig. 2) as a heating element. The length of this wire is 0 cm for the bottom, 60 cm for the next compartment, 80 cm for the middle, 125 cm for the next, and 200 cm for the top.

One terminal of the heating wire protrudes from the next to the bottom ring through an appropriate hole. The other terminal comes through a similar hole in the top ring. All resistances are connected in series through the compartments, and only one rheostat is needed.

By means of screws and winged nuts the assembly is pressed tightly into place between two brass plates of 5-mm thickness.

At the bottom, middle, and top rings holes are provided (Fig. 1 and 3) for the insertion of therocouples (I.C.) and hypodermic needles for feeding or sampling.

For better insulation, the second and fourth rings are made of plastic.

The capacity of the 5-ring column is about 120 ml.

The feed used throughout this work was 50% by volume mixture of tetralin and normal decane purified by fractionation.

The refractive index of tetralin and n-decane is 1.541 and 1.4118, at 20 C correspondingly, and the density 0.972 and 0.7301 at 20/4.

The feed is introduced very slowly at the bottom port and fills the apparatus after several hours. In this way most of the air bubbles are eliminated.

The mechanism of thermal diffusion in this apparatus is supposed to be a multistaged form of the convection-free cell picture. In each compartment, the molecules are

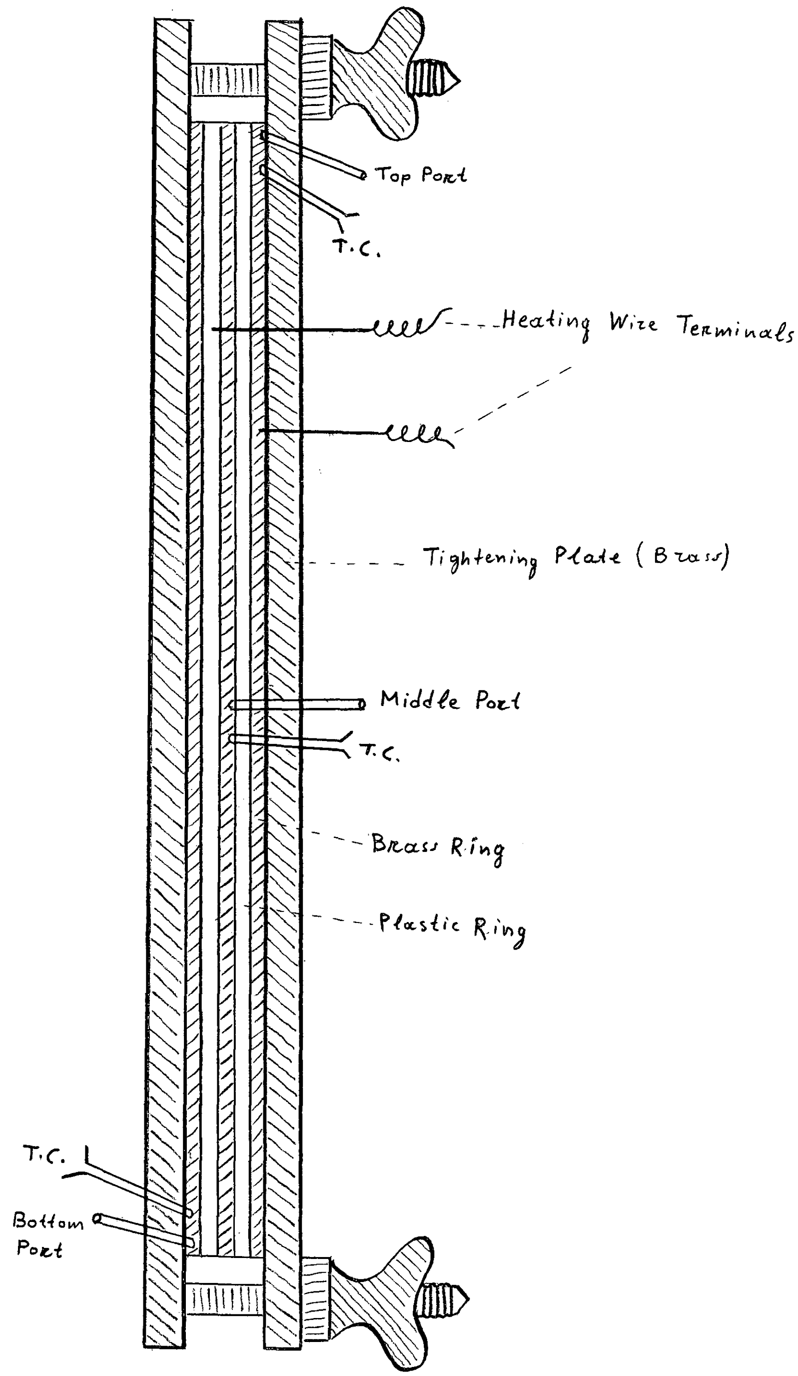

Figure 1

Outside View of the Apparatus.

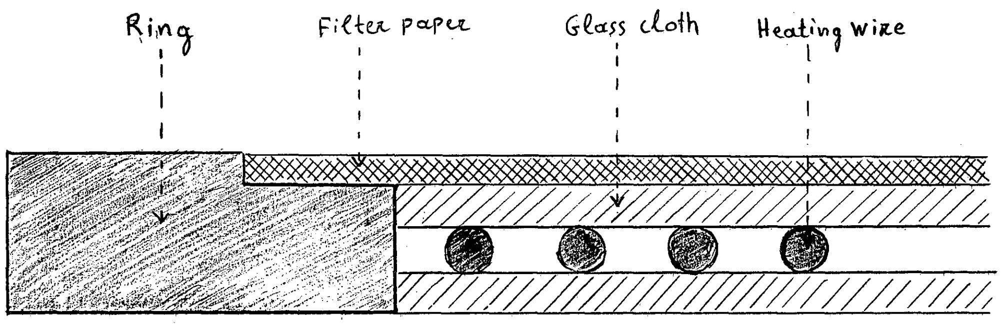

Figure 2

Magnified Cross-section of an Assembled Ring.

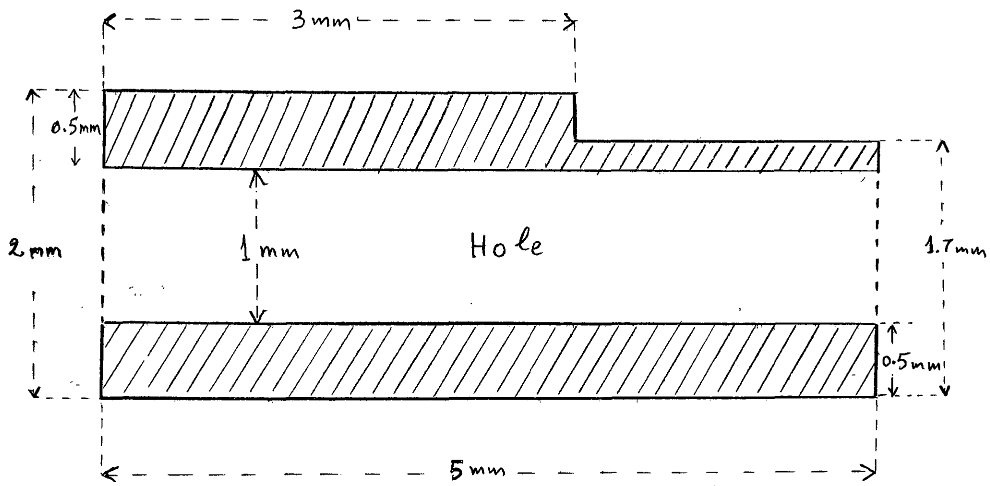

Figure 3

Magnified Cross-section of a Ring with a Hole.

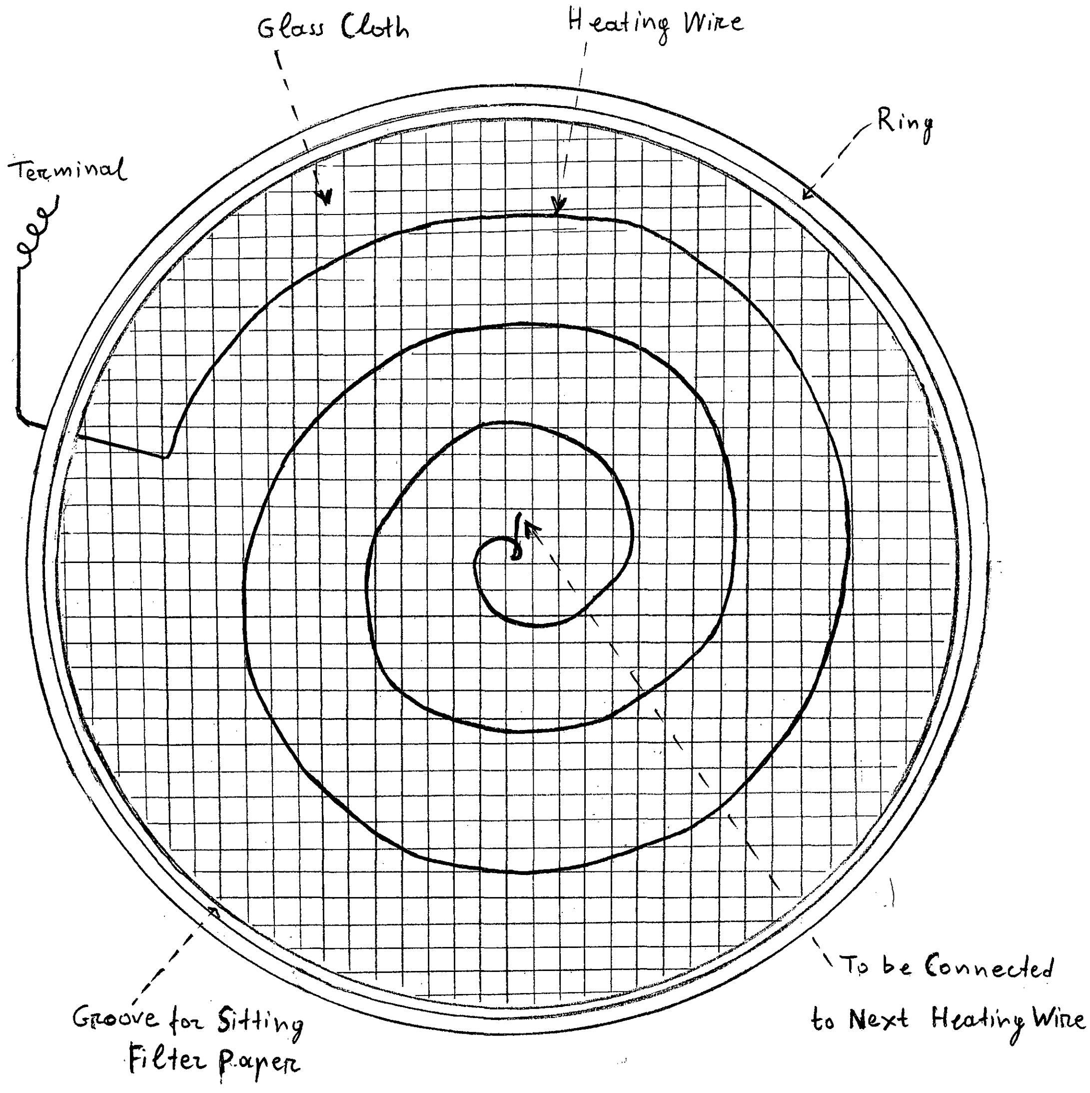

Figure 4

Exploded Inside View of a Ring

placed in a gradient of temperature; the ones migrating towards, say, the hot wall, enter through the filter paper in the next warmer compartment where again another temperature gradient gives them a second push towards the next warmer compartment, and so on. In this way, a continuous fractionation is taking place throughout the apparatus which acts as a column.

The above mechanism is good only for a horizontal position of the apparatus. When the column is in a vertical position gravitational forces are acting at right angles with thermal diffusion forces, and the separation is better.

Operation

A. The above described column was used at first in a horizontal position with the hot wall upwards and the cold wall downwards. The temperature of the top was approximately 135F and of the bottom 75F. The cooling was effected by placing the apparatus in running water in such a way as to keep only the bottom tightening plate wet. With the single exception of run shown in Table A3, two glass sheets were put in each ring. In Table A3 were put four.

Frpm time to time samples were drawn and the refractive indexes determined. From the difference in refractive index of the products, the percent separation was computed by the following formula:

Percent separation =

$$\frac{\text{Difference in refractive index of products X 100}}{\text{Difference in refractive index of pure materials}}$$

B. A similar apparatus was used, but the rings were all of plastic and the whole assembly was exactly fitted into a shallow glass vessel of 1 cm height and ID equal to the OD of the rings. The apparatus was placed in a horizontal position with the hot wall facing up and the cold wall facing down.

C. The same apparatus as in (A) was used in reversed position; the cold wall was up and the hot down. Dripping water and blown air at the outer surface of the top (tightening plate maintained a low temperature on the cold wall.

D. The same apparatus was placed in a vertical position in such a manner as to have the top port at the left, where the cold wall, and the bottom port at the right, where the hot wall. A woolen cloth attached at the cold wall was kept wet by dripping water and cool by air blown. In this way a constant low temperature was maintained (75F) on the cold wall; the temperature of the hot wall was again maintained at 135F.

E. The same column, in the same conditions, and in a vertical position but the top port was at the right where the hot wall, and the bottom port at the left where the cold wall.

F. The same column in the same conditions and position as in (D) was run in a continuous operation. The feed was introduced at the middle port and the products were collected from the top and bottom ports.

Data

The experimental data obtained in the above-mentioned runs are listed in the following tables marked with the corresponding letter-number.

TABLE A1 (Run No. 1)

Horizontal position, hot wall up. R.I. of feed = 1.475

Hours	R.I. of Top	R.I. of Middle	R.I. of Bottom	Percent Separation
2	1.479	1.475	1.473	4.7
6	1.481	1.475	1.471	7.8
15	1.4815	1.480	1.470	9.1
24	1.484	1.482	1.468	12.6
38	1.484	1.4752	1.467	13.

TABLE A2 (Run No. 2)

Horizontal position, hot wall up. R.I. of feed = 1.477

Hours	R.I. of Top	R.I. of Middle	R.I. of Bottom	Percent Separation
2	1.4805	1.477	1.473	6.
12	1.4843	1.477	1.4713	10.

TABLE A3 (Run No. 3)

Horizontal position, hot wall up. R.I. of feed = 1.475

Four glass sheets in each compartment.

Hours	R.I. of Top	R.I. of Middle	R.I. of Bottom	Percent Separation
2	1.4725	1.479	1.4733	5.1
8	1.471	1.485	1.4678	13.4
17	1.470	1.486	1.470	12.6
24	1.460	1.487	1.472	21.
36	1.453	1.481	1.484	24.5

TABLE B

Horizontal position, hot wall up. R.I. of feed = 1.475

All plastic rings fitted in a glass vessel.

	Hours	R.I. of Top	R.I. of Bottom	Percent Separation
Run 1	5	1.483	1.467	15.
Run 2	13	1.4866	1.4478	30.5
Run 3	6	1.489	1.442	37
Run 4	12	1.486	1.440	36

TABLE C

Horizontal position, hot wall down. R.I. of feed = 1.472

Hours	R.I. of Top	R.I. of Middle	R.I. of Bottom	Percent Separation
7	1.4712	1.473	1.4712	1.4
16	1.470	1.472	1.474	3.15
27	1.4698	1.4717	1.474	3.3

TABLE D

Vertical position, top port at cold wall.
R.I. of feed = 1.475

	Hours	R.I. of Top	R.I. of Middle	R.I. of Bottom	Percent Separation
Run 1	2	1.473		1.481	6.3
"	4	1.471		1.485	11.
"	6	1.468		1.488	15.8
Run 2	6	1.4677	1.476	1.482	11.
Run 3	6	1.465	1.475	1.486	16.6
Run 4	2	1.468	1.475	1.487	15.
"	4	1.465	1.475	1.489	19.

TABLE E1 (Run 1)

Vertical position, top port at hot wall.

R.I. of feed = 1.477

Hours	R.I. of Top	R.I. of Bottom	Percent Separation
2	1.478	1.476	2
8	1.479	1.477	2

TABLE E2 (Run 2)

Vertical position, top port at hot wall.

R.I. of feed = 1.475

Hours	R.I. of Top	R.I. of Middle	R.I. of Bottom	Percent Separation
4	1.473	1.4746	1.4763	2.5
9	1.473	1.4716	1.478	4

TABLE F

Vertical position, top port at cold wall.

R.I. of feed = 1.475

Continuous operation

	Hours	R.I. of Top	R.I. of Bottom	Percent Separation
	6	1.466	1.480	11.
Amount Collected		30 ml	30 ml	

A run was performed with the Jones and Milberger column using the same mixture as before with R.I. of feed 1.474. The feed was introduced at the middle and the products removed for R.I. determination from the bottom and top ports. The temperature difference was 60F. The data are shown in the Table G below.

TABLE G

Jones and Milberger Column

R.I. of feed = 1.474

Hours	R.I. of Top	R.I. of Bottom	Percent Separation
5	1.468	1.481	10.2
10	1.463	1.4855	17.7
15	1.460	1.4892	23.
20	1.4565	1.494	29.5

Figure 5 illustrates a comparison of Table G (obtained with the 186 cm high Jones and Milberger column) with Table D (obtained with the 14 cm high new column in a vertical position).

Figure 6 illustrates a comparison of Table A1, A2, and A3 with Table B.

Figure 7 illustrates a comparison of Table E1, and E2 with Table D. The superiority of results obtained in Table D is obvious.

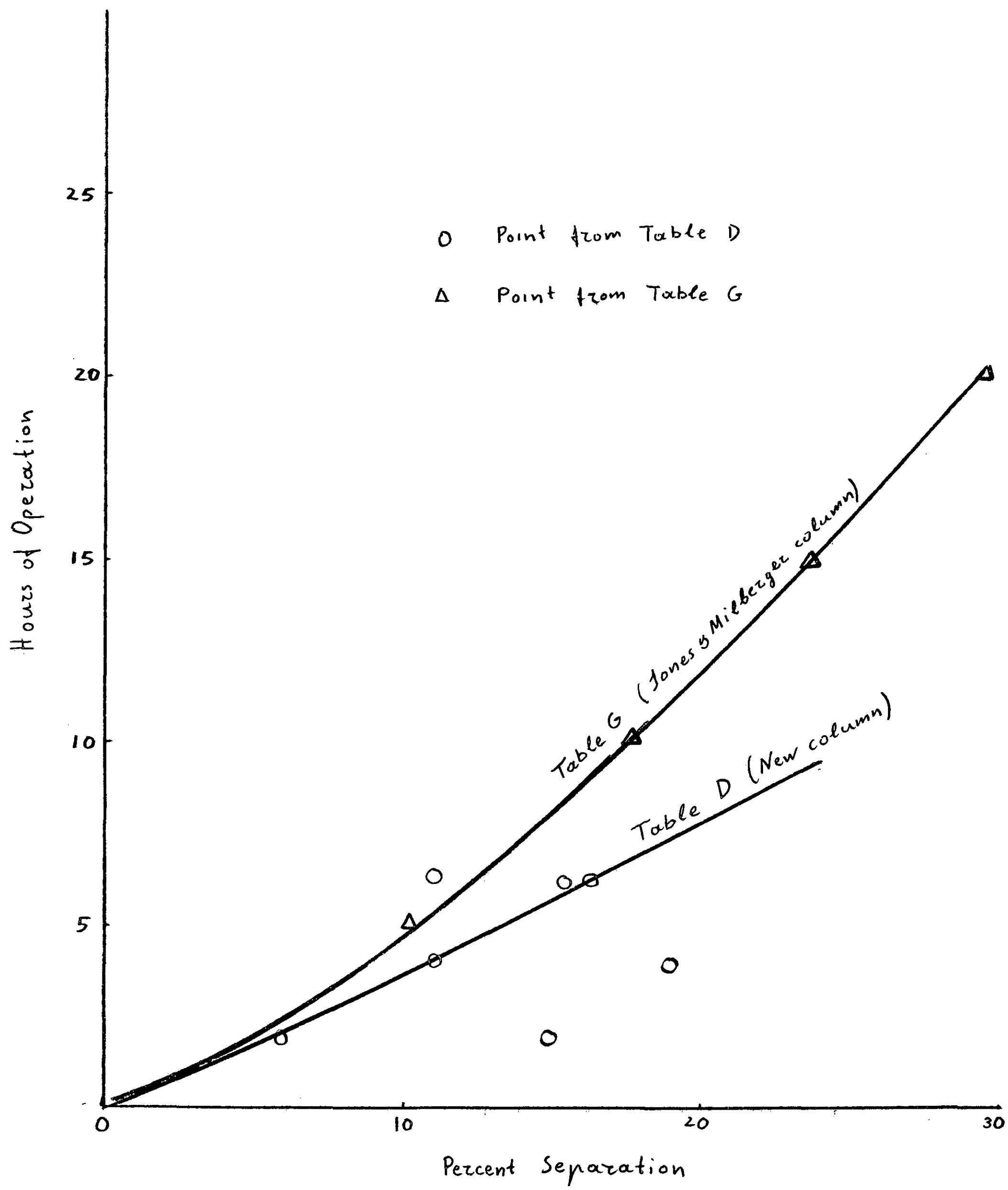

Figure 5

Comparison of Table D with Table G
(Jones and Milberger Column)

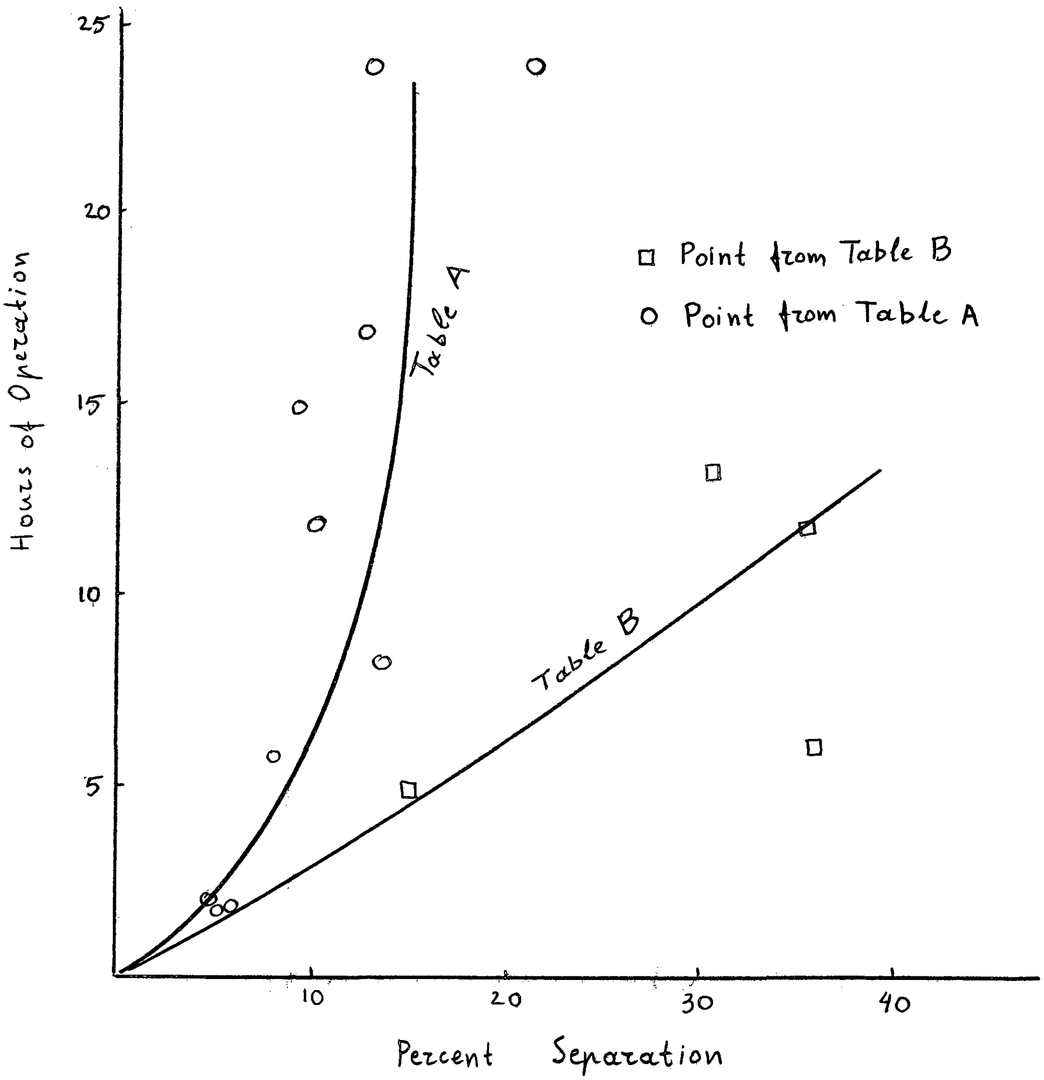

Figure 6

Comparison of Tables A1, A2, and A3 with Table B.

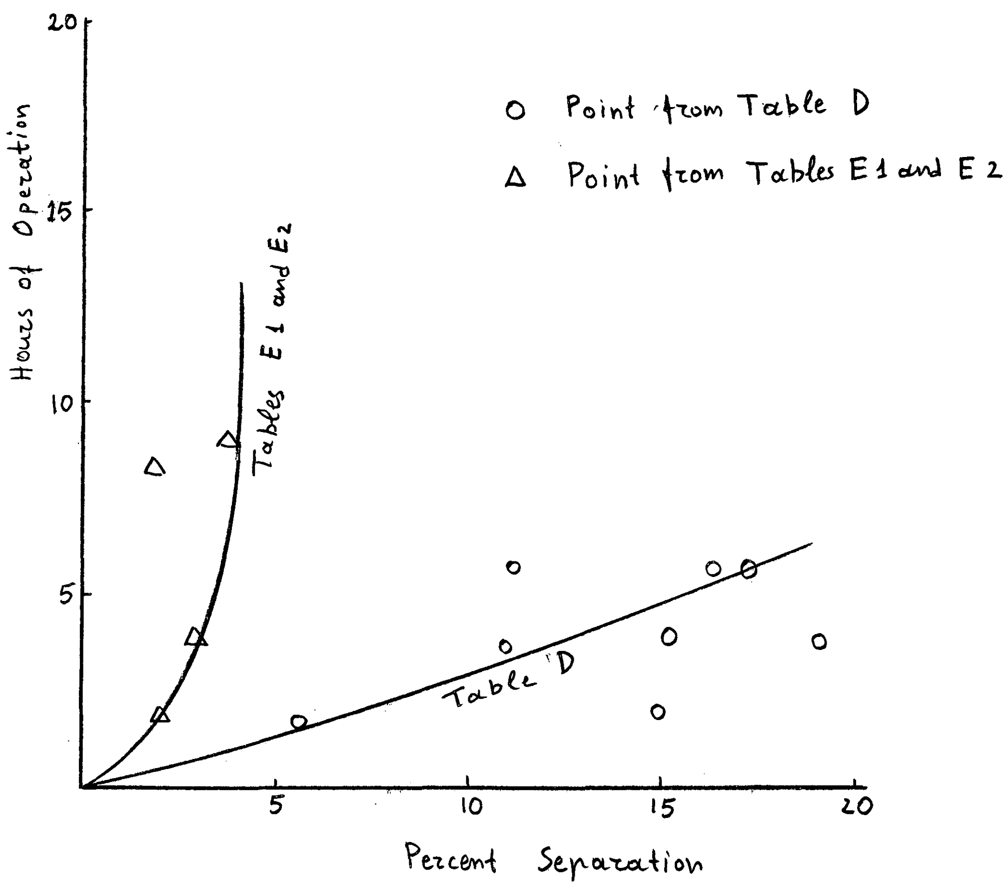

Figure 7

Comparison of Tables E1 and E2 with Table D.

DISCUSSION

Comparison with Previous Columns

One of the differences between this column and the previous ones is the path of thermal diffusion. In this column, the gap between the hot and the cold wall is 0.4 in. or more as compared to 0.03 in. open-annulus column or 0.12 in. in a packed column (Sullivan, 1957, p. 110). This fact makes the construction of columns with a large capacity much easier and more economical. Incidentally the ratio of capacity to the size of the column is 0.018 for the Jones and Milberger apparatus but for this new column this ratio is 0.4.

The second difference of this column, in contrast to that of Jones and Milberger, or the packed column of Sullivan, is the lower energy consumption. In Jones and Milberger, for the gap of 0.03 in., a temperature difference of 60F must be applied in order to effect the same separation as in the new column with the same time factor and temperature difference but with a gap 13 times larger. This difference means the energy consumed for the separation of, say, 25 ml in the Jones and Milberger column will suffice for the separation of 325 ml in this new column. However, in view of the electric energy consumed in each column, the new column needs only 40 times less energy than the Jones and Milberger column. 1/

1/ For the Jones and Milberger column: R = 19 ohm, V = 90 volt, I = 4.73 amp, Capacity = 25 ml, Power/ml = 17.0 watt/ml.
For the new column: R = 50 ohm, V = 50 volt, I = 1 amp, Capacity = 120 ml, Power/ml = 0.418 watt/ml.

Significantly an open annulus of 0.06 in. or more would give no separation in a Jones and Milberger column (Sullivan, 1957, p. 111).

The apparent conclusion from this comparison is that the open-annulus column is outmoded by the packed column which in turn is outmoded by the partitioned type described in this thesis.

Limiting Factors

The most important limiting factor in liquid thermal diffusion is the effective path of diffusion. In all previous columns this path was very small: from 0.03 to 0.06 in. for open-annulus spacing or from 0.06 to 0.12 in. for packed columns. This difference was caused by strong convection currents whose effects were primarily to remix the separated molecules thus decreasing the efficiency of the column. In the packed column the convection currents are eliminated to the degree that the spacing can be increased to 0.12 in. In the column presented in this thesis another factor radically alters the existing situation. The partitions in 2-mm spacings prevent the convection currents from spoiling the separation and thus increase the effective path of thermal diffusion. Therefore the limiting factor referring to the path of thermal diffusion is no longer as critical as it was before; the restriction pertaining to the distance between the hot and the cold wall becomes easier to cope with.

There must be, however, a limit to the increase of the path of thermal diffusion even with this improved method; but this limit must lie beyond 0.4 in., and only further investigations will establish its true magnitude.

Another limiting factor in liquid thermal diffusion is the maximum temperature applicable to the hot wall to effect separation. This temperature must be lower than the boiling point of the liquids processed. In this new column, small temperature differences are needed for the separation of large amounts of feed. In other words, a temperature gradient lower than that in any other column is necessary to effect separation. Consequently this limitation for the temperature of the hot wall is not so critical with this new column. This leads to the important conclusion that separations near the critical point are now possible. This was impossible with other columns. Furthermore, mixtures sensitive to temperature can now be considered for thermal-diffusion processing. These mixtures would include some medicines, proteins and peptides, some optical active substances, and even perhaps living viruses that respond easily to temperature differences.

Position

The position of the column affects separation and order of arrangement of the constituents.

In the horizontal position with the hot wall up and the cold wall down, the aromatic molecules start rising to the top, though the density of tetralin is 0.971 as compared to 0.730 of n-decane. This fact means that the liquid thermal-diffusion forces have to overcome gravity in order to put the heavier component higher than the lighter one. The fact that thermal diffusion emerges means that it is a very strong antigravity force. What is most important is that in this position with gravity counteracting, the separation is better because of useful convection.

The "forgotten effect," i.e. the effect by which the density gradient resulting from thermal diffusion separation may oppose the thermal density gradient responsible for the countercurrent convection to limit separation or reverse the direction of separation as a function of time (Jones, 1953, p. 2689), is observed here in Table A3.

The fact that this "forgotten effect" -- which occurs when the less dense component diffuses toward the cold wall -- is observed only in one set of data and in horizontal position allows for the conclusion that this column is capable of handling this difficulty well enough. Needless to say that in a convection-free cell the "forgotten effect" would spoil every separation. In the vertical position no "forgotten effect" appears, and the separation proceeds very smoothly, the heavy component concentrating at the bottom and the lighter at the top.

In the vertical position a good example of the cooperation of the two forces, thermal diffusion and gravity, is observed in the comparison of Table D and E1. For instance, in Table E1, an increase in aromatics takes place at the top on the hot wall. This increase, however, is much larger at the bottom on the hot wall as seen in Table D.

Limitations and Recommendations

One limitation in the experimental apparatus was the variation of the voltage applied for heating, a diversity resulting in a corresponding variation in the temperature of the hot wall. This phenomenon was caused by the unavailability of a convenient voltage stabilizer. Similarly the cooling means used (water and/or air) was not at a constant temperature.

These variations in temperature, especially during the nights when no adjustment was possible, affected to a certain degree the accuracy of the data. However, this deficiency is not so acute as in the example of the Jones and Milberger column where a slight variation in temperature produces considerable disturbance in separation.

It is recommended that if this work is going to be carried further the voltage for heating be kept constant through a suitable voltage stabilizer. In addition the cooling water should be kept at a constant temperature by circulating it through a constant-temperature cooling bath regulated with a thermostat. The application of the cooling water would be easier and better if the cold-wall plate were hollow and the water were introduced at a bottom port and overflowed from a top port.

With respect to the amount of packing in each ring, the results shown in Table A 3 (where four pieces of glass cloth were used instead of two as in every other run) seem to suggest that a certain amount of convection currents is useful for separation. The optimum amount of packing, however, is something which needs investigation.

APPLICATIONS

Petroleum Industry

The application of this column in the petroleum industry may prove of great value. Since this novel separation process utilizes the differences in shape or configuration of the molecules, separations now can be accomplished in petroleum fractions which were impossible or extremely difficult with conventional processes. An expected application of this column is in the pattern of upgrading of fuels and lubricants.

Chemical and Petrochemical Industry

In the chemical industry, especially the branches of fine chemicals, reagents, and dyestuffs, this column may prove to be a useful tool for purification of costly materials.

In the petrochemical industry both preparation of suitable feed for processing and purification of petrochemicals obtained might be facilitated by this column.

Pharmaceutical Industry

As in the chemical industry, purification in drugs is a very important requirement in production. Therefore this new tool of separation will be helpful in several ways.

Military Applications

The preparation and purification of nuclear and thermonuclear materials is of military importance. Hence, this column may be of value in such operations as the Manhattan Project, in which liquid thermal diffusion was an important factor (Smyth, 1945, p. 162).

CONCLUSIONS

An attempt to determine whether the path of liquid thermal diffusion could be increased above the limits set by previous investigators and whether the high energy consumption observed in ordinary thermal diffusion columns could be decreased to a more economical level resulted in satisfactory data.

The method employed was the reduction of the convection currents by glass packing and the creation of successive steps of fractionation by introducing partitioned compartments which would give each diffusing molecule a series of "pushes" toward separation.

The established limit for the length of liquid thermal-diffusion path in a column by previous investigators was proven inaccurate, and the new limit is now left open with a magnitude of no less than 1 cm.

Respecting construction costs and operational expenses, the new column is much more economical than any previously used column.

The results of this study justify further investigations of this type of column and of the operational methods in the use of the column.

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