SEPARATION OF BENZENE AND NORMAL HEPTANE

IN CONTINUOUS THERMAL DIFFUSION   COLUMNS

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February, 1956

IP-155

ACKNOWLEDGEMENTS

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NOMENCLATURE

B   Bottom product rate--gm/sec,

C   Mass fraction of n-heptane in the n-heptane-benzene system,

D   Top product rate--gm/sec,

D_1 Diffusivity--cm^2/sec,

E   Circumference of column--cm,

F   Feed rate--gm/sec,

H   Transport coefficient--gm/sec,

K   Transport coefficient--gm cm/sec,

L   Height of column--cm,

M   Molecular weight,

S   Separation--weight fraction,

T   Temperature--°C or °K,

ΔT Temperature gradient across spacing--°C or °K,

W   Transport up column--gm/sec,

a   Spacing--cm,

g   Acceleration of gravity--cm/sec^2,

m   Viscosity--gm/cm sec,

s   Density--gm/cm^3,

q   Separation factor,

w   Velocity component--gm/sec,

x   Radial co-ordinate in column,

z   Longitudinal co-ordinate in column,

α Thermal diffusion coefficient,

β Coefficient of volume expansion--gm/cm^3 °C,

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Subscripts

B   Bottom product,

D   Top product,

F   Feed,

o   Average value,

r   Reference value,

'   Total reflux,

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I. INTRODUCTION

The phenomenon of thermal diffusion is not new; however, the ap-
plication of the process to continuous separation columns is relatively
recent (2, 7, 10). It has been reported (8) that liquid thermal diffusion
may have a range of applications equally as broad as distillation. It is
not yet apparent how thermal diffusion would stand in the economic picture
when compared with conventional means of separation, since operating data
are practically non-existent. It is evident, however, that the process
would be applicable to the separation of highly valuable materials which
are difficult or impossible to separate by other means. The reported use
of the process at Oak Ridge to separate isotopes of uranium is a case in
point.

The following discussion describes the operation of continuous
thermal diffusion columns in separating liquid mixtures of n-heptane and
benzene. The effect of column height, spacing, feed rate, temperature
gradient and feed composition have been studied in their relation to the
separation attainable.

II. PREVIOUS WORK

The literature is quite extensive in describing thermal diffu-
sion in both the liquid and gaseous states. In their article on isotope
separation by thermal diffusion, Jones and Furry (11) give an extensive
listing of references to work conducted prior to 1946. However, the pre-
ponderance of the literature is confined to theroretical aspects and gen-
eral description of the application of thermal diffusion to specific cases.
Very few data have appeared on the operation of continuous columns. Indeed,
the relatively recent conception of the thermal diffusion column has pre-
cluded the accumulation of extensive data.

An important development in the study of thermal diffusion was the theoretical work of Furry, Jones and Onsager (5, 6, 7, 11). They integrated the heat and mass transfer equations which describe the performance of thermal diffusion columns. These equations correlate the separation attainable with the column characteristics, operating conditions, and physical properties of the system.

Trevoy and Drickamer (16) studied thermal diffusion in binary mixtures of paraffin hydrocarbons with each other and with benzene. They used a total reflux or batch column with a constant feed composition of 50 mol per cent. In addition, they used small temperature differences so they could study the thermal diffusion coefficient. They found that the thermal diffusion coefficient is only slightly affected by temperature.

Jones and Milberger (9) reported the results of their study of a great many organic liquid systems. Their results were obtained for binary and a few ternary systems at total reflux with the column design and operating conditions held constant so they could study the variation of separation between systems. They found that the shape of the molecule was the controlling factor in determining the direction of separation. In addition, they determined that the maximum separation normally occurred when the composition of the feed was 50 per cent by volume. It is significant that the volume composition determined the maximum separation rather than the molecular composition.

Jones and Hughes (10) patented a variety of thermal diffusion columns for liquids as well as methods for using thermal diffusion on a continuous basis. Jones (8) discusses the effect of column height, spacing and temperature in relation to separation in an article describing some industrial applications. A number of other investigators studied thermal diffusion in liquids. These investigations were made in columns operating at total reflux for the purpose of establishing that thermal diffusion would occur in the system studied and of determining the direction of separation. In some cases, the magnitude of the thermal diffusion effect was also determined. Among these investigators are Carr (1), Clusius and Dickel (2, 3), Fournier (4), Korsching (12, 13), Prigogine et al. (15), van Dranen and Bergsma (17), van Velden et al. (18), and Wirtz (19).

III. THEORETICAL CONSIDERATIONS

Furry, Jones, and Onsager (7) carried out the integration of the heat and mass transfer equations applicable to the operation of cylindrical thermal diffusion columns, so that only a minimum of theoretical considerations are discussed here. Analysis of an infinitesimal height of

column yields the so-called basic transport equation which applies only to batch or total reflux* operation.

$$W_1 = HC(1 - C) - (K_c + K_d)(dC/dz) .$$ (1)

For details of the development of this equation reference should be made to Jones and Furry (5). In Equation (1), W_1 is defined as the transport of a component according to the relation

$$W_1 = \int_0^1 EaswC \, dX .$$ (2)

In these relations C is the mass fraction of the component going to the top of the column, Z is the vertical distance along the column, E is the column circumference, a is the spacing or width of the diffusion section, s is the density of liquid, w is the vertical velocity, X is the radial distance, g is gravitational acceleration, D_1 is the diffusivity of a component, m is viscosity, T_o is the average temperature across the diffusion section, ΔT is the temperature drop across the section and β is the volume expansion coefficient. The other terms, H, K_c and K_d are transport coefficients defined by:

$$H = \frac{sg\beta Ea^3 (\Delta T)^2}{6!mT_o} ,$$ (3)

$$K_c = \frac{sg^2 \beta^2 Ea^7 (\Delta T)^2}{9!m^2 D_1} ,$$ (4)

and

$$K_d = EasD_1 .$$ (5)

The three transport coefficients can be interpreted as follows: The first term, H, represents flow of component 1 in the radial direction due to thermal diffusion. The two K terms represent remixing due to convection and ordinary diffusion. Generally, remixing coefficients are combined as

$$K = K_c + K_d$$ (6)

to yield the simplified transport equation:

$$W_1 = HC(1 - C) - K(dC/dz) .$$ (7)

Equation (5) describes the effect of ordinary diffusion in the longitudinal direction when substituted in Equation (1). However, this effect is

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*Total reflux has the same significance as in distillation. It implies a continuous column operated with no take-off of product.

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usually small, so that the K of Equation (7) is practically equal to the K_c of Equation (4). With q defined in terms of the top concentration C_D and the bottom concentration C_B,

$$q = \frac{C_D/(1 - C_D)}{C_B/(1 - C_B)} . \tag{8}$$

Equation (7) can be integrated over the whole column height for the total reflux or batch case where $W_1 = 0$, giving

$$\ln q = HL/K . \tag{9}$$

Here, L is the height of the column.

It is desirable to adapt the transport equation to the case of continuous operation, in which products are removed from the top and bottom of the column while a feed is introduced in the middle. Jones and Furry have indicated this modification in their work. Effectively, Equation (7) becomes:

$$W_1 = DC + HC (1 - C) - K (dC/dz), \tag{10}$$

where D is the flow rate of the top product. The material balance over the top portion of the column above the feed requires that:

$$W_1 = DC_D . \tag{11}$$

Thus, Equations (10) and (11) reduce to:

$$D (C_D - C) = HC (1 - C) - K (dC/dz). \tag{12}$$

Similarly for the bottom half of the column:

$$B (C - C_B) = HC (1 - C) - K (dC/dz), \tag{13}$$

where B is the flow rate of the bottom product. Equations (12) and (13) can be integrated over the length of the column with no further assumptions; however, if C (1 - C) is held constant, a simpler and more useful result is obtained as

$$\exp [LBD/K (B + D)] = \frac{HC (1 - C)}{HC (1 - C) - (BD/F)(C_D - C_B)} \tag{14}$$

where F is the feed rate. It should be noted that for the case in which C (1 - C) is taken as a constant, the batch or total reflux separation S' is given from the integration of Equation (7) as

$$S' = C_D' - C_B' = \frac{HL}{K} [C (1 - C)] . \tag{15}$$

In the special case where $D = B = F/2$, Equation (14) can be simplified even further and combined with Equation (15) to yield:

$$\frac{S}{S'} = \frac{1 - \exp (-FL/4K)}{FL/4K} . \tag{16}$$

Equation (16) gives the ratio of the separation or variation between top and bottom products in a continuous thermal diffusion column to the separation in a batch or total reflux column as a function of the feed rate, column length, and the variables contained in the transport coefficient K.

It is emphasized that Equation (16) is a simplification resulting from assuming a constant $C(1 - C)$ throughout the column and equal bottom and top product flow rates. In cases where C varies from approximately 0.3 to 0.7 in weight fraction units, the first, assumption is quite good. If the ratio of the top product flow to the bottom product flow (B/D) does not vary more than two-fold from unity, the second assumption holds very well.

IV. DESCRIPTION OF APPARATUS

Concentric-tube thermal diffusion columns were used in this study. A schematic diagram of a typical column is shown in Figure 1. Each column was constructed of three pieces of aluminum tubing arranged concentrically, with suitable end pieces and piping connections welded in place. The inner tube contained circulating hot water, while the outer tube contained circulating cold water. The system to be separated, n-heptane and benzene, was contained in the intermediate tube. A feed port was located midway up each column, and product removal ports were provided at the top and bottom. The height of a column was considered to be the length of the outer tube, while the spacing was defined as the distance between the hot and cold walls. Circumference was determined as the average of the hot and cold walls bounding the system. The dimensions of each column are listed in Table 1. Also included are the dimensions of a column used by Trevoy and Drickamer with the n-heptane-benzene system.

Considerable care was taken to maintain constant spacing throughout the length of the column. During the construction of the columns, a number of wooden blocks approximately one-eighth of an inch square and of the proper thickness were impregnated with phenolic resin and dried. These small blocks were placed between the concentric tubes to provide a hard, non-conducting spacer which would resist the n-heptane and benzene. Small

TABLE I

COLUMN DIMENSIONS

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

projections were raised on the outside surface of the inner tube where the spacers were to be located. The spacers were forced on to each of these projections so that when the inner tube was inserted into the column, the spacers were held in place between the tubes forming the diffusion section. Three spacers were installed circumferentially 120 degrees apart approximately every two feet along the length of the column.

Cold water was supplied directly from the tap while a small gear pump was used to circulate the hot water. The hot water was heated by low pressure steam in a steam-jacketed exchanger located downstream from the pump. Hot water was introduced at the top of the thermal diffusion column, while the cold water entered from the bottom. By this arrangement, any convection patterns contributed by virtue of a temperature gradient from top to bottom were more or less stabilized. Feed was supplied by gravity to the middle of the column from an overhead container. Flow rates of the hot and cold water streams were measured with a size 8 Fischer and Porter rotameters, and the feed and product rates were measured with size 07 or 08 rotameters. Thermocouples were located at the inlets and outlets of the hot and cold water streams. Junctions were placed directly in the water and on the hot and cold walls. Figure 2 is a flowsheet of the arrangement of the various pieces of equipment and Figure 3 is a photograph taken during an experimental run.

V. EXPERIMENTAL PROCEDURE

At the beginning of a run, the hot and cold water streams were adjusted to flow rates of approximately 15 gallons per minute. The steam was then turned on so that the hot water would be heated to the desired temperature. At the same time, the feed and product streams were turned on and set at the proper flow rate. Control of the flow rates was accomplished by adjusting the valve on the two product streams, the valve on the feed being left open. The column was allowed to reach a steady state before recording data. With the operating conditions used, it was felt that if the separation changed less than 0.1 weight per cent in four hours, the column had attained steady-state conditions.

The feed and products were analyzed by measurement of their refractive indices. For the samples from columns 1, 2 and 3, the analysis was accomplished at 25.0°C in a Zeiss-Abbe refractometer capable of measuring refractive indices to $\pm$0.0001. The samples from column 4, along with pure samples of n-heptane and benzene, were measured at room temperature with a Zeiss precision refractometer which measured refractive indices to $\pm$0.00003. Compositions derived from these refractive indices are believed accurate to approximately 0.1 weight per cent.

Since the feed and product rates were quite low in many runs, the rotameters used in the rate measurements were markedly affected by the viscosity of the material. For this reason, it was necessary to calibrate the rotameters with liquids of varying viscosities. The liquids used in calibration were acetone, ethanol, benzene, and ethyl acetate. Correlation of these measurements was accomplished by the method proposed by Martin (14) to account for the effect of viscosity and density.

Prior to assembly of the columns, the outside diameter of the hot wall and inside diameter of the cold wall were carefully measured at different points along the length of the tubes, and the spacing was calculated as the difference between the average of these diameters. The spacings determined by this method are believed accurate to $\pm$0.002 cm.

It was necessary to correct the spacing of each column for the thermal expansion or contraction of the hot and cold walls during a run. It was assumed that the tubes comprising these walls behaved like thin cylindrical shells so that the dimensions would change linearly with temperature. Thus, the following relation was derived for correction of the spacing:

$$\frac{a}{a_r} = 1 - \beta\Delta T \left[\frac{R_r H}{a_r} + \frac{T_r - T_c}{T}\right] \qquad (17)$$

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where a is the spacing at the temperature difference T, a_r is the spacing measured at temperature T_r, R_{rH} is the radius of the hot wall at temperature T_r, and β is the expansion coefficient for aluminum. This correction amounted to a maximum of less than 2 per cent of the total spacing. However, spacing occurs to the seventh power in the correlations so that an ultimate error of about 15% may result from a 2% error in spacing.

VI. RESULTS

Table 2 lists a summary of the data and the calculations that have been made in accordance with the theoretical deductions. These results are considered separately for the continuous column operation and for total reflux operation.

A. Continuous Operation

1. Effect of FL/4K

The group FL/4K, given by the equation

$$\frac{FL}{4K} = \frac{9! \; FL \; m^2 \; D_1}{4g^2 \; a^7 \; \beta^2 \; E \; (\Delta T)^2} \tag{18}$$

includes the variables; feed rate, spacing, height, circumference and temperature gradient. The feed composition and average column temperature are also included through their effect on the physical properties.

Equation (16) suggested that the data could be properly correlated through the group FL/4K. The effect of this group on the separation may be seen from Figures 4-14. Although the function described by Equation (16) appears rather complex, it may be roughly approximated by

$$\ln \frac{S}{S'} = b \; (FL/4K) \tag{19}$$

up to FL/4K $\simeq$ 1.5, thus suggesting the semi-logarithmic plots of Figures 4-12.

The data from column 1 are seen to be rather well represented by a straight line; however, the theoretical curve lies above the line drawn through the data except for Figure 7. The feed concentration for the runs depicted in Figure 7 was 0.572 mass fraction n-heptane. For the case of column 3, the theoretical curve is practically coincident with the line drawn through the data points in Figures 9 and 10. The theoretical curve lies above the data line in Figure 11. The data from columns 2 and 4 show

TABLE II

SUMMARY OF CALCULATIONS AND RESULTS

Run No.	F $\frac{gm}{sec}$	C_F wt fract. n-heptane	D/B	ΔT °C	T_O °C Avg. Temp. of Liquid	a/a_r	K $\frac{gm\text{-}cm}{sec}$	FL/4K	S wt fract. n-heptane
1-60	0.0098	0.433	0.68	42.3	36.1	0.978	14.6	0.050	0.147
1-61	0.0062	0.438	1.00	40.9	34.6	0.979	13.5	0.035	0.148
1-62	0.0128	0.441	1.08	36.9	31.8	0.982	11.0	0.089	0.134
1-63	0.0083	0.443	0.60	35.1	30.8	0.982	9.86	0.066	0.131
1-65	0.0062	0.471	1.18	32.4	32.0	0.983	9.26	0.052	0.129
1-66	0.0069	0.474	0.97	38.7	36.6	0.980	12.5	0.042	0.141
1-67	0.0053	0.467	1.03	42.2	38.5	0.979	14.5	0.029	0.150
1-68	0.0072	0.249	0.95	35.3	36.0	0.982	10.8	0.052	0.128
1-69	0.0049	0.250	1.10	33.4	34.4	0.983	9.59	0.038	0.125
1-70	0.0655	0.250	0.29	33.1	35.0	0.983	9.43	0.533	0.096
1-71	0.0093	0.255	1.33	25.3	31.2	0.987	5.57	0.126	0.113
1-72	0.0097	0.255	2.22	27.1	31.3	0.986	6.31	0.119	0.105
1-73	0.0158	0.258	2.96	26.9	31.8	0.986	6.27	0.194	0.101
1-74	0.0062	0.258	0.95	35.0	36.6	0.982	10.7	0.044	0.128
1-75	0.0083	0.257	0.56	37.2	37.9	0.981	12.2	0.053	0.123
1-76	0.0120	0.255	0.33	38.5	39.3	0.980	13.2	0.069	0.135
1-77	0.0139	0.257	0.57	36.7	38.2	0.989	11.9	0.088	0.132
1-78	0.0334	0.261	0.61	37.9	39.0	0.989	12.8	0.097	0.118
1-79	0.0067	0.262	1.00	2.7	20.6	0.998	0.067	7.70	0.104
1-80	0.0048	0.263	0.81	7.3	22.9	0.996	0.467	0.792	0.070
1-81	0.0115	0.272	1.16	32.0	36.8	0.984	9.00	0.099	0.115
1-82	0.0109	0.272	1.38	38.0	38.9	0.981	12.8	0.064	0.131
1-83	0.0096	0.276	1.68	42.2	42.6	0.979	13.1	0.045	0.136
1-84	0.0106	0.275	1.40	19.7	29.4	0.990	3.44	0.235	0.087

Note: First digit of run number denotes column.

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TABLE II (cont.)

Run No.	F gm/sec	C_F wt fract. n-heptane	D/B	ΔT °C	T_o °C Avg. Temp. of Liquid	a/a_r	K gm-cm/sec	FL/4K	S wt fract. n-heptane
1-85	0.0068	0.097	0.97	17.0	28.6	0.991	2.35	0.216	0.046
1-86	0.0113	0.097	1.19	17.8	29.4	0.991	2.58	0.340	0.046
1-87	0.0058	0.099	1.26	32.1	37.8	0.984	8.58	0.053	0.067
1-88	0.0083	0.099	2.34	29.8	37.5	0.985	7.45	0.085	0.064
1-89	0.0128	0.101	4.66	31.7	37.5	0.984	8.35	0.117	0.057
1-90	0.0491	0.098	0.90	37.7	38.0	0.981	11.6	0.324	0.064
1-91	0.0137	0.099	4.12	36.9	38.2	0.981	11.2	0.093	0.060
1-92	0.0360	0.099	12.50	37.0	39.1	0.982	11.3	0.248	0.055
1-93	0.0074	0.103	1.97	35.3	38.5	0.982	10.2	0.056	0.071
1-94	0.0052	0.103	1.07	33.7	37.6	0.983	9.33	0.043	0.074
1-95	0.0133	0.805	0.58	16.5	27.8	0.993	1.65	0.617	0.034
1-96	0.0061	0.806	0.95	16.5	27.8	0.993	1.65	0.282	0.036
1-97	0.0063	0.806	0.95	7.1	22.1	0.996	0.415	1.16	0.026
1-98	0.0067	0.815	1.08	28.7	34.0	0.985	4.89	0.104	0.051
1-99	0.0116	0.817	1.06	26.1	34.5	0.987	4.05	0.219	0.045
1-100	0.0225	0.821	0.97	25.1	32.5	0.987	3.72	0.451	0.037
1-101	0.0107	0.825	0.96	21.8	32.0	0.989	2.82	0.260	0.044
1-102	0.0173	0.824	0.99	33.8	37.5	0.983	6.72	0.198	0.052
1-103	0.1045	0.827	0.79	31.2	35.8	0.984	5.72	1.40	0.024
1-104	0.0062	0.826	0.96	32.6	35.8	0.983	6.25	0.077	0.054
1.105	0.1237	0.829	0.74	32.7	36.1	0.984	6.27	0.151	0.052

TABLE II (cont.)

Run No.	F $\frac{gm}{sec}$	C_F wt fract. n-heptane	D/B	ΔT °C	T_o °C Avg. Temp of Liquid	a/a_r	K $\frac{gm\text{-}cm}{sec}$	$FL/4K$	S wt fract. n-heptane
106	0.0082	0.569	1.10	23.5	30.7	0.988	4.25	0.149	0.092
107	0.0209	0.570	0.99	23.5	30.6	0.988	4.25	0.378	0.089
108	0.0697	0.574	1.02	25.5	31.6	0.987	4.92	1.08	0.066
109	0.0093	0.571	0.65	22.0	30.4	0.989	3.74	0.191	0.089
110	0.0547	0.573	0.99	23.9	31.4	0.988	4.39	0.954	0.076
111	0.0109	0.573	1.07	22.1	30.4	0.989	3.74	0.223	0.090
112	0.151	0.575	0.83	22.7	31.6	0.988	3.97	2.90	0.042
113	0.153	0.574	0.84	24.6	31.6	0.987	4.62	2.53	0.044

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TABLE II (cont.)

Run No.	F gm/sec	C_F wt fract. n-heptane	D/B	ΔT °C	T_0 °C Avg. Temp. of Liquid	a/a_r	K gm-cm/sec	FL/4K	S wt fract. n-heptane
2-1	0.0103	0.587	0.96	28.0	33.9	0.991	144	0.0037	0.031
2-2	0.0059	0.608	1.13	25.3	33.2	0.992	116	0.0026	0.028
2-3	0.0106	0.608	1.13	21.5	31.8	0.993	83.5	0.0066	0.027
2-4	0.0092	0.608	1.27	24.1	33.6	0.992	106	0.0045	0.027
2-5	0.0102	0.610	1.06	31.8	37.5	0.990	186	0.0028	0.024
2-6	0.0096	0.578	1.01	33.2	31.8	0.989	194	0.0025	0.027
2-7	0.0151	0.579	0.94	46.4	42.5	0.985	405	0.0019	0.033
2-8	0.0390	0.582	1.32	46.4	42.0	0.985	402	0.0050	0.032
2-9	0.0045	0.589	1.06	46.6	42.7	0.985	404	0.0057	0.036
2-10	0.0053	0.589	1.03	31.3	34.3	0.990	179	0.0016	0.030
2-11	0.0150	0.593	0.99	31.7	34.3	0.990	182	0.0042	0.027
2-12	0.0358	0.596	1.75	32.3	34.0	0.989	189	0.0106	0.029
3-1	0.0099	0.554	0.90	31.5	35.0	0.983	9.26	0.041	0.065
3-1a	0.0097	0.563	0.98	31.1	33.6	0.983	8.86	0.042	0.070
3-2	0.0049	0.565	0.95	29.9	33.5	0.984	8.23	0.023	0.068
3-2a	0.0056	0.565	0.93	29.6	33.2	0.984	8.67	0.026	0.073
3-3	0.0048	0.563	0.98	25.0	31.0	0.987	5.82	0.031	0.068
3-4	0.0817	0.573	0.78	25.9	30.8	0.986	6.19	0.504	0.049
3-5	0.0097	0.576	0.98	27.5	32.0	0.985	6.95	0.053	0.063
3-6	0.0266	0.576	0.86	28.2	32.6	0.985	7.29	0.140	0.059
3-7	0.0133	0.584	0.94	27.3	31.9	0.985	6.75	0.075	0.061
3-8	0.0600	0.595	0.80	47.8	42.2	0.974	20.3	0.113	0.065
3-9	0.0111	0.591	0.98	47.4	42.8	0.975	20.3	0.021	0.063

TABLE II (cont.)

Run No.	F $\frac{gm}{sec}$	C_F wt fract. n-heptane	D/B	ΔT °C	T_o °C Avg. Temp of Liquid	a/a_r	K $\frac{gm\text{-}cm}{sec}$	FL/4K	S wt fract. n-heptane
3-10	0.0289	0.602	0.85	46.6	42.6	0.975	19.4	0.057	0.066
3-11	0.0141	0.602	0.96	45.2	41.5	0.976	18.2	0.030	0.068
3-12	0.0051	0.611	1.03	46.5	42.4	0.975	19.1	0.010	0.071
3-12a	0.0059	0.621	0.99	41.6	42.4	0.978	15.5	0.015	0.062
3-13	0.0094	0.627	1.03	8.9	39.8	0.995	0.78	0.460	0.041
3-14	0.0957	0.630	0.74	10.0	21.8	0.994	0.874	3.31	0.011
3-15	0.0100	0.629	0.98	10.1	22.6	0.994	0.897	0.426	0.039
3-16	0.0518	0.630	0.73	17.3	25.5	0.991	2.62	0.756	0.037
3-17	0.0087	0.633	0.98	17.6	27.0	0.990	2.71	0.123	0.050
3-18	0.0242	0.633	0.73	19.7	27.3	0.989	3.36	0.276	0.046
3-19	0.0058	0.639	1.02	21.0	28.3	0.989	3.83	0.058	0.061
3-20	0.0089	0.257	0.53	10.0	22.0	0.994	1.04	0.326	0.055
3-21	0.0073	0.260	0.93	20.6	27.4	0.989	4.46	0.063	0.066
3-22	0.0743	0.261	0.83	25.7	30.4	0.986	6.92	0.410	0.052
3-23	0.0127	0.261	0.71	23.6	29.3	0.987	5.83	0.084	0.065
3-24	0.126	0.262	0.85	25.6	30.6	0.986	6.87	0.698	0.053
3-25	0.0078	0.262	0.61	35.8	36.5	0.981	13.3	0.023	0.071
3-26	0.148	0.263	0.77	38.2	37.5	0.980	15.4	0.368	0.061
3-27	0.0060	0.263	0.87	39.3	38.2	0.979	16.3	0.014	0.071

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TABLE II (cont.)

Run No.	F $\frac{gm}{sec}$	C_F wt fract. n-heptane	D/B	ΔT °C	T_o °C Avg. Temp. of Liquid	a/a_r	K $\frac{gm\text{-}cm}{sec}$	FL/4K	S wt fract. n-heptane
3-28	0.0652	0.447	0.56	14.4	24.8	0.993	2.11	1.18	0.044
3-29	0.0083	0.452	1.36	9.2	21.7	0.995	0.85	0.372	0.052
3-30	0.0089	0.447	0.89	16.6	25.6	0.992	2.81	0.120	0.068
3-31	0.0136	0.449	0.83	8.9	21.0	0.996	0.791	0.657	0.044
3-32	0.0907	0.454	0.87	41.8	39.2	0.980	17.7	0.197	0.069
3-33	0.0132	0.453	0.79	40.2	38.2	0.890	16.5	0.031	0.070
3-34	0.0266	0.456	0.99	42.9	39.6	0.979	18.7	0.54	0.071
3-35	0.0050	0.458	1.02	41.5	39.1	0.980	17.5	0.011	0.077
3-36	0.128	0.465	3.20	30.5	33.7	0.985	9.30	0.527	0.055
3-37	0.0095	0.471	2.44	28.7	31.6	0.986	8.20	0.045	0.067
3-38	0.120	0.472	0.84	27.6	31.4	0.986	7.57	0.607	0.055
3-39	0.0085	0.471	0.85	27.6	31.6	0.986	7.55	0.043	0.069
3-40	0.114	0.473	14.4	26.4	30.4	0.987	6.95	0.627	0.057
3-41	0.0068	0.473	1.35	28.0	31.8	0.986	7.80	0.033	0.068
3-42	0.128	0.473	0.17	26.2	29.4	0.987	6.76	0.736	0.052
3-43	0.0068	0.473	0.75	26.3	29.3	0.987	6.82	0.038	0.063
3-44	0.0376	0.478	0.79	26.1	29.4	0.987	6.66	0.216	0.065
4-1	0.0121	0.491	0.87	30.8	29.0	0.994	4670	0.0000997	0.0112
4-2	0.0705	0.491	0.58	32.7	30.0	0.994	5290	0.000509	0.0091
4-3	0.0123	0.488	1.49	54.0	41.1	0.990	15100	0.0000312	0.0131
4-4	0.0486	0.487	1.76	57.2	41.8	0.989	16900	0.000110	0.0106
4-5	0.0048	0.486	0.87	52.3	39.8	0.990	14000	0.0000132	0.0106

TABLE II (cont.)

Run No.	F $\frac{gm}{sec}$	C_F wt. fract. n-heptane	D/B	ΔT °C	T_0 °C Avg. Temp. of Liquid	a/a_r	K $\frac{gm\text{-}cm}{sec}$	$FL/4K$	S wt. fract. n-heptane
4-1a	0.651	0.23	0.89	32.1	28.3	0.994	5.40×10^3	6.96×10^{-5}	0.00835
4-2a	0.900	0.23	0.82	30.2	27.4	0.994	4.84	10.6	0.00728
4-3a	0.323	0.23	0.99	33.5	25.4	0.994	5.76	2.78	0.00775
4-4a	0.498	0.23	0.96	32.6	25.1	0.994	5.43	4.61	0.00882
4-5a	3.52	0.23	0.73	20.0	18.6	0.996	1.99	118.0	0.00615
4-6a	0.672	0.23	0.94	19.0	17.8	0.996	1.81	21.9	0.00552
4-7a	0.605	0.23	0.51	53.2	36.4	0.990	14.89	2.13	0.01298
4-8a	0.755	0.23	1.03	52.8	35.4	0.990	14.5	3.19	0.01360
4-9a	0.628	0.23	0.90	50.2	35.5	0.991	13.2	2.45	0.01386
4-10a	1.68	0.23	0.73	49.4	33.9	0.991	12.6	8.68	0.01262
4-11a	0.61	0.23	0.99	33.2	25.3	0.994	5.69	6.15	0.00738
4-12a	0.617	0.23	0.96	49.6	34.0	0.991	12.8	2.97	0.01295
4-13a	0.448	0.23	0.92	49.8	33.6	0.991	12.9	1.88	0.01255
4-14a	5.05	0.23	0.82	48.0	32.3	0.991	12.0	24.7	0.01148
4-15a	0.646	0.23	0.98	34.1	25.0	0.994	5.95	6.40	0.00747
4-16a	1.45	0.23	0.87	35.9	26.1	0.993	6.65	13.7	0.00826

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that the values of FL/4K are so small that the separation is practically independent of FL/4K, indicating that these columns were operating at essentially total reflux.

2. Effect of ΔT

According to theory ΔT should be properly accounted for in FL/4K. However, it is noted in Figures 12 and 13 that there is a definite grouping of points according to temperature distribution. Theory predicts that separation at total reflux is independent of temperature difference. Runs depicted in Figures 12 and 13 are apparently near enough to total reflux that they are not correlated by the function FL/4K which includes $(\Delta T)^{-2}$.

3. Effect of D/B

The effect of the top-to-bottom ratio D/B may be seen in Figure 15, in which separation is plotted versus D/B for a single D/B and for two different feed rates. These data indicate that separation is independent of D/B. With the remainder of the runs, D/B was maintained at approximately 1.0, although there was some deviation from 0.5 to 1.50. Although not completely conclusive, the trend depicted in Figure 15 indicates that the variations in D/B can be neglected.

B. Operation at Total Reflux

1. Effect of Spacing

The total reflux separations for columns 1 and 3 were obtained from the curves in Figures 4-11 by extrapolation to FL/4K equals zero. The total reflux separations for columns 2 and 4 were obtained by averaging all the values of separation obtained experimentally, since these columns were operating at essentially total reflux. The separations were converted to separation factors q by use of Equation (8) and the material balance relations.

$$ C_O = C_F + S/2 \; ; \; C_B = C_F - S/2 $$

which are noted for the case in which top and bottom product rates are equal.

Thermal diffusion coefficients were calculated by the theoretical equation.

$$ \alpha = \frac{\ln q}{HL/\alpha K} . \tag{20} $$

The values of α thus determined are presented as a function of composition in Figure 16. Examination of the data points reveals that the values of α for column 1 and 3 agree quite well with theory, in that they are a function of

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composition only. The values of α for columns 2 and 4 are far removed from the curve representing the data for columns 1 and 3. Inasmuch as column 1 and 3 had approximately the same spacing q and columns 2 and 4 had higher spacings (Table 1), indications are that the theory does not predict the correct function to describe the total reflux case.

2. Effect of Temperature Difference

The theoretical relation for the total reflux case predicts that the separations are independent of temperature gradient. Some data demonstrating this point may be seen in Figures 17 and 18, which are graphs of separation versus feed rate with temperature gradient as a parameter. Extrapolation of the curves to zero feed rate tends to corroborate the theory. Further, Figures 12 and 13 indicate that the function $(\Delta T)^{-2}$ does not correlate the data as FL/4K approaches zero.

VII. CORRELATION

A. Continuous Operation

The results for continuous operation as presented in Figures 4-14 did not exhibit any consistent deviation from the theoretical curves. The curves representing the experimental data were constructed as a least square fit of the form

$$S = ab^{FL/4K}$$

where the extrapolated value of S at FL/4K equals zero would be the constant a. Although the extrapolation is subject to considerable error, it was felt that the scatter of the data precluded a more critical treatment.

All of the results for columns 1 and 3 are shown in Figure 19 as ln S/S' versus FL/4K. The results for columns 2 and 4 are not included, inasmuch as the values of FL/4K were relatively low and the separation values were largely unaffected by FL/4K as shown in Figures 12, 13, and 14. The theoretical curve has been drawn in Figure 19 and it would appear to give a good representation of the data. A slightly modified curve might better represent the data but this would be an arbitrary choice. The theoretical curve reproduces the values of S/S' with an average error of 8.4 percent with a maximum error of approximately 30 percent. For operations involving simultaneous mass and heat transfer, such deviations are not unusual.

1. Operation at Total Reflux

For the case of total reflux, the values of α as determined from the extrapolated values of separation show considerable variation with column spacing. Examination of Figure 16 indicates that the calculated thermal diffusion coefficients increase with larger column spacings. This apparently shows that the wrong function has been used to calculate the thermal diffusion

coefficient, which should be a property of the fluid alone. Since no one of the thermal diffusion coefficients determined through use of Equation (20) is more reliable than any other, it is difficult to examine the total reflux case further. However, recalling that the group of physical properties in HC/K is nearly independent of temperature, the function $\ln q/(L/a^n)$ should behave as an absolute thermal diffusion coefficient, that is, be a function of composition alone. It was apparent from Figure 16 that total reflux separation is not correctly predicted by the inverse fourth power of spacing in accordance with Equation (9). With this in mind, the results were replotted as $\ln q/(L/a^2)$ versus feed composition as shown in Figure 20. Also plotted on the same graph is the average of the function as determined by Trevoy and Drickamer in a column operating only at total reflux. It is apparent that the results of this experimentation and that of Trevoy and Drickamer are in good agreement. Without recourse to the introduction of a modified thermal diffusion coefficient, the results can be correlated as a function of spacing, length of column and feed composition:

$$\ln q = \frac{L}{a^2} (3.30 \times 10^{-5} - 2.60 \times 10^{-5} \, C_p) . \tag{21}$$

As an illustration of the correlation for total reflux and the theoretical equation as originally developed by Furry, Jones and Onsager for continuous operation, an example will be presented.

A thermal diffusion column is to be operated on the system n-heptane-benzene. A feed is available with a concentration, 0.50 weight fraction n-heptane. The following additional data are available:

$$E = 15.0 \text{ cm}$$

$$a = 0.100 \text{ cm}$$

$$\Delta T = 40.0°C$$

$$T_o = 35.0°C$$

$$B/D = 1.0 .$$

(a) Calculate the maximum separation which may be attained with a column length of 300 cm?

(b) What would be the maximum rate at which feed could be introduced to produce one-half the separation calculated in (a) above?

For part (a) it is necessary to use the total reflux relationships.

From Equation (21) or more directly from Figure 20,

$$\frac{\ln q}{L/a^2} = 0.000020$$

$$\ln q = \frac{300 \ (0.000020)}{(0.100)^2} = 0.600 \ .$$

From Equation (8) and the relationships in Equation (20),

$$q = \frac{c_D'/(1 - c_D')}{c_B'/(1 - c_B')}$$

$$c_D' = c_F + S'/2 \quad ; \quad c_B' = c_F - S'/2 \ .$$

The primes indicate the case for total reflux or maximum separation. Substituting for c_D' and c_B',

$$\ln \frac{(0.50 + S')(1 + S')}{(1 - S')(0.50 - S')} = 0.600$$

$$S' = 0.100$$

Thus, a top product with a composition 0.550 weight fraction n-heptane would be attained at total reflux. In part (b),

$$.S' = 0.100 \ ,$$

$$S = 0.50 \ (0.100) = 0.050 \ ,$$

$$\frac{S}{S'} = 0.500 \ .$$

We can now use the relationship:

$$\frac{S}{S'} = \frac{1 - \exp \ (-FL/4K)}{FL/4K} = 0.500 \ ,$$

$$\frac{FL}{4K} = 1.60 \ .$$

The physical properties in the constant K are evaluated at the average temperature 35°C and feed composition 0.50 weight percent n-heptane.

$$S = 0.765 \ \frac{gm}{cm^3}$$

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$$\beta = 0.00096 \ \frac{gm}{cm^3 - {}^\circ C}$$

$$m = 0.380 \ \text{centipoise} \ ,$$

$$D_1 = 0.0000278 \ \frac{cm^2}{sec} \ ,$$

$$K = \frac{Sg^2 \ \beta^2 \ Ea^7 \ (\Delta T)^2}{9! \ m^2 \ D_1} \ ,$$

$$K = \frac{(0.765)(980)^2 \ (0.00096)^2 \ (0.100)^7 \ (15)(40)^2}{9! \ (0.0038)^2 \ (0.0000278)} \ ,$$

$$K = 11.2 \ \frac{gm - cm}{sec} \ ,$$

$$F = \frac{(1.60)(4)(11.2)}{300} \ ,$$

$$F = 0.239 \ gm/sec \ ,$$

VIII. SUMMARY

The separation of n-heptane and benzene in thermal diffusion columns under continuous operation is fairly well correlated by the equations of Furry, Jones and Onsager. For the total reflux case, the theory yields thermal diffusion coefficients which appear to be a function of the column spacing, rather than a function of the liquid mixture alone. For the columns operated in conjunction with this work the separation factor ln q was inversely proportional to the square of the spacing rather than the fourth power as predicted by theory. The results of this work further indicated that the separation attainable at total reflux is independent of temperature gradient across the spacing.

Although more complete data would be desirable for the system n-heptane-benzene and other liquid systems, it is believed that the theoretical equations should prove generally applicable to liquid systems.

IX. LITERATURE CITED

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HEIGHT-L

HOT WATER INLET

TOP PRODUCT PORT

COLD WATER OUTLET

FEED→
PORT

COLD WATER INLET

BOTTOM PRODUCT PORT

HOT WATER OUTLET

OUTER TUBE
INTERMEDIATE TUBE
INNER TUBE

SPACING - a
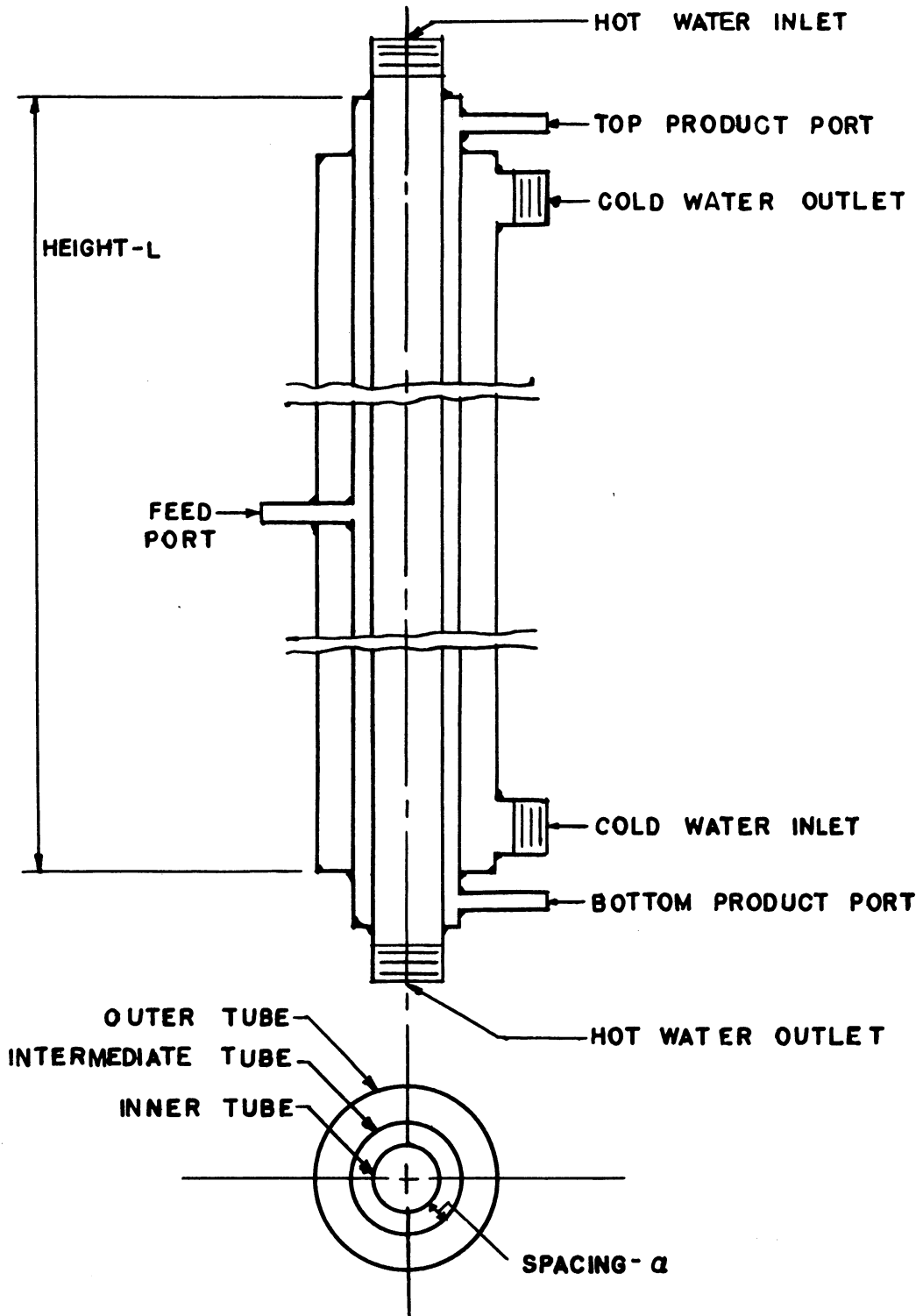
Fig. 1. Diagram of a Thermal Diffusion Column.
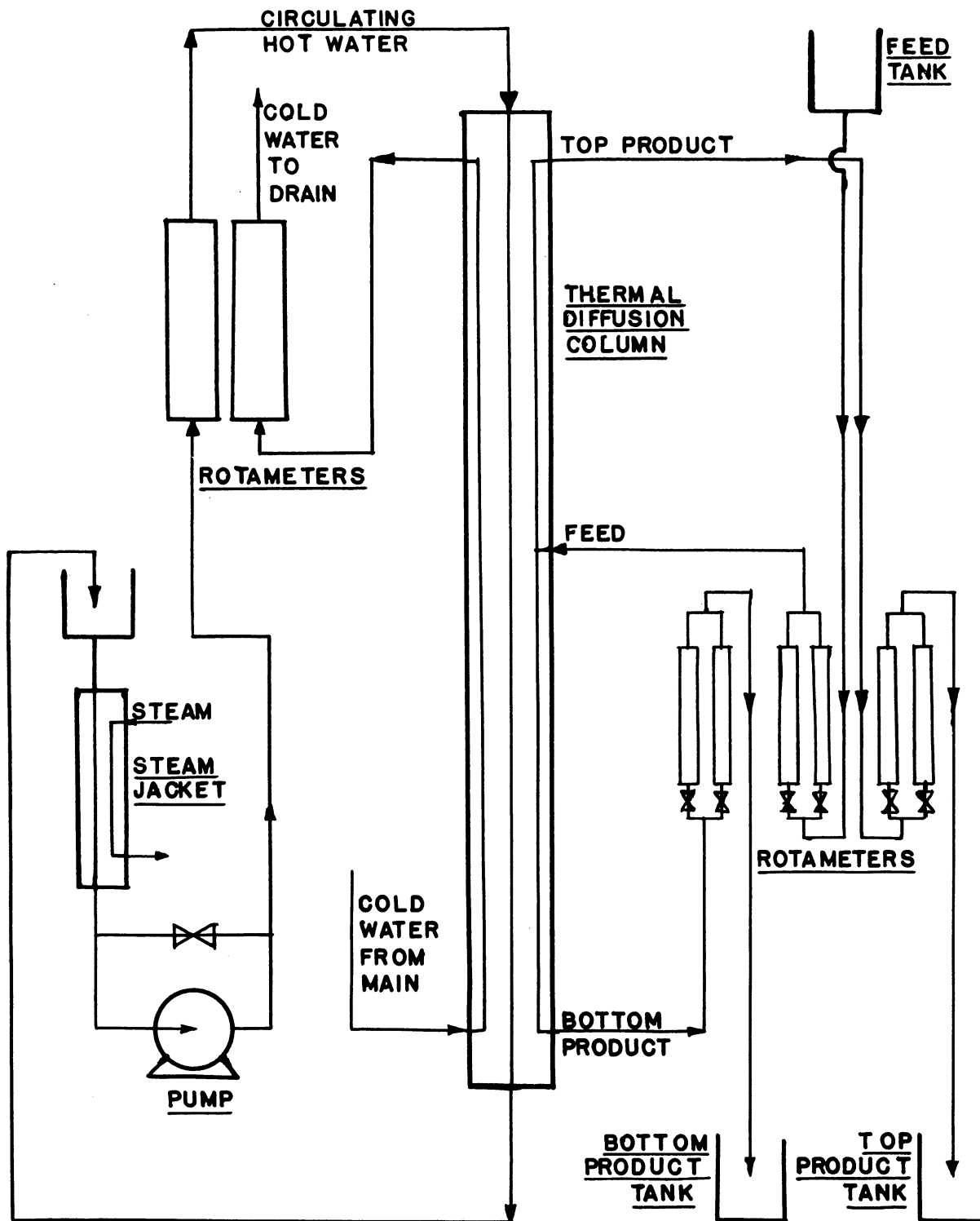
Fig. 2. Flow Diagram for Thermal Diffusion Column and Accessories.
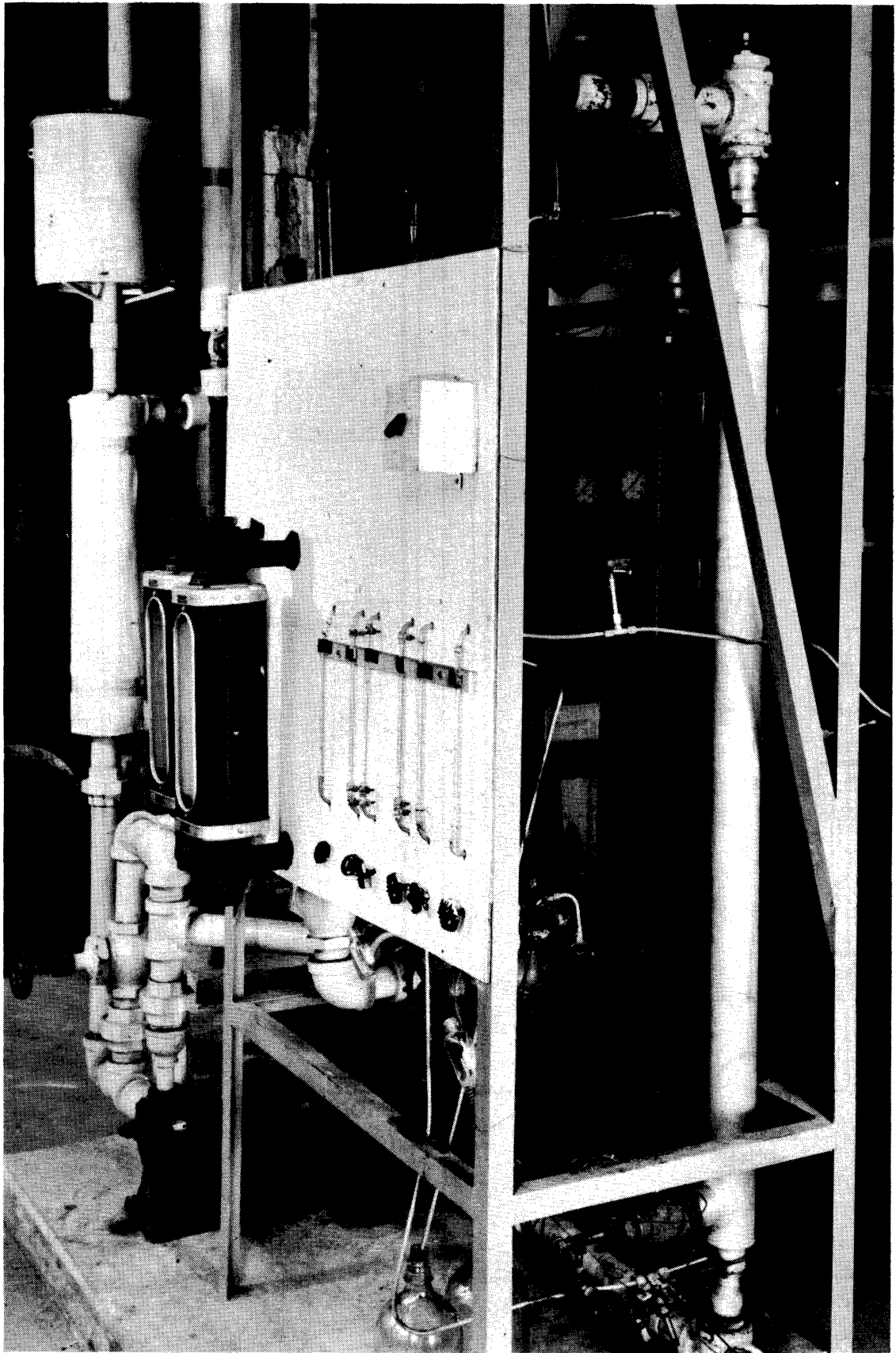
Fig. 3. Photograph of Experimental Equipment.
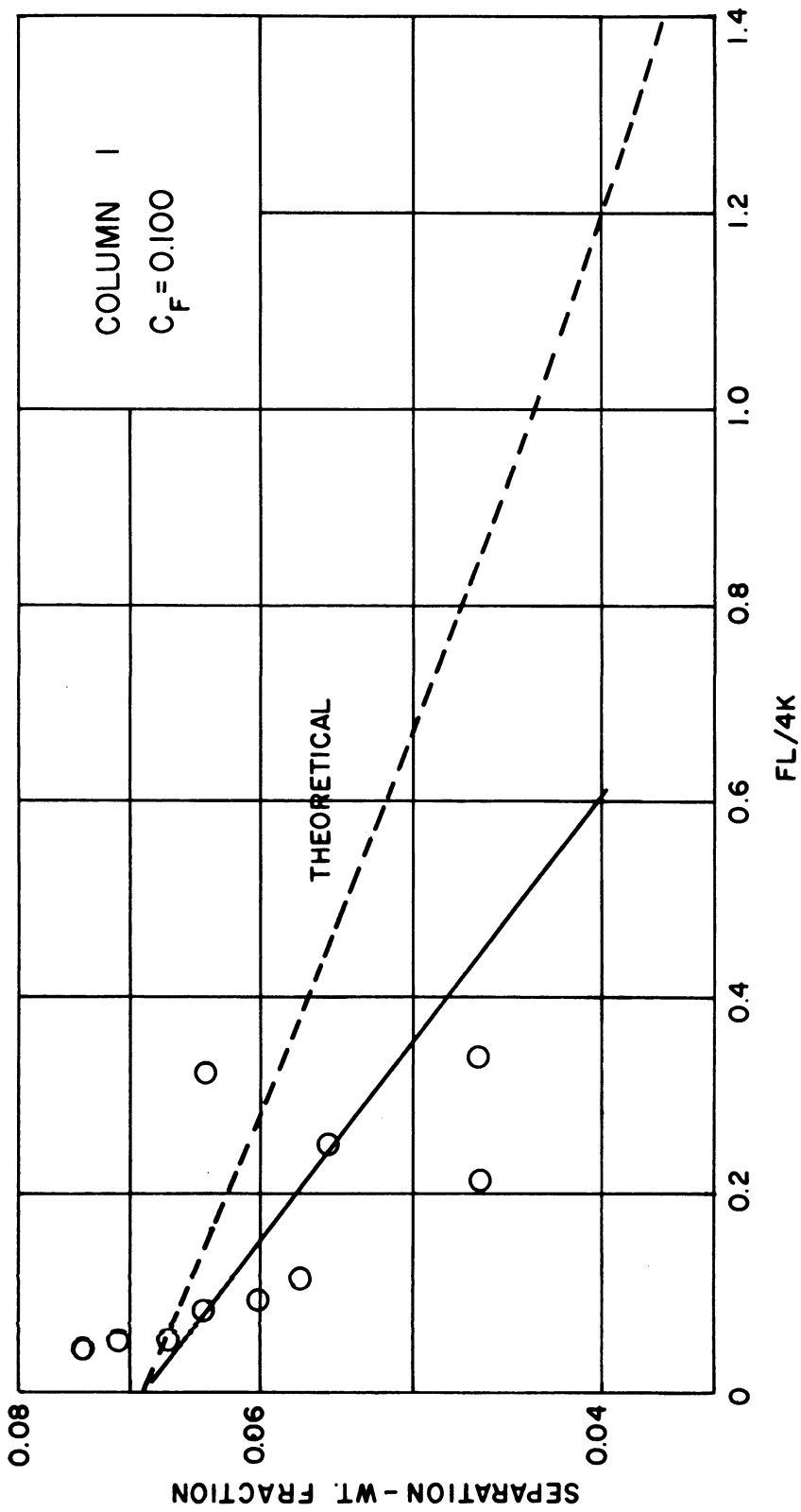
Fig. 4. Performance of Column 1 at a Feed Concentration of 0.100.
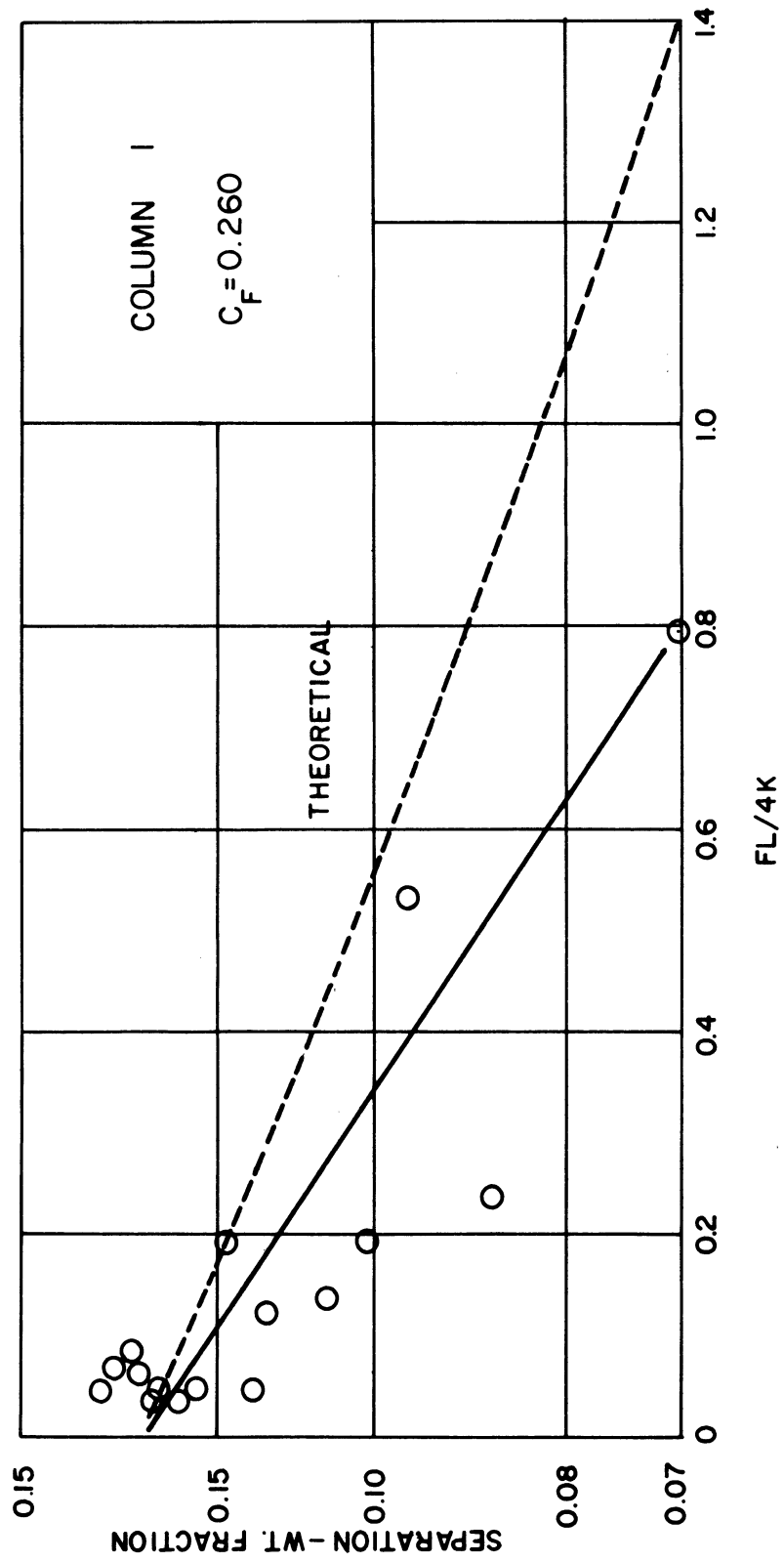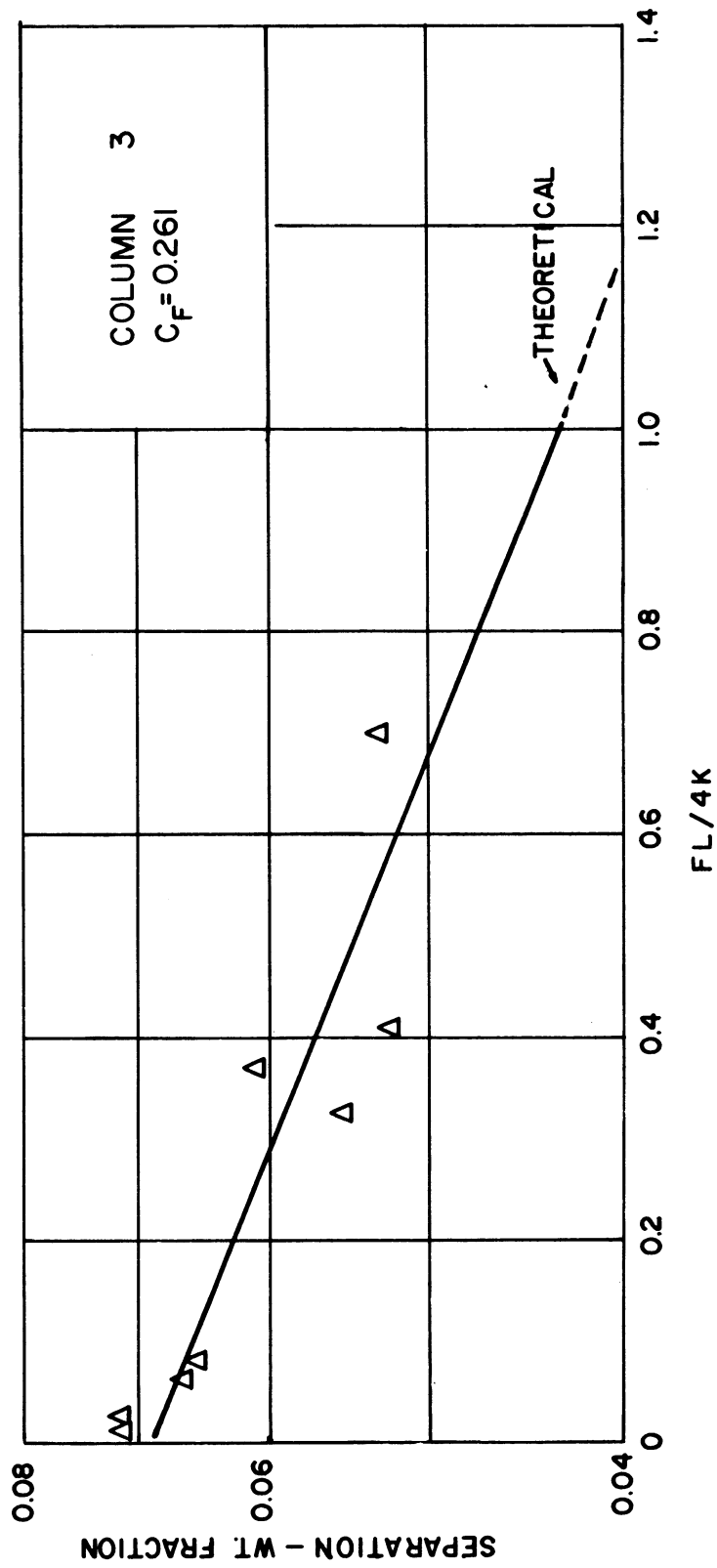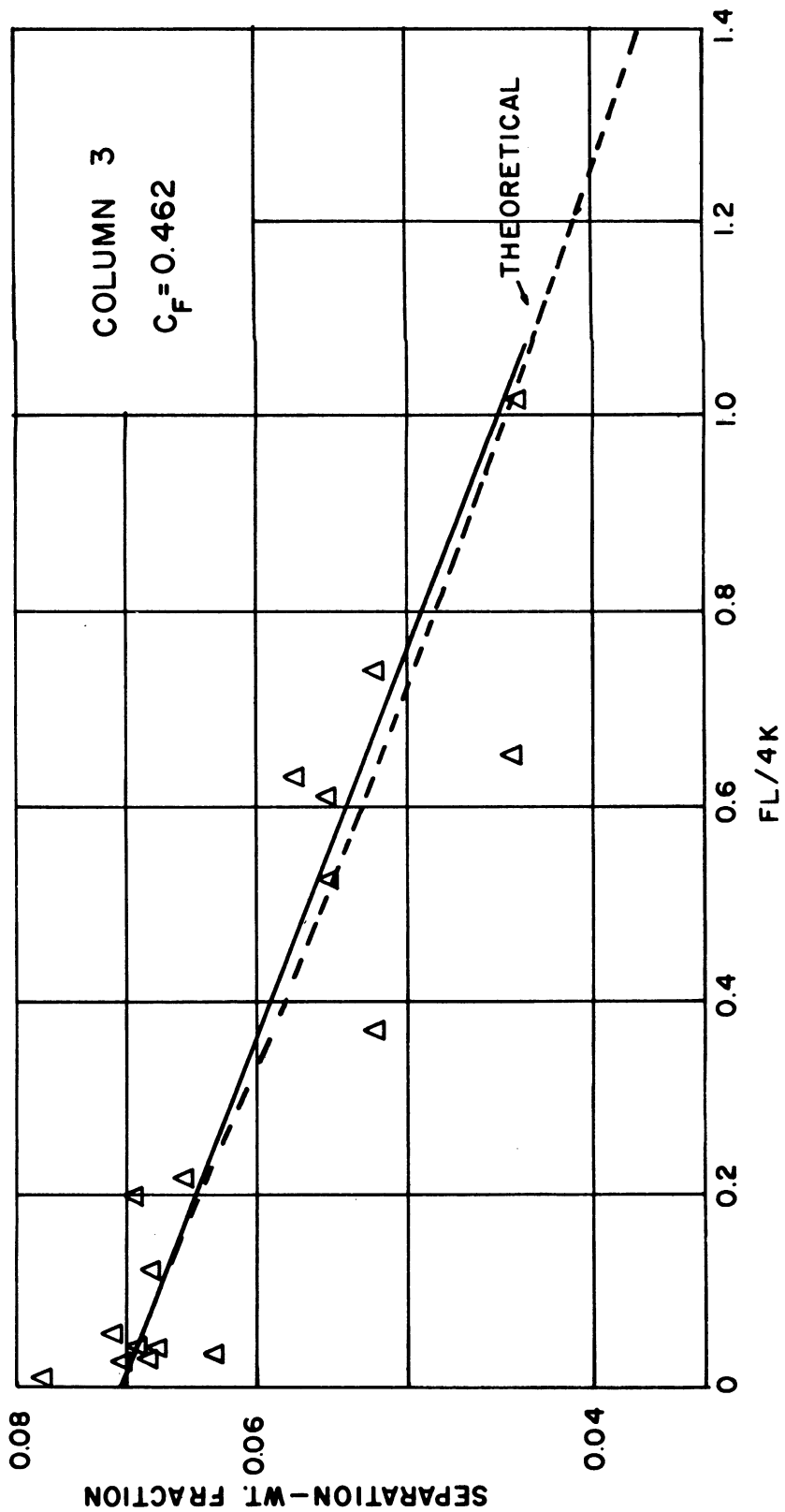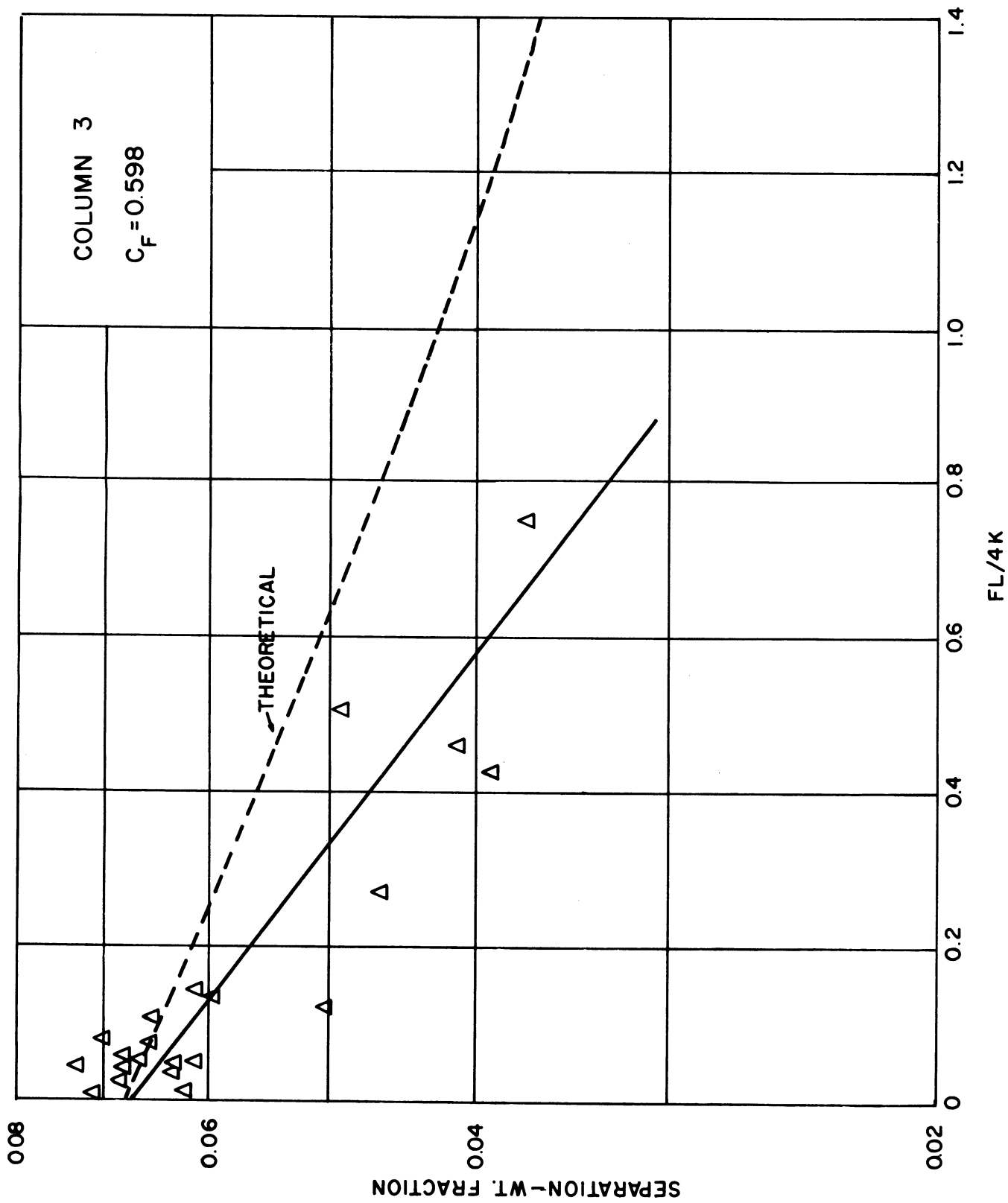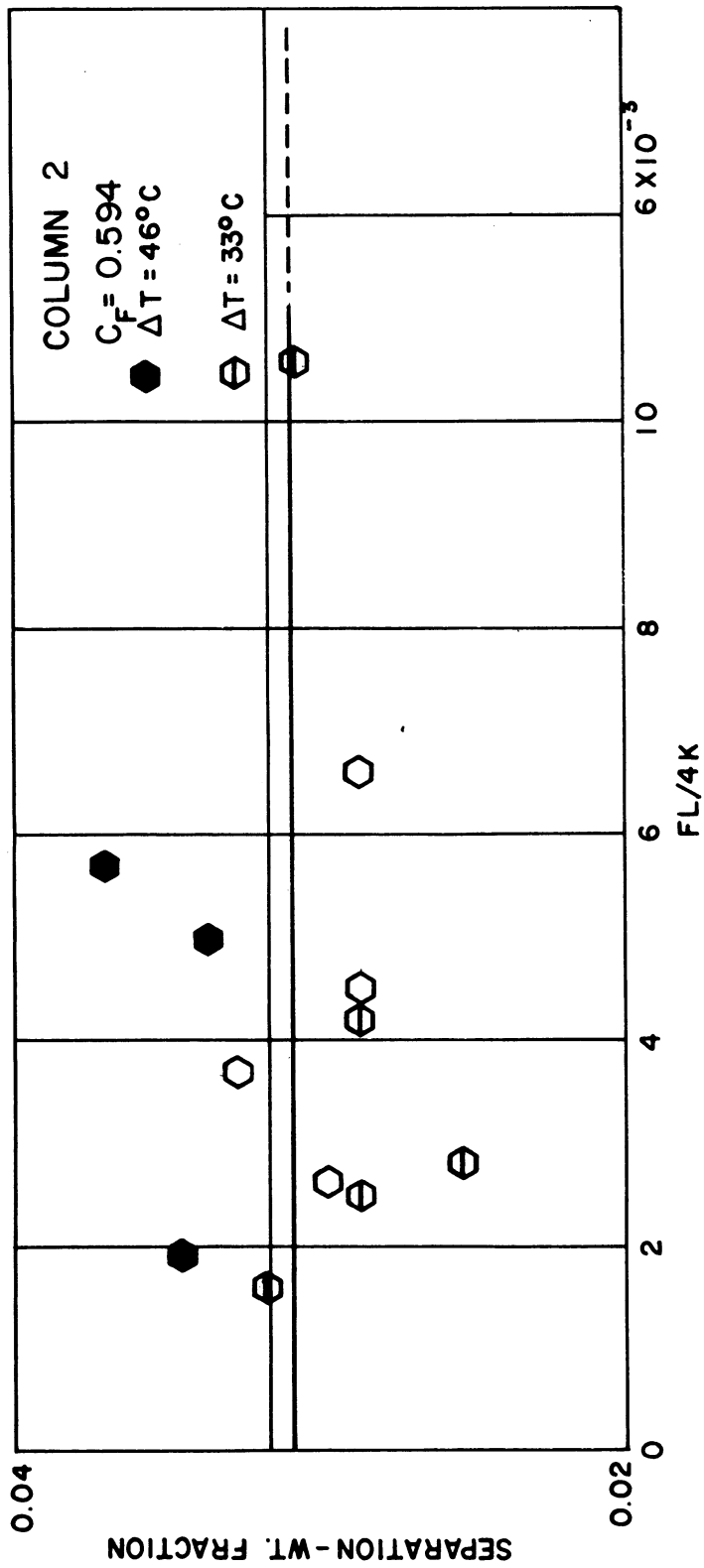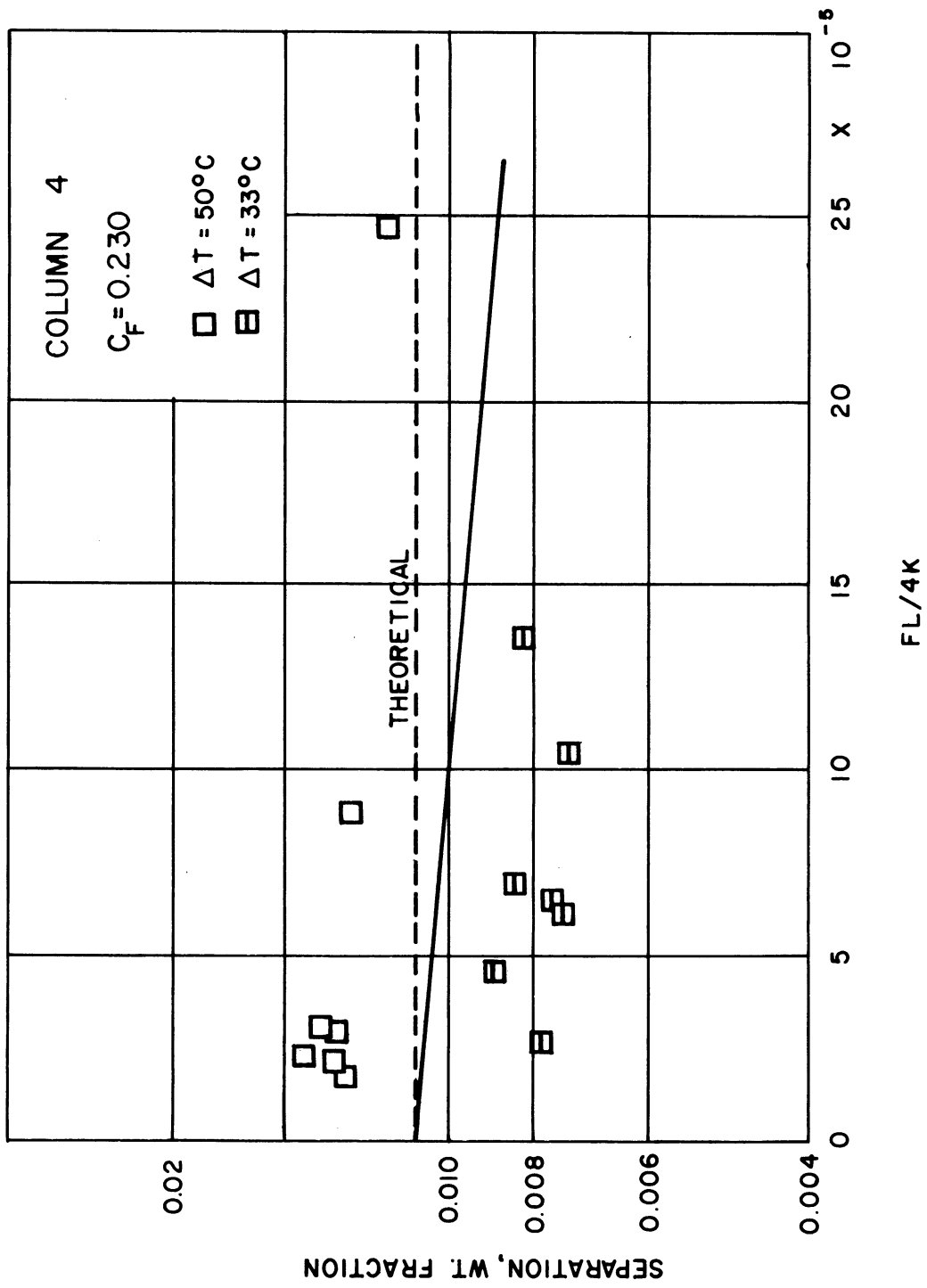
Fig. 5. Performance of Column 1 at a Feed Concentration of 0.260.
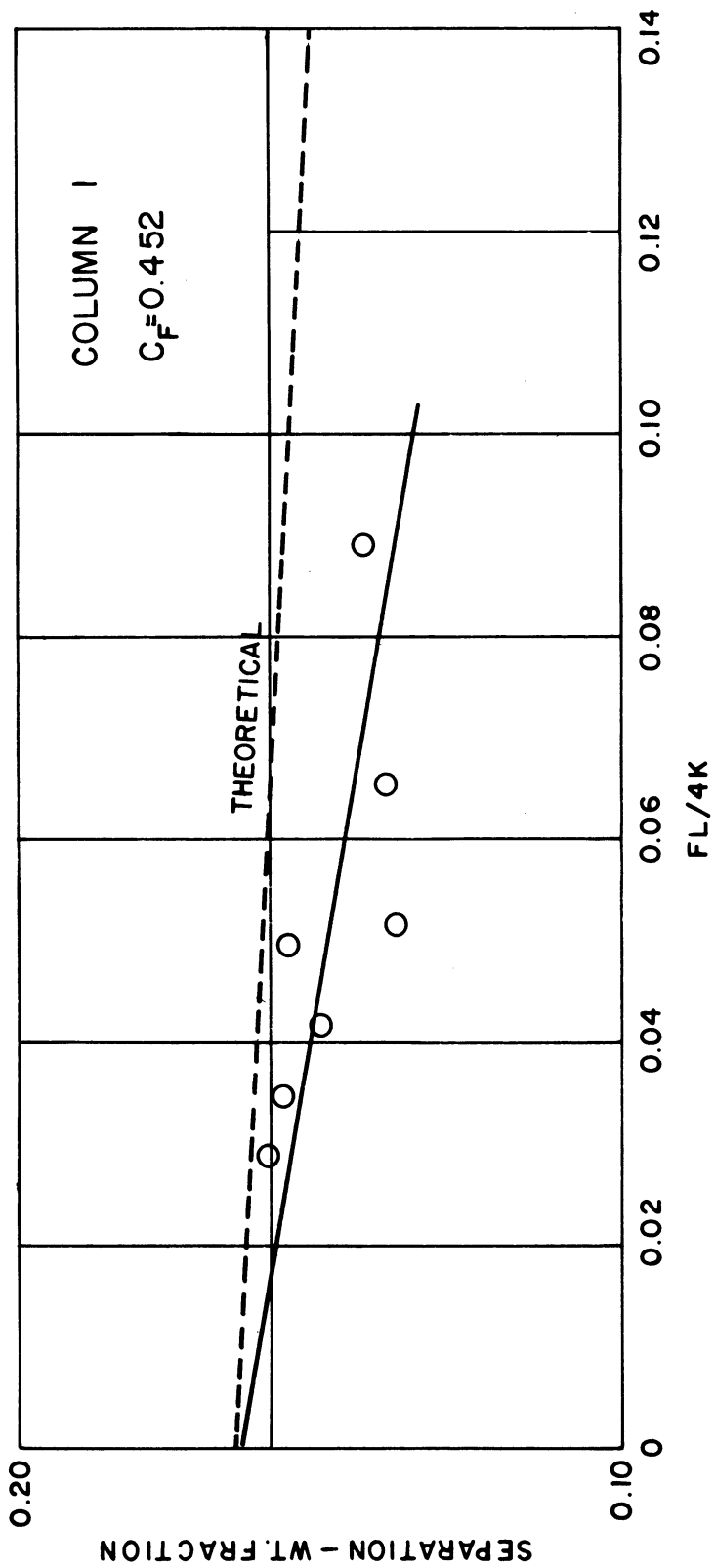
Fig. 6. Performance of Column 1 at a Feed Concentration of 0.452.
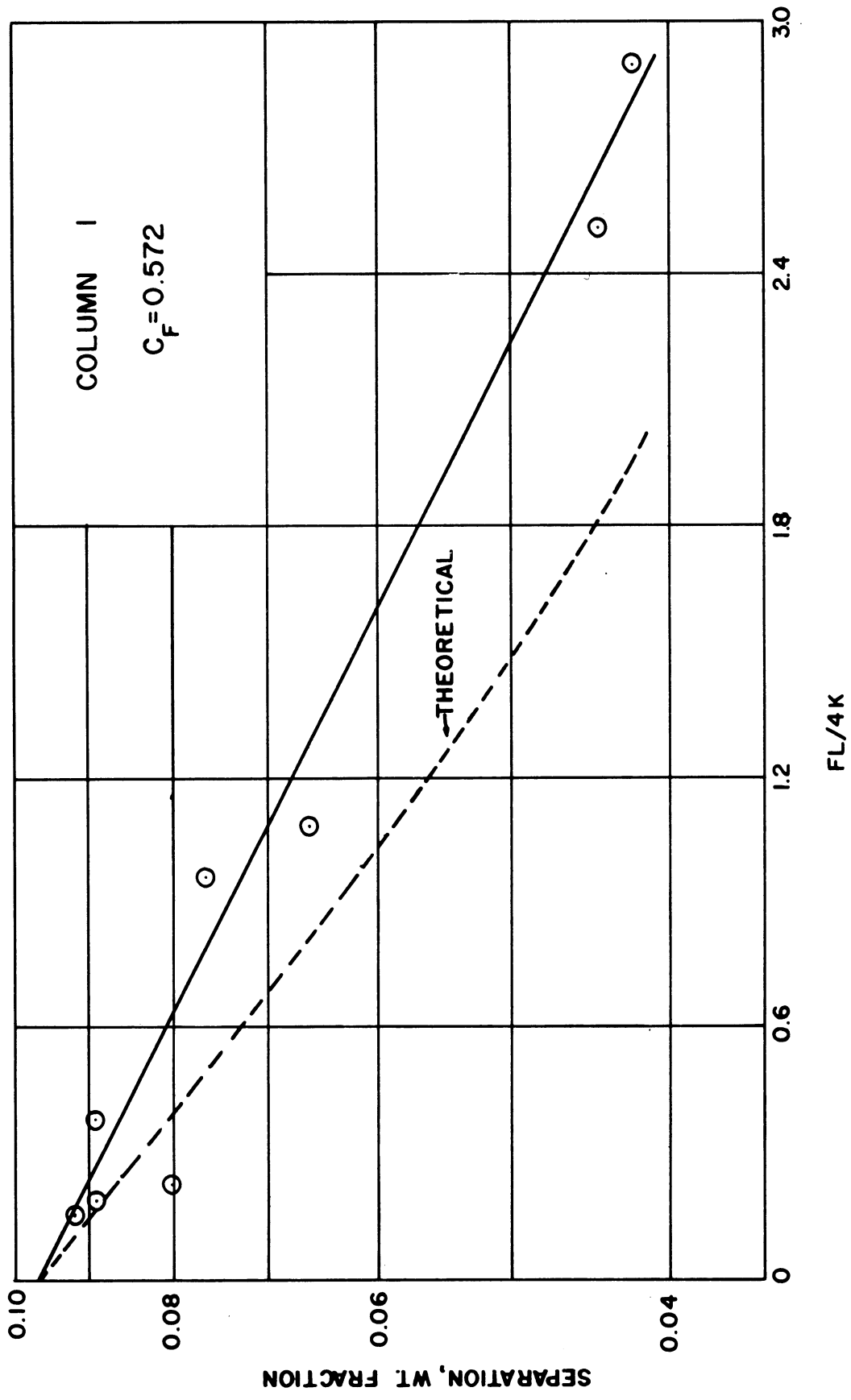
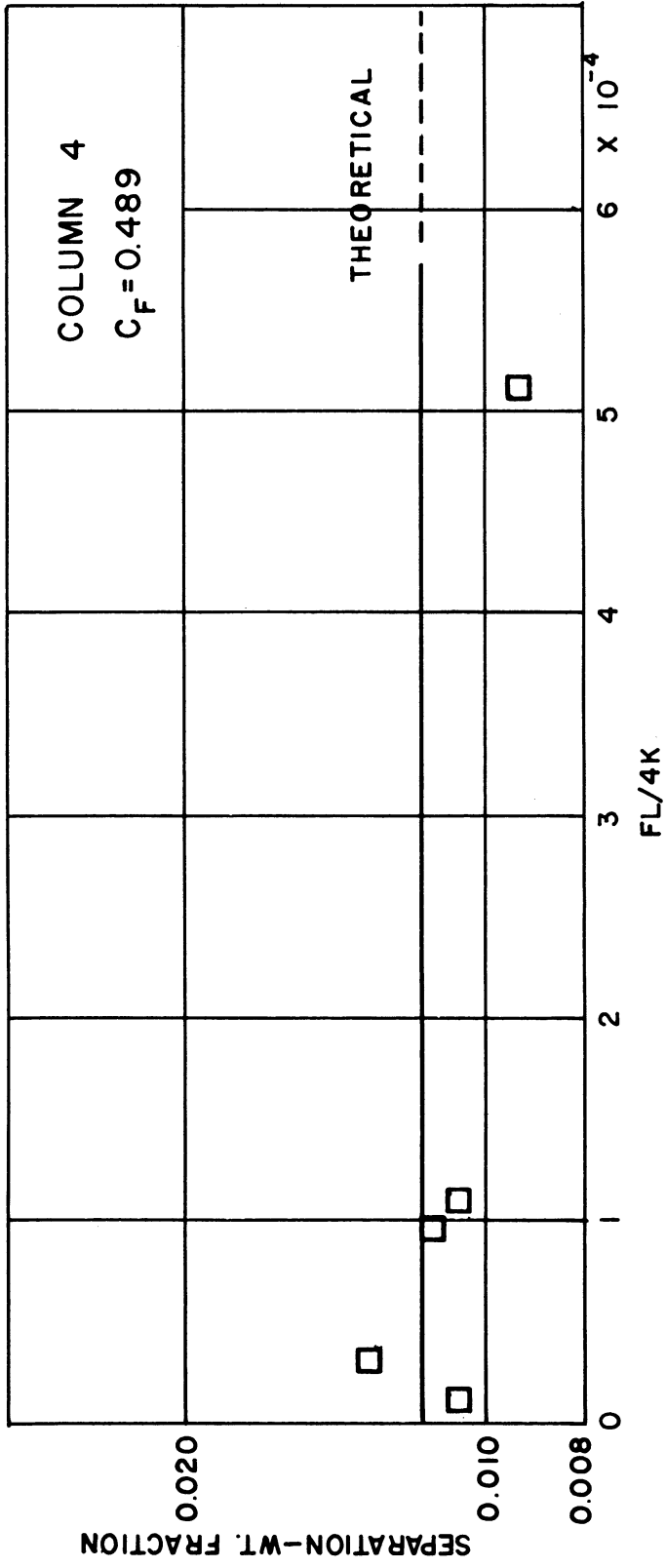Fig. 7. Performance of Column 1 at a Feed Concentration of 0.572.

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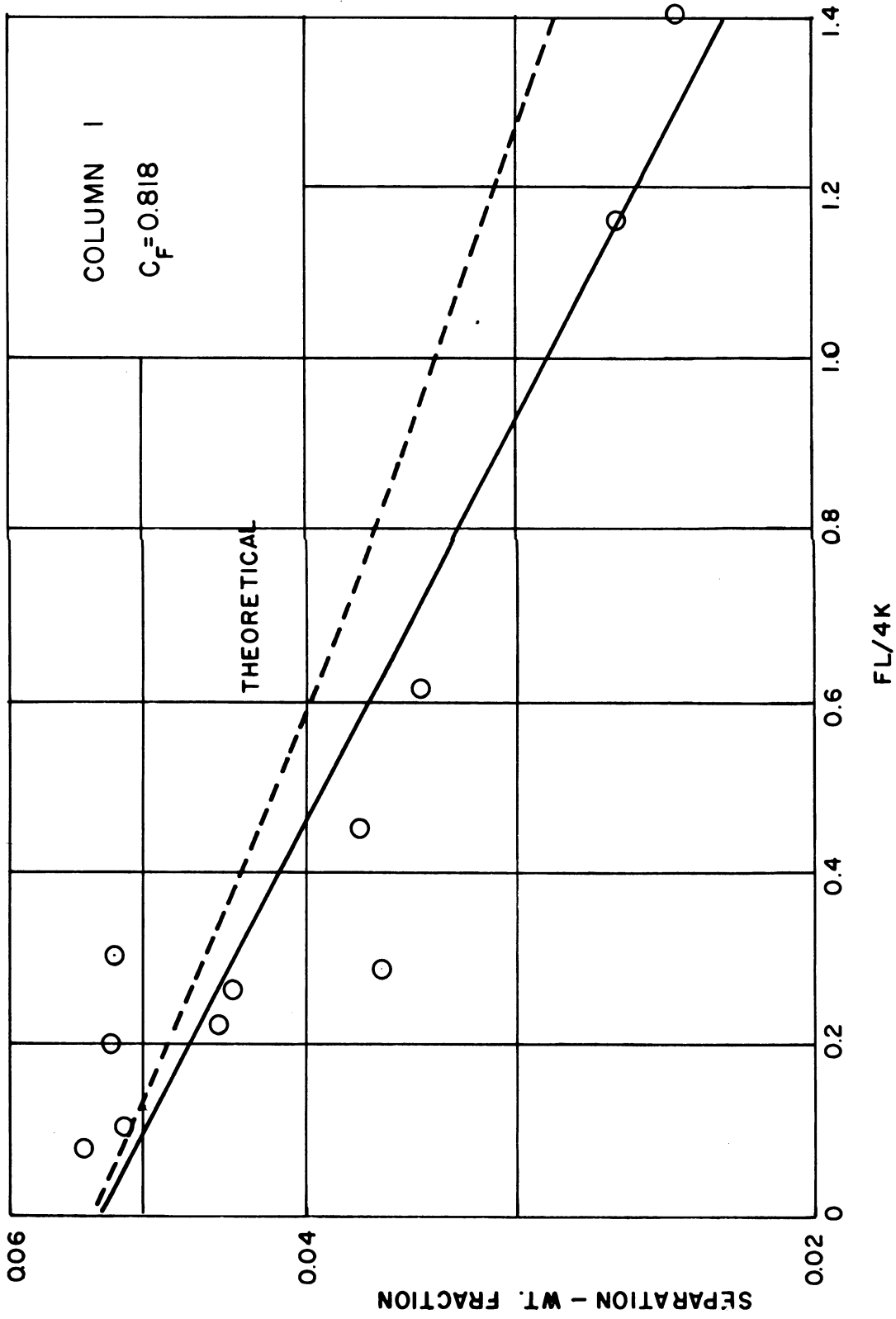
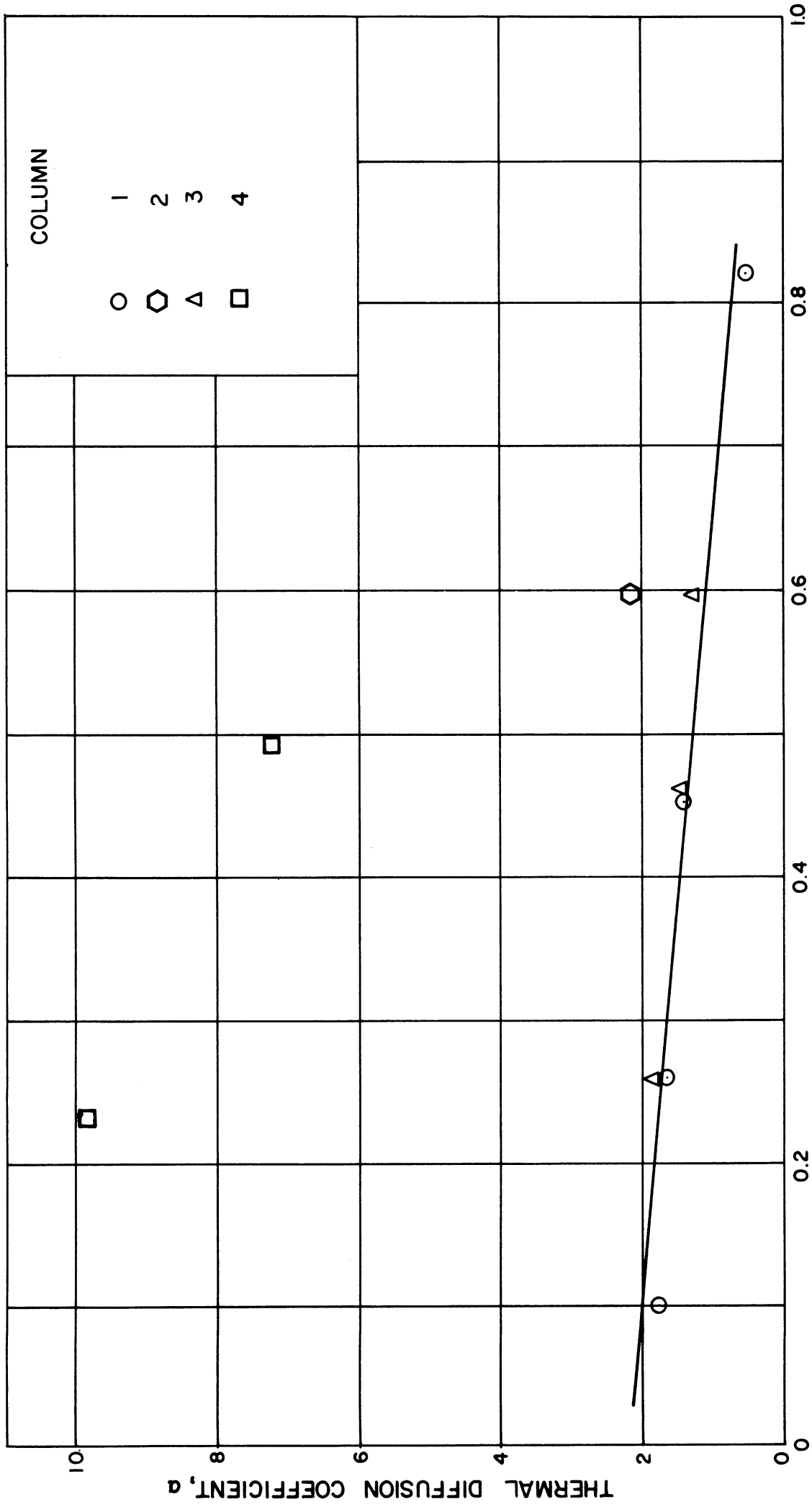Fig. 8. Performance of Column 1 at a Feed Concentration of 0.818.

Fig. 9. Performance of Column 3 at a Feed Concentration of 0.261.

Fig. 10. Performance of Column 3 at a Feed Concentration of 0.462.

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Fig. 11. Performance of Column 3 at a Feed Concentration of 0.598.

Fig. 12. Performance of Column 2 at a Feed Concentration of 0.594.

Fig. 13. Performance of Column 4 at a Feed Concentration of 0.230.

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Fig. 14. Performance of Column 4 at a Feed Concentration of 0.489.
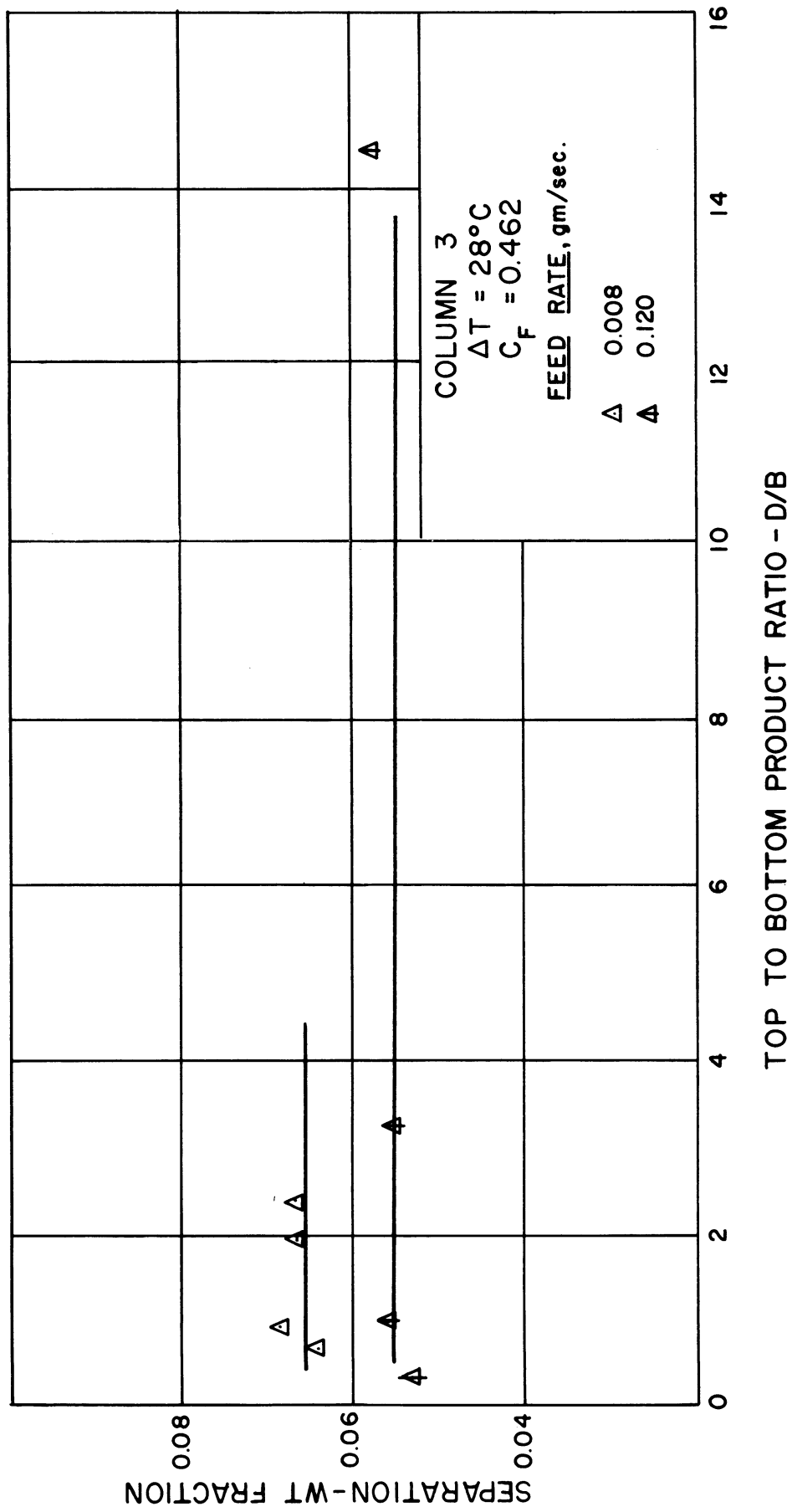
Fig. 15. Effect of Ratio of Top to Bottom Product Flow on Separation.

COLUMN 3
$\Delta T = 28°C$
$C_F = 0.462$

FEED RATE, gm/sec.

△   0.008
▲   0.120

TOP TO BOTTOM PRODUCT RATIO – D/B

SEPARATION–WT FRACTION

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WT. PERCENT N-HEPTANE

Fig. 16. Thermal Diffusion Coefficient Determined
from Performance of Several Columns.

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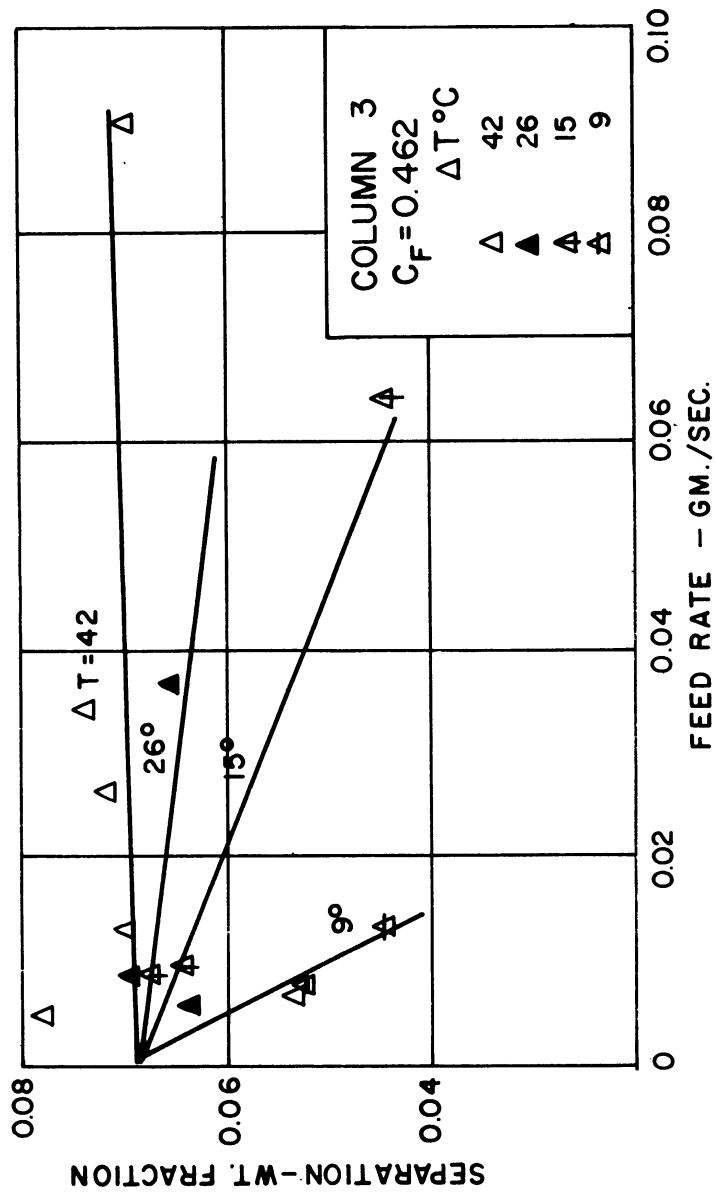
Fig. 17. Effect of Temperature Difference on Separation at a Feed Concentration of 0.462.
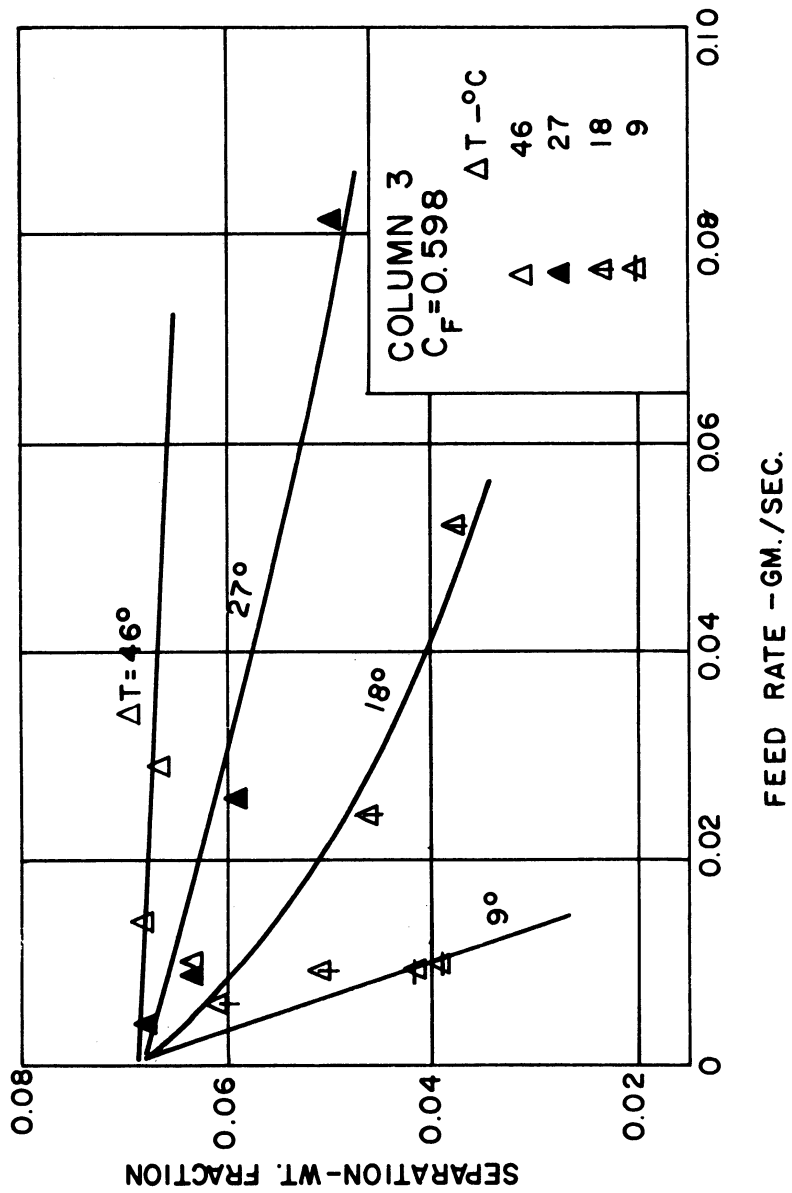
Fig. 18. Effect of Temperature Difference on Separation at a Feed Concentration of 0.598.
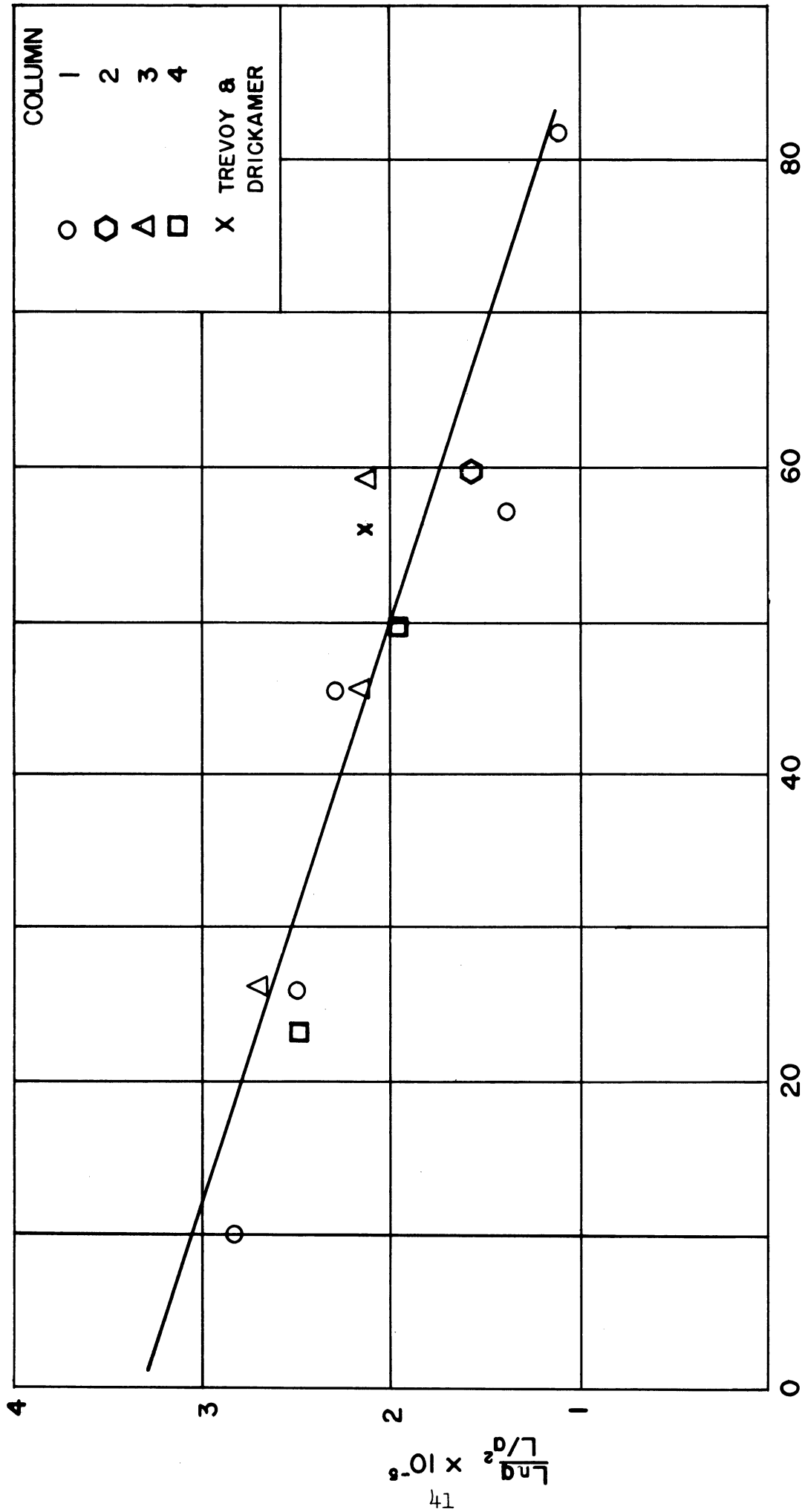
Fig. 19. Final Correlation for Continuous Separation.

Fig. 20. Correlation of Total Reflux Results.

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