$$N = \frac{E_1(y_0 - y_N)}{(y_N + A - E_1)(y_0 + A - E_1)} \qquad (12A)$$

If the roots of the discriminant (3A) are complex, a case which often arises in practical applications, one may write (3A) in two forms:

$$E_1 = \frac{A-B}{2} + ip \qquad (13A)$$

and

$$E_2 = \frac{A-B}{2} - ip \qquad (14A)$$

where

$$ip = \sqrt{\left(\frac{A+B}{2}\right)^2 - C} \qquad (15A)$$

When (6A) and (8A) are combined

$$\left(\frac{E_1}{E_2}\right)^n = \frac{(E_2 - y_n - A)(y_0 + A - E_1)}{(E_2 - y_0 - A)(y_n + A - E_1)} \qquad (16A)$$

When (13A) and (14A) are inserted, the equation may be rearranged to obtain, at $n = N$ and $y_n = y_N$

$$\left[\frac{\dfrac{A-B}{2} + ip}{\dfrac{A-B}{2} - ip}\right]^N = \frac{\left(y_N + \dfrac{A+B}{2} + ip\right)\left(y_0 + \dfrac{A+B}{2} - ip\right)}{\left(y_N + \dfrac{A+B}{2} - ip\right)\left(y_0 + \dfrac{A+B}{2} + ip\right)} \qquad (17A)$$

The complex numbers may then be represented as follows:

$$re^{i\theta} = \frac{A-B}{2} + ip \qquad (18A)$$

where

$$\arctan \frac{2p}{A-B} = \theta \qquad (19A)$$

$$r_2 e^{i\theta_2} = y_N + \frac{A+B}{2} + ip \qquad (20A)$$

where

$$\arctan \frac{p}{y_N + (A+B)/2} = \theta_2 \qquad (21A)$$

$$r_1 e^{i\theta_1} = y_0 + \frac{A+B}{2} + ip \qquad (22A)$$

where

$$\arctan \frac{k}{y_0 + (A+B)/2} = \theta_1 \qquad (23A)$$

When these are inserted into (17A) one obtains

$$e^{2iN\theta} = e^{2i\theta_2} \cdot e^{-2i\theta_1} \qquad (24A)$$

When logarithms are taken

$$N = \frac{\theta_2 - \theta_1}{\theta} \qquad (25A)$$

Thermal Diffusion of Liquids in Columns

DAVID T. HOFFMAN, JR., and ALDEN H. EMERY, JR.

Purdue University, Lafayette, Indiana

A number of studies of the operating variables of the thermal diffusion column have been made since the war. Most of these show that the early theory is essentially correct, but that certain irregularities may prevail. The purpose of the present work is to continue the study of the theory of the column in transient batchwise operation and in continuous flow. The work was limited to liquids in annular columns without end reservoirs.

PREVIOUS WORK

The early studies of thermal diffusion were made in the single-stage, convection-free apparatus in which separations are very small. In 1938 Clusius and Dickel (*1*) devised the thermal diffusion column which acts as a multistage device and thus greatly magnifies the possible separations. In 1939 Furry, Jones, and Onsager (2) and, independently, Debye (3) published theories to explain the behavior of the column. A number of investigations followed which demonstrated the approximate validity of the theory of the column for gases.

David T. Hoffman, Jr., is with the du Pont Company, Buffalo, New York.

TABLE 1.

Investigation		Liquid system	Slopes of plots against ΔT, slope divided by average ordinate $(\frac{m}{y} \pm 2s)\ 10^2$			Slopes of logarithmic plots against $\log w$			Comparison of various investigations, n-heptane-benzene system	
			Y	$\frac{H}{\Delta T^2}$	$\frac{K}{\Delta T^2}$	$\frac{Y(2w)^4}{L}$	$\frac{\overline{HT}\eta}{\Delta T^2(2w)^3}$	$\frac{\overline{KT}\eta}{\Delta T^2(2w)^7}$	$\frac{Y(2w)^3}{L} \times 10^6$	$\frac{H}{B\Delta T^2(2w)^2} \times 10^5$
Batch operation:										
Present authors		cumene-cetane	0.4 ± 0.1	—0.7 ± 0.3	—1.1 ± 0.5	0.5 ± 0.4	0.8 ± 0.3	0.5 ± 0.6		
Longmire (*10*)	Runs I C 1-4, 7	benzene-carbon tet.	1.2 ± 0.8			1.1 ± 0.6				
	Run II C 1	n-heptane-benzene				1.5			3.3	
	Run II C 2	n-heptane-benzene							4.3	
Powers (*12*)	all	n-heptane-benzene	0.2 ± 0.1			0.4	—0.1			
	Exp. 18 II	n-heptane-benzene							2.8	9
	Exp. 17 III	n-heptane-benzene							2.2	16
Continuous operation:										
Longmire (*10*)	Runs I 1-27	benzene-carbon tet.		—4 ± 7			—1 ± 2			
	Runs II 7-21	n-heptane-benzene								5.4
Powers (*9*)	Groups A, B, C, D	ethanol-water	0.5 ± 0.2	—2.6 ± 0.9	—2.3 ± 0.9					
	Groups F, G, I	ethanol-water	0.6 ± 1.0	—0.8 ± 1.1	—1.4 ± 1.7					
	Groups Q, U, V, W, Z	ethanol-water				1.1 ± 0.3	—1.6 ± 0.4	—3.0 ± 0.6		
	Group BB	n-heptane-benzene				0.4	—1.2		2.9	5.1
	Group BC	n-heptane-benzene							2.4	4.8
Heines et al. (*11*)	Col. 3, $c_f = 0.462$	n-heptane-benzene				2			2.3	

Early exploratory work on the separation of organic liquids, and recent work on optimum column arrangements, has been done by A. L. Jones and his coworkers (*4* to *6*). Several studies have been made of the application of the theory to columns containing liquids. Jones and Furry (*7*) presented a thorough review of the subject in 1946; Powers (*8*, *9*) reviewed the field to 1954; Longmire (*10*) recently extended the review to 1957. Recent papers concerned with the application of the theory to reservoir-less columns containing liquids are discussed below.

Powers and Wilke (*9*) investigated the effects of feed rate, column length, plate spacing, $2w$, temperature difference, ΔT, and column inclination on the separation of two binary solutions, ethanol-water and n-heptane-benzene, in continuous flow in parallel-plate columns. They concluded that the theory correctly accounts for the effects of all variables except w, for which large discrepancies were found. They found that the constants H and K vary with w raised to the powers 1.5 and 5, respectively, instead of 3 and 7 as predicted by theory. This gives an empirical variation of the constant Y, defined by the ratio of H and K, as in Equation (4), with the —3.5 power of w instead of —4 predicted theoretically. They devised an empirical correlation which successfully accounts for a large amount of data on both liquids and gases.

Heines, Larson and Martin (*11*) studied the effects of all the same variables, except inclination, in continuous flow of n-heptane-benzene solutions in annular columns. They found that Y varied as w raised to the power —2, as compared to the Powers and Wilke value of —3.5 and theoretical value of —4. They concluded from their data that ΔT has no effect on Y, but does have an effect on K which is not included in the theory.

Longmire (*10*) investigated the effects of w, ΔT, and feed concentration on the steady state batch separation and these variables plus feed rate in continuous flow of benzene-carbon tetrachloride, n-heptane-benzene, and one ternary system in annular columns. His conditions of operation were unique in that he frequently approached complete separation. As he points out, his empirical correlation involves almost the same groups of variables as the theory, but not always the same group functions. One may judge from the batch results that the theoretical variation of Y with w and ΔT satisfactorily correlate the data. In the continuous results, however, Longmire's function is not the theoretical one, and no direct comparison may be made with the theory.

Powers (*12*), using concentric columns, studied the effects of w, ΔT, and time in transient batch operation with the system n-heptane-benzene. He found an effect of ΔT contrary to theory in both Y and K, corroborated the extraneous effect of annular spacing on Y that he found earlier (*9*), but found no extraneous effect of w on K.

The four studies above were all made with organic liquids in fairly long, reservoir-less columns, and yet seem to give conflicting results, rarely recording the same deviations from theory. The largest deviations from theory and from each other seem to come in the effect of w. This variable is always suspect because it is usually small and difficult to determine and is raised to large powers in the theoretical equations. Are the reported deviations due to magnification of experimental error, or are they real? To answer this question the present authors employed statistics in an analysis of the data reported here and also selected data from the four studies above. The results, summarized in Table 1 and discussed later, show that the deviations are real, and further that some were overlooked in the original analysis.

EQUATIONS

The complete theoretical differential equations with some solutions were first published by Furry, Jones, and Onsager in 1939 (*2*). Their system of notation, as amended by Jones and Furry (*7*), is followed here for the most part.

Continuous Flow

Jones and Furry presented the general solution of the differential equations for steady state continuous operation of the column, exact for all concentrations. The present authors obtained the same equation using Laplace transforms:

$$\tanh \frac{b' Y_e}{2} = \frac{b'\,(c_f - c_i)}{c_f + c_i - n_e\,(c_f - c_i) - 2c_f c_i} \tag{1}$$

in which

$$n_e = \frac{\sigma_e}{H},\quad b' = [(1 + n_e)^2 - 4 n_e c_f]^{1/2}$$

$$H = \frac{g\,B\,(2w)^3\,(\Delta T)^2\,\alpha\,\beta\rho}{6!\,\bar{T}\,\eta} \tag{2}$$

$$K = g^2\,\frac{B\,(2w)^7\,(\Delta T)^2}{9!\,D\,\eta^2}\,\beta^2\rho \tag{3}$$

$$Y_e = \frac{H L_e}{K} = \frac{504\,\alpha\,D\,\eta\,L_e}{g\,(2w)^4\,\beta\,\bar{T}} \tag{4}$$

Equation (1) applies to the enriching section of the column, that section of the column above the feed point. An equation for the stripping section, that section of the column below the feed point, can be obtained by substituting $(1 - c)$ for all the c's, and the proper physical parameters in Y and n.

Equation (1) is too complicated to be illuminating, according to Jones and Furry, and they list simpler solutions for limited ranges of concentration which show the variation of separation with the parameters in a clearer fashion. No one has bothered to use Equation (1) and most investigators limit their concentration range to correspond to one of the approximations, while some correlate their results empirically. The authors used a computer to effect a least-squares determination of the constants Y and H for each set of data, and it was little extra trouble to use Equation (1). This also enabled the authors to obtain values of these constants for data in the literature for which the simplifications of Jones and Furry did not apply.

A more convenient form of Equation (1) is

$$\Delta_e \equiv c_f - c_i = \frac{2c_i(1 - c_i)}{n_e - 1 + 2c_i + b' \coth \dfrac{b' Y_e}{2}} \tag{5}$$

This form converges rapidly in an iterative solution and reduces readily to simpler forms. In the limit of zero flow rate, b′ is unity, and Equation (5) becomes

$$\Delta_e = \frac{c_i(1 - c_i)\,(e^{Y_e} - 1)}{c_i(e^{Y_e} - 1) + 1} \tag{6}$$

Equation (6), the exact solution for zero flow in the continuous case, differs from Equation (15), the exact solution for infinite time in the batch case, because of the difference the material balance makes in the two cases. If Y_e is small, then Equation (5) becomes

$$\Delta_e = c_i(1 - c_i) Y_e \tag{7}$$

and this is in exact agreement with the corresponding simplification for the batch case.

When the flow rate is large, $b' = n_e$ and Equation (5) reduces to

$$\Delta_e = c_i(1 - c_i)/n_e \tag{8}$$

One of the simpler solutions of the differential equation listed by Jones and Furry is that for the case in which $c(1 - c)$ is constant throughout the column. This is

$$\Delta_e = c_i(1 - c_i)\,(1 - e^{-n_e Y_e})/n_e \tag{9}$$

In the limit of zero flow rate, this reduces immediately to Equation (7), and for high flow rates it reduces to Equation (8). Thus at high flow rates the simpler Equation

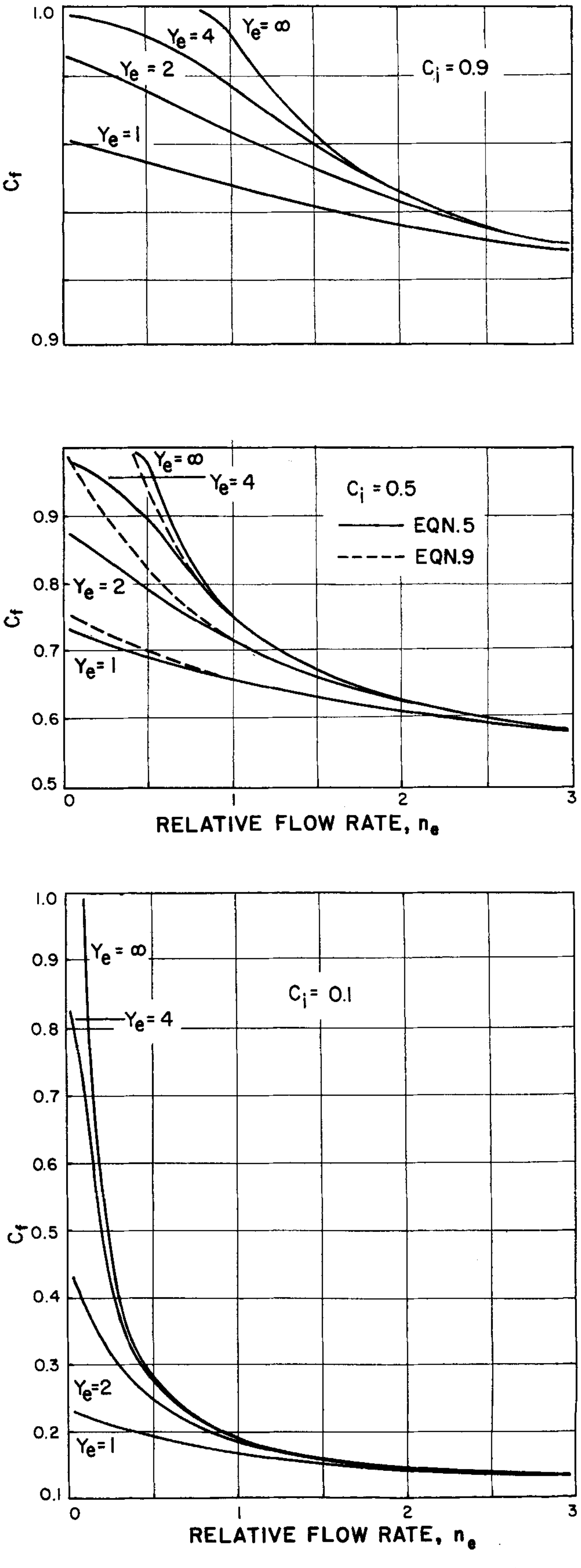

Fig. 1. Influence of flow rate and column parameters on outlet concentration in continuous operation. Some examples of the solution of Equation (5).

(9) and the exact Equation (5) give the same results; elsewhere they give different results unless Y is small.

Several examples of the manner in which c_f varies with flow rate as calculated from Equation (5) are shown in Figure 1. For the group of curve for $c_i = 0.5$, the results of Equation (9) are also shown for comparison. The curve for $Y_e = \infty$ is the hyperbola given by Equation (8) down to about $n = c_i$, below which it approaches unity asymptotically. Curves for other values of Y_e approach the hyperbola asymptotically as n increases.

These curves are drawn for the enriching section, but are also valid for the stripping section if $(1-c)$ is substituted for c. Thus the enriching section curves of c_f vs. n_e for $c_i = 0.9$ are also stripping section curves of $(1-c_f)$ vs. n_s for $(1-c_i) = 0.9$. For example, if $c_i = 0.9$, $Y_e = 1$, $Y_s = 2$, $n_e = 1$, $n_s = 1/2$, then from the curve for $c_i = 0.9$, c_f for the enriching section is 0.947, and from the curve for $c_i = 0.1$, $(1-c_f)$ for the stripping section is 0.247, or c_f for the stripping section is 0.753, and $\Delta_e = 0.047$, $\Delta_s = 0.147$, $\Delta = \Delta_e + \Delta_s = 0.194$.

By applying these equations to the data collected in tests in which flow rate is the only quantity varied, one obtains values of the two fundamental constants, Y and H (or Y and K, or H and K). Continuous tests at different operating conditions are compared by observing the effects of the variables on Y and H.

Batch Operation

The first solutions of the differential equations for the batch case in the reservoir-less column by Debye (*3*) and Bardeen (*13*) were for dilute solutions. Powers (*12*) solved the equations for the case in which $c(1-c)$ is constant with position and time. Majumdar (*14*) has presented the exact solution for all concentration ranges. His solution for c as a function of vertical position z and time t involves a ratio of infinite series, but after a time $t = 0.3\tau$, when only the first term of each series is retained, there is less than 1% error as shown by trial calculations for extreme cases. This gives

$$c = \frac{1}{2} + \frac{1}{2}\frac{(k_1 e^{y} - 1)}{(k_1 e^{y} + 1)} + k_2 \cos\frac{\Pi z}{L}\, e^{-\frac{t}{\tau}} \qquad (10)$$

in which

$$\tau = 2wB\rho L/HY\left(\frac{1}{4} + \frac{\Pi^2}{Y^2}\right) \qquad (11)$$

$$k_1 = (e^{c_0 Y} - 1)/(e^{Y} - e^{c_0 Y})$$

$$k_2 = \frac{2\,c_0\,(1-c_0)\,\Pi^2\,(e^{Y}-1)\,(1+e^{-b_0 Y})}{Y^3\left(b_0{}^2 + \frac{\Pi^2}{Y^2}\right)\left(\frac{1}{4} + \frac{\Pi^2}{Y^2}\right)\left[(e^{c_0 Y} - 1)\, e^{\frac{y}{2}} + (e^{Y} - e^{c_0 Y})\, e^{\frac{-y}{2}}\right]}$$

$$Y = \frac{HL}{K},\ y = \frac{Hz}{K},\ b_0 = \frac{1}{2} - c_0$$

The difference in concentration Δ between samples taken at two points in the column is

$$\Delta = \Delta_\infty\,(1 - k_3\, e^{-\frac{t}{\tau}}) \qquad (12)$$

If one sample is taken from the bottom of the column and the other from some point below the top of the column, as was done in the experiments reported below, then

$$\Delta_\infty = \frac{(e^{Y}-1)\,(e^{c_0 Y}-1)\,(e^{Y}-e^{c_0 Y})}{(e^{Y}-1)\,[e^{c_0 Y}\,(e^{Y}-1) + e^{Y} - e^{y}]} \qquad (13)$$

$$k_3 = \frac{2\,c_0(1-c_0)\,\Pi^2\,(1+e^{-b_0 Y})\,(e^{Y}-1)}{Y^3\left(b_0{}^2 + \frac{\Pi^2}{Y^2}\right)\left(\frac{1}{4} + \frac{\Pi^2}{Y^2}\right)} \left\{\frac{1}{e^{Y} - e^{c_0 Y}} + \frac{(e^{Y}-1)\left(1 - e^{\frac{y}{2}}\cos\frac{\Pi z}{L}\right)}{(e^{Y}-1)\,(e^{Y}-e^{c_0 Y})\,(e^{c_0 Y}-1)}\right\} \qquad (14)$$

On the other hand, if the samples are removed from the top and bottom

$$\Delta_\infty = \frac{(e^{c_0 Y}-1)\,(e^{Y}-e^{c_0 Y})}{e^{c_0 Y}\,(e^{Y}-1)} \qquad (15)$$

$$k_3 = \frac{2\,c_0(1-c_0)\,\Pi^2\,(1+e^{-b_0 Y})\,(e^{Y}-1)\,(e^{c_0 Y} + e^{\frac{y}{2}})}{Y^3\left(b_0{}^2 + \frac{\Pi^2}{Y^2}\right)\left(\frac{1}{4} + \frac{\Pi^2}{Y^2}\right)(e^{c_0 Y}-1)\,(e^{Y}-e^{c_0 Y})} \qquad (16)$$

The constant k_3 changes very slowly with Y, which facilitates calculations. If y and Y are small, Equations (11), (13), and (14) reduce to

$$\Delta_\infty = c_0(1-c_0)y,\quad k_3 = \frac{4L\left(1 - \cos\frac{\Pi z}{L}\right)}{\Pi^2 z} \qquad (17)$$

and

$$\tau = 2wB\rho LY/\Pi^2 H$$

If $y = Y$, and Y is small

$$k_3 = 8/\Pi^2$$

These last results coincide with those of Powers (*12*), after $t = 0.3\tau$, when all but the first term of his series may be neglected.

Thus all experiments involving transient operation at any concentration may be treated with Equation (12), but different expressions for Δ_∞, k_3, and τ will be involved, depending on the conditions of sampling and degree of separation. When these equations are applied to the data collected in tests in which time is the only variable, one obtains values of the two fundamental constants, Y and H. Tests at different operating conditions are compared by observing the effects of the variables on Y and H.

EXPERIMENTAL WORK

Three different concentric-tube thermal-diffusion columns with annular spacings of 0.0159, 0.0204, and 0.0244 in. were used. The working space in the columns was 54.5, 56.7, and 54.1 cm., respectively, and the column circumference was 7.78 cm. Sample taps were located at the top, middle, bottom, and 2 in. below the top. Each wall contained four thermocouples for the measurement of temperature. Warm water or steam was passed through the center tube, cooling water around the outside tube. A gravity flow system, with head tank, shunted capillary tubes, and hypodermic-needle sampling ports similar to that used by Powers (*8*), was used in the continuous-flow work.

Two liquid systems were used: 0.324 mole fraction cetane (n-hexadecane) in cumene (isopropyl benzene), and 0.528 mole fraction 1,1,2,2-tetrachloroethane in 1,1,2,2-tetrabromoethane.

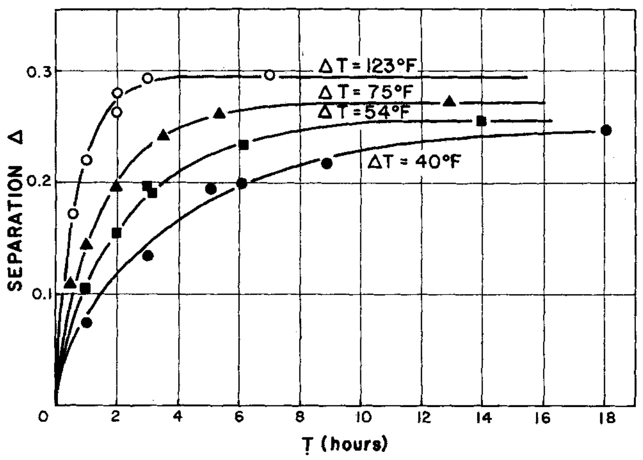

Fig. 2. Separation as a function of time, batch operation. Series 6, 7, 8, 9, average temperature, 140°F. Lines are Equation (12) with the least-square values of the two constants.

A series of about six batch runs was made with all conditions held constant except time. Typical data are shown in Figure 2. A series of about eight continuous runs was made with all conditions held constant except feed rate. Typical data are shown in Figure 3 in which $\Delta = \Delta_e + \Delta_s$ is plotted against $\sigma = \sigma_e + \sigma_s$. The best values of the constants Y and K in Equation (5) or (12) were determined by least squares, with the assumption that error occurs only in Δ and not in *t* or σ. The curves in Figures 2 and 3 were calculated from Equations (5) and (12) with the resulting least-square values of Y and K. The trial-and-error least-squares calculations were made on a digital computer in programs which also determined the standard deviations S_Y and S_H of the two constants. The results, shown in Table 2, were then further analyzed for the effects of the three variables studied: temperature difference ΔT, average temperature T, and annual spacing 2w.

RESULTS OF THE BATCH OPERATION

Effect of Temperature Difference

One significant deviation from theory observed from the results is in the effect of ΔT. The values of Y for series 6 through 9 are shown in Figure 4 plotted against ΔT; $2s$ limits are also shown. The fact that the points cluster closely to the line while the $2s$ limits for each point are large is coincidental; other comparable plots behaved more typically with the points scattering from a line and compatible with the $2s$ values for the points. It seems clear from the plot that the variation is significant, whereas theoretically Y should be independent of ΔT as indicated in Equation (4).

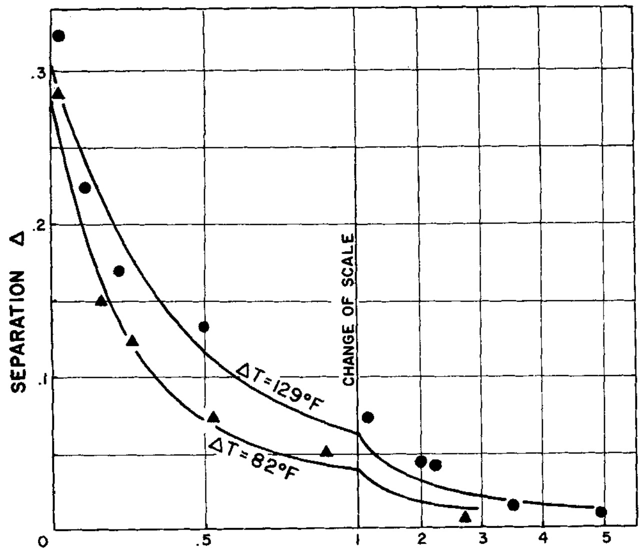

Fig. 3. Separation as a function of feed rate, continuous operation. Series 24 and 25. Lines are Equation (5) with the least-square values of the two constants.

TABLE 2.

Series	$2w$, in.	T, °F.	ΔT, °F.	Y or Y_e	S_Y	$H, \frac{g.}{sec.} \cdot 10^4$	$S_H \cdot 10^4$
Batch operation. System: cumene-cetane							
1	0.0159	140	120	3.14	0.067	3.93	0.22
2	│	140	73	3.02	0.22	1.52	0.27
3	│	130	75	2.87	0.11	1.61	0.15
4	│	116	75	2.75	0.26	1.40	0.34
5	↓	168	77	3.49	0.12	1.93	0.15
6	0.0204	140	123	1.526	0.036	9.29	0.95
7	│	140	75	1.394	0.023	3.94	0.24
8	│	140	54	1.302	0.028	2.45	0.16
9	│	140	40	1.281	0.048	1.38	0.16
10	│	130	72	1.306	0.011	3.97	0.13
11	│	115	74	1.344	0.032	3.34	0.27
12	↓	168	77	1.327	0.020	6.46	0.42
13	0.0244	140	72	0.703	0.012	9.08	0.69
14	│	129	73	0.695	0.015	7.05	0.66
15	│	116	74	0.675	0.010	7.17	0.46
16	│	168	76	0.689	0.014	9.31	0.82
17	↓	142	125	0.708	0.0045	20.20	0.64
System: tetrachloroethane-tetrabromoethane							
18	0.0159	142	124	3.52	0.16	29.4	4.9
19	0.0204	170	78	1.251	0.018	23.8	1.5
20	│	139	72	1.151	0.031	26.9	3.6
21	↓	142	126	1.289	0.013	65.2	4.6
22	0.0244	143	133	0.654	0.0096	87	11
Continuous flow. System: cumene-cetane							
23	0.0244	144	133	0.3679	0.0063	19.55	0.75
24	0.0204	146	129	0.817	0.058	11.9	1.8
25	0.0204	176	82	0.735	0.030	6.82	0.50

As a test of significance in this and later cases, the slope m and standard deviation s_m of a straight line on the plot were calculated with the calculated s of the points and not the scatter from the line. This test is crude because the proper relationship is not a straight line; but since s_m is obtained from the calculated s of the points, it gives a first approximation of significance. The results of the application of this test are clear-cut. They indicate no significant deviation from the predictions of theory in the case of T and significant deviations from theory in the case of w and ΔT, as explained below.

The slope of the line in Figure 4 is $(4.1 \pm 1.5)10^{-3}$ in which $2s$ is indicated. This shows that the slope is significantly different from zero at the 5% level. From Equation (2), the group $H/\Delta T^2$ should be independent of ΔT, but the slope of a plot of this group against ΔT is $(-10 \pm 7)10^{-3}$, and in the case of $K/\Delta T^2$, $(-6 \pm 3)10^{-2}$. All these are significantly different from zero. These same slopes, divided by the average value of the ordinate to make them comparable to the results of other investigations, are shown in Table 1.

Also shown in Table 1 are some results from the data of other investigations obtained by use of the least-squares program. Almost all of these other results, when so analyzed, corroborate the existence of these discrepancies in the theoretical effect of ΔT, and even show the same directions of deviation.

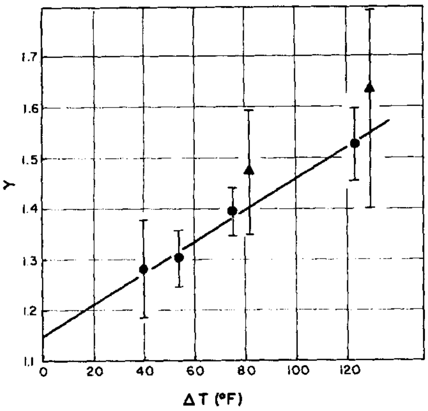

Fig. 4. Variation of Y with temperature difference. The straight line was placed through the circles, taken from batch operation, series 6, 7, 8, 9. The triangles are from continuous operation, series 24 and 25, and show that the continuous results are not significantly different from the batch.

No aspect of the data or anything observed during operation of the column suggests the reason for these variations. The sizable variations of viscosity and diffusion coefficient in the annular pace, ignored in the statement and usage of the constants Y and H given by Equations (2) and (4), contribute negligibly to any alteration of Y and H with ΔT in this case (*15*). It may be, as some authors have suggested, that the fluid dynamics of the column is not completely understood.

Effect of Average Temperature

Four series of runs at each of the three annular spacings were made to test the effect of $\overline{T}$, a variable which has received little attention. All of the system properties change with temperature, but the change in ρ and β may be neglected, and the change in α, while not completely negligible, is usually slight (*16*). The variables η and D are the most important. From Equation (2), then, $H\,\overline{T}\,\eta$ should theoretically be independent of $\overline{T}$.

For many systems, the group $(D\,\eta/\overline{T})$ is independent of temperature (*17*). Measurements here indicate that this is true of the cumene-cetane system involved. Consequently, according to Equation (4), Y should be independent of $\overline{T}$. Equation (3) can be rearranged to give

$$K\overline{T}\,\eta = g^2\,\frac{B\,(2w)^7}{9!}\,\Delta T^2\,\beta^2\,\rho\left(\frac{\overline{T}}{D\eta}\right) \qquad (18)$$

which, in conjunction with the above conclusions, indicates that $K\overline{T}\eta$ should theoretically be independent of $\overline{T}$.

Three quantities, Y, $\dfrac{H\overline{T}\eta}{\Delta T^2}$, and $\dfrac{K\overline{T}\eta}{\Delta T^2}$, were calculated for each series and plotted against $\overline{T}$. ΔT^2 was used to eliminate the effect of small variations in ΔT. Only one of the nine resulting slopes, that for Y at $2w = 0.0159$ in., was significantly different from zero, which shows that the variation of column behavior with $\overline{T}$ is correctly given by the theory.

The viscosity η of 0.324 mole fraction cetane in cumene used in two of these quantities was calculated from the equation

$$\ln\eta = c\left(\frac{1975}{\overline{T}} - 5.525\right) + (1-c)\left(\frac{1115}{\overline{T}} - 4.048\right) + 0.34\,c(1-c) \qquad (19)$$

which represents an empirical fit of data taken in this laboratory from 20°C. to 60°C. and over the entire concentration range. Here c is the mole fraction of cetane and T is absolute temperature in degrees Kelvin.

Effect of Annular Spacing

Since $\overline{T}$ is correctly accounted for by the theory, weighted averages were taken of the three groups above for all the values of $\overline{T}$, at $\Delta T = 75F$, weighted according to $1/s^2$. From these were calculated the groups

$$\frac{Y(2w)^4}{L},\quad \frac{H\overline{T}\eta}{\Delta T^2(2w)^3},\quad \frac{K\overline{T}\eta}{\Delta T^2(2w)^7} \qquad (20)$$

which, according to the theory, should be independent of w. The slope, m, and s_m of a log-log plot of each group against w were calculated. The results are shown in Table 1 with some results of other investigations.

There appears to be a significant deviation from the theoretical prediction of the effect of w on Y and H. The numbers in the first row indicate that Y varies as w raised to the power 3.5 ± 0.4 and H as w to the power 3.8 ± 0.3, instead of the theoretical values 4 and 3, respectively. The cause of these deviations is likewise unknown.

The results from other investigations corroborate this conclusion, but the significance of the deviation, and the agreement on the direction of deviation, is less than in the case of the variation with ΔT.

RESULTS, CONTINUOUS OPERATION

The constants calculated from Equation (12), shown in Table 2, are not significantly different from those calculated from the batch data at comparable conditions, but there are not sufficient data to draw independent conclusions on the effects of the variables. Note that the values of Y_e tabulated for the continuous runs must be multiplied by two to correspond to the values of Y tabulated for the batch runs. To show the similarity of results, the values of $2Y_e$ from series 24 and 25 are plotted in Figure 4 along with the values of Y from the batch runs: these values were not used in calculating the slope of that plot mentioned above.

ABSOLUTE VALUES OF Y, H, AND K

The theory predicts both trends in and absolute values of the experimentally determined Y, H, and K. For this comparison, weighted averages of the groups (20) from the batch data at $\Delta T \cong 75$°F. and all three annular spacings were taken. The same groups were calculated from the continuous data, and were corrected to a ΔT of 75°F. by the evidence from the batch runs. Fluid properties for the two binary systems are shown in Table 3. The data is

TABLE 3. SYSTEM PROPERTIES
2s values indicated

	Cumene-cetane	Tetrachloroethane-tetrabromoethane
ρ, $\dfrac{\text{g.}}{\text{cc.}}$	0.79 ± 0.01	2.20 ± 0.02
β, $\dfrac{\text{g.} \times 10^3}{\text{cc. °C.}}$	0.73 ± 0.02	1.92 ± 0.02
$\dfrac{D\eta}{T}$, $\dfrac{\text{dyne}}{\text{°K.}} \times 10^{10}$	0.77 ± 0.07	$0.72 \pm \sim 0.07$
	3.4 ± 0.5	3.0 ± 0.6

TABLE 4. ABSOLUTE COMPARISON OF RESULTS

	$\frac{Y(2w)^4}{L} \times 10^7$	$\frac{H\bar{T}\eta}{\Delta T^2(2w)^3} \times 10^3$	$\frac{K\bar{T}\eta}{\Delta T^2(2w)^7} \times 10^{-4}$
System: cumene-cetane			
Theoretical	1.8 ± 0.3	4.7 ± 0.5	2.6 ± 0.4
Batch	1.7 ± 0.1	4.8 ± 0.2	2.7 ± 0.2
Continuous	1.8 ± 0.1	5.0 ± 0.4	2.7 ± 0.3
System: tetrachloroethane-tetrabromoethane			
Theoretical	0.6 ± 0.1	32 ± 5	55 ± 11
Batch	1.7 ± 0.1	49 ± 6	28 ± 4

all taken from measurements made here except for α for the halogen system which was taken from Saxton and Drickamer (*16*). The results are shown in Table 4.

The most important conclusions to be drawn from Table 4 are that the results of continuous and batch measurements are not significantly different, and for the cumene-cetane system neither differs significantly from the predicted value. However, for the halogen system, the results are quite different. In view of the fact that there are imperfections in the theoretical predictions of the effect of ΔT and w, the agreement in the one case and disagreement in the other may mean nothing. Perhaps one should be pleased that the orders of magnitude are the same. Comparisons of this sort rarely agree, partly, at least, because of a notorious uncertainty in the value of thermal diffusion constant, α. One investigator may get a value four times that of another (*8, 13*).

COMPARISON OF VARIOUS INVESTIGATIONS

Selected results of Powers (*8*) and Longmire (*10*) were subjected to the same statistical treatment as the data reported here. The results are shown in Table 1 with the results of the present investigation. Some other values not treated statistically are also shown. Most of the slopes differ significantly from zero, whereas they should all be zero according to the theory. Thus all of these investigations indicate some significant deviations from theory. Furthermore, there is some agreement in the kind of deviation. For example, Table 1 shows that Y increases and the groups involving H and K decrease with increasing ΔT.

Powers, Longmire, and Heines et al. each made at least a few tests with the system n-heptane-benzene. In comparing these results, the non-theoretical effect of ΔT can be ignored because it is small, but the effect of w should be taken into account. The data on the effect of w in this system, shown in Table 1, are sketchy and conflicting but for the purpose of comparison it is assumed that Y varies as w^{-3} and H as w^2. The groups in the last two columns of Table 1 should then be the same for all investigations.

The agreement is remarkable in view of the different circumstances in which the data were collected. Powers' continuous data were taken in parallel-plate columns and the rest of the data in annular columns. Longmire obtained very large separations, Heines et al. very small. The only peculiarity of the collection is that the H group seems to be different in batch and continuous work. None of these data were analyzed statistically, but from the nature of other results, it seems unlikely that the uncertainty in these figures could be large enough to make the difference uncertain. In the experiments reported here on the cumene-cetane system in which batch and continuous runs were made in the same apparatus, there was no significant difference in either in the Y or the H group between batch and continuous. The implication is that there are large experimental flaws in thermal diffusion work, possibly in the critical nature of the annular spacing.

NOTATION

B = column circumference, or plate width
b_o, b' = groupings of constants and variables
c = concentration
c_i, c_f = inlet and outlet concentrations, continuous flow operation
c_0 = initial concentration, batch operation
D = diffusion coefficient
g = acceleration of gravity
H, K = phenomenological constants
k_1, k_2, k_3 = groupings of constants and variables
L = total column length
n = relative flow rate
t = time
$\bar{T}$ = average temperature in the column
ΔT = temperature difference between the parallel solid surfaces
w = half width of the column, perpendicular to the surfaces
Y = phenomenological constant
y = dimensionless vertical distance variable
z = vertical distance variable

Greek Letters

α = thermal diffusion constant
β = $-\partial\rho/\partial T$
Δ = concentration difference between two points in column
Δ_∞ = value of Δ at infinite time in batch operation
η = viscosity
ρ = density
σ = rate of flow, continuous operation
τ = relaxation time

Subscripts

e = variables in the enriching section of the column in continuous flow operation
s = variables in the stripping section in continuous operation

LITERATURE CITED

1. Clusius, Klaus, and Gerhard Dickel, *Naturwissenschaften*, **26**, 546 (1938).
2. Furry, W. H., R. C. Jones, and L. T. Onsager, *Phys. Rev.*, **55**, 1083 (1939).
3. Debye, Peter, *Ann. Physik*, **36**, 284 (1939).
4. Jones, A. L., *Ind. Eng. Chem.*, **47**, 212 (1955).
5. Frazier, David, *Ind. Eng. Chem., Process Des. and Dev.*, **1**, 237 (1962).
6. Grasselli, Robert, and David Frazier, *ibid.*, p. 241 (1962).
7. Jones, R. C., and W. H. Furry, *Rev. Mod. Phys.*, **18**, 151 (1946).
8. Powers, J. E., Ph.D. thesis, Univ. of California, Berkeley, Calif. (1954).
9. ———, and C. R. Wilke, *A.I.Ch.E. Journal*, **3**, 213 (1957).
10. Longmire, D. R., *ibid.*, **6**, 304 (1960).
11. Heines, T. S., O. A. Larson, and J. J. Martin, *Ind. Eng. Chem.*, **49**, 1911 (1957).
12. Powers, J. E., *Proceedings of the Joint Conference on Thermodynamic and Transport Properties of Fluids*, p. 198, Institution of Mechanical Engineers, London, England (July, 1957).
13. Bardeen, John, *Phys. Rev.*, **57**, 35 (1940).
14. Majumdar, S. D., *ibid.*, **81**, 844 (1951).
15. Emery, A. H., Jr., *Ind. Eng. Chem.*, **51**, 651 (1959)
16. Saxton, R. L., and H. G. Drickamer, *J. Chem. Phys.*, **22**, 1287 (1954).
17. Wilke, C. R., *Chem. Eng. Progr.*, **45**, 218 (1949).

Manuscript received November 29, 1962; revision received March 4, 1963; paper accepted March 11, 1963. Paper presented at A.I.Ch.E. Buffalo meeting.