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The Effect of Column Length on Separation in Thermogravitational Thermal Diffusion Columns

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A series of experiments was designed to test the phenomenological theory of thermogravitational thermal diffusion columns by obtaining data on the steady state separation and approach to equilibrium in a batch column as a function of column length. Data were obtained on the separation of an equimolar n-heptane-benzene solution at five different values of column length varying from 14.5 in. to 6 ft. All measurements were made in one concentric cylinder column in which the effective length was varied by controlling the liquid level in the annulus. Helium gas was used to displace the air in the annulus above the liquid in order to provide even temperature distribution throughout the column. The data were found to substantiate the effect of length predicted by application of the phenomenological theory and to be in very good agreement with other aspects of the theory.

If a temperature gradient is applied to a homogeneous, binary solution, a concentration gradient will usually be established. The name applied to this phenomenon is *thermal diffusion.* Although this effect was reported as early as 1856 (*11*), it remained primarily a laboratory curiosity until Clusius and Dickel introduced the thermogravitational thermal diffusion column in 1938 (*1*). This device makes use of convection currents to achieve a multistaging effect in one piece of equipment.

Several phenomenological theories describing thermogravitational thermal diffusion columns have been presented in the literature (*2, 3, 6, 9*). The treatment of Furry, Jones, and Onsager (*6*) has been widely applied. This treatment is based on the reduction of a complicated differential equation in two space dimensions to an equation involving only one space dimension corresponding to the length of the column. The reduced equation resulting from their analysis is called the *transport equation.*

The transport equation has been applied to predict the effect on separation of column dimensions, operating variables, and various physical properties of the solution being separated for both batch and continuous-flow columns operating under steady state and transient conditions. Many investigations have been reported which demonstrate the qualitative agreement between theory and experiment. Several investigators have considered the effect of column length as one of several column parameters being studied, but no one investigation has covered a large enough range of column length to substantiate or repudiate the theory.

As part of an extensive investigation of the effect of pressure on the steady state separation of gas mixtures in batch columns, Drickamer and coworkers (*5*) used columns which differed in length by a factor of two. Drickamer, Mellow, and Tung (*4*) used these results in preparing an empirical correlation which predicts a

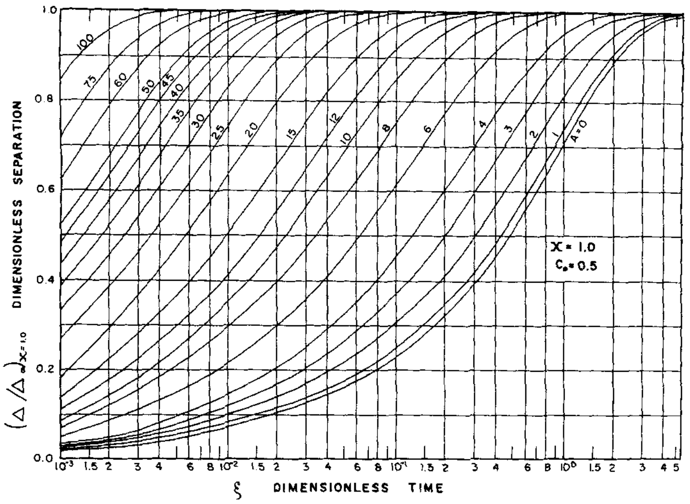

Fig. 1. Results of numerical solution of Equations (2) and (3*a*), (3*b*), (3*c*), and (3*d*) for $X = 1.0$ and $C_0 = 0.5$.

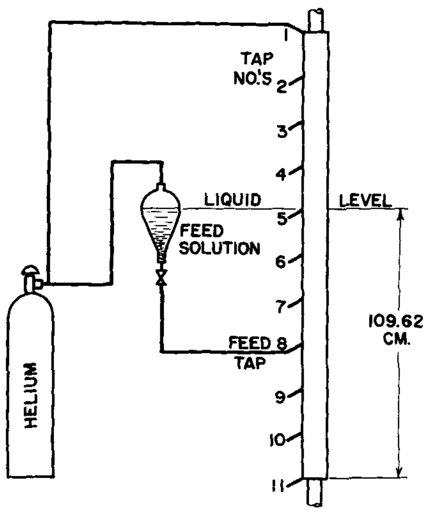

Fig. 2. Batch thermogravitational column illustrating method of adjusting effective length.

length effect in marked disagreement with basic theory in certain regions of column operation.

Other investigators working with the separation of liquid systems in continuous flow columns (*7, 16*) have also considered column length as a parameter, but their investigations were likewise limited to a factor of two in length. These investigators found the theoretically predicted effect of variation in length to be in substantial agreement with their experimental results. In addition independent investigators working with the same binary systems [ethyl alcohol-water (*12, 18*); *n*-heptane-benzene (*7, 12, 15, 17*)] in columns greatly different in length have reported values of the thermal diffusion constant α which are in close agreement. Such agreement lends strong support to the theoretical developments.*

The study of the behavior of thermogravitational columns with either the effect of pressure on steady state separation in a batch column as employed by Drickamer and co-workers or the effect of flow rate on the steady state separation in a continuous flow column as used by others has several disadvantages. Reasonable pressures have little influence on the physical properties and hence the separation of liquid mixtures. The theory of continuous-flow columns is not as well-developed as that of batch columns. On the other hand the theoretical analyses of the steady state separation and the rate of approach to equilibrium of batch columns have been well-established and are applicable to both liquid and gaseous mixtures. Recent reports in the literature have presented the theoretical bases of such analyses and illustrated their application to the comparison of theory and experimental results (*13, 15*). Therefore it was decided to obtain transient and steady state data in columns differing greatly in length in an effort to check the theoretically predicted effect of column length. It was decided to make use of the batch thermogravitational columns without reservoirs presently in the Thermal Diffusion Laboratory at the University of Oklahoma and to study the separation of an equimolal *n*-heptane-benzene mixture. Numerous other investigators have used this system (*7, 10, 12, 13, 15, 17*), and the essential basic data are available.

THEORY

The transport equation of Furry, Jones, and Onsager (*6*) results from the reduction of a complicated differential equation in two space dimensions to an equation involving only one space dimension corresponding to the length of the column:

$$\tau = HC(1-C) - K\frac{\partial C}{\partial y} \qquad (1)$$

This equation serves well as a basic rate expression in the study of the phenomenological behavior of batch thermogravitational thermal diffusion columns, and its development has been discussed in detail elsewhere (*12*). Application of Equation (1) in combination with the continuity condition to the analysis of the transient behavior of batch columns yields the following expression:

$$m\frac{\partial C}{\partial t} = K\frac{\partial^2 C}{\partial y^2} - H\frac{\partial[C(1-C)]}{\partial y} \qquad (2)$$

Equation (2) has been solved subject to the following boundary conditions:

$$@\ t = 0;\ C = C_0 \text{ for all } y \qquad (3a)$$

$$@\ y = 0;\ C = C_0 \text{ for all } t \qquad (3b)$$

$$@\ y = L;\ \frac{\partial C}{\partial y} = \frac{HC(1-C)}{K} \text{ for all } t \qquad (3c)$$

A solution of Equation (2) subject to boundary conditions (3*a*) and (3*b*) which relates the concentration C to the position in the column y under steady state conditions is readily found by integration:

$$\ln\left[\frac{C}{1-C}\right] = \frac{H}{K}y + \ln\left[\frac{C_0}{1-C_0}\right] \qquad (3)$$

$$= 2A(y/L_T) + \ln\left[\frac{C_0}{1-C_0}\right] \qquad (4)$$

The results of a numerical solution of Equations (2) and (3*a* to *c*) under transient conditions for $C_0 = 0.5$ have been published by Powers (*15*). Von Halle (*20*) has presented an analytical solution of an analogous set of equations, but unfortunately there is a typographical error in his result.

A typical set of curves as presented by Powers (*15*) is shown in Figure 1. Powers describes how steady state data can be analyzed using Equation (4) to obtain a value of A and how this value is then used in conjunction with the transient data to yield values of the ratio (t/ξ). In accordance with theory these parameters are related to column length (and other column dimensions, operating variables and

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* Since this manuscript was submitted, it has been reported that data obtained on units 2 and 6 ft. in length had been applied in conjunction with column theory to predict accurately the performance of a column 34 ft. in length (Grasselli, R., G. R. Brown, and C. E. Plymale, *Chem. Eng. Progr.*, 57, No. 5, p. 59 (1961).)

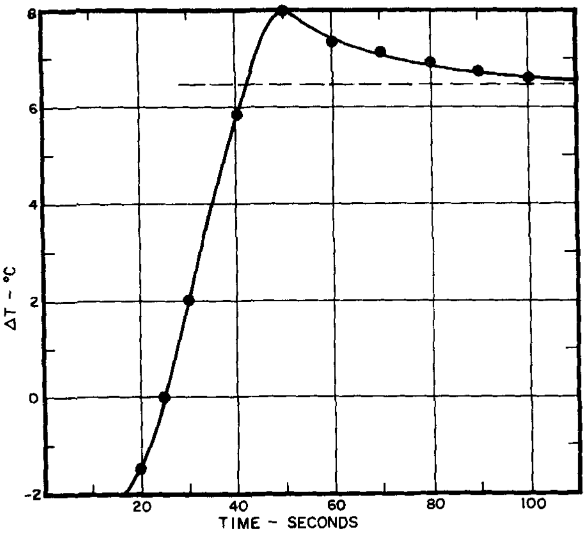

Fig. 3. Determination of time required to attain temperature equilibrium.

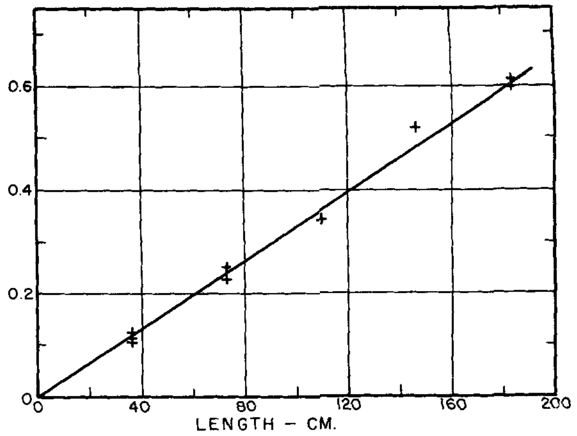

Fig. 5. Linearity of the dimensionless grouping A as a function of column length.

physical properties of the solution) in the following manner:

$$A \equiv \left(\frac{H}{2K}\right) L_T \qquad (5)$$

$$(t/\xi) = \left(\frac{m}{\Pi^2 K}\right) L^2_T \qquad (6)$$

In the development of the theory all factors within the parentheses on the right-hand side of Equations (5) and (6) are assumed to be independent of column length. Thus it was felt that if transient and steady state data could be obtained in columns significantly different in length and analyzed as described above, Equations (5) and (6) would serve as the basis of a meaningful comparison of data and theory.

EXPERIMENTAL

Equipment

The column used in this investigation is of the concentric cylinder type, and a similar column has been described in detail elsewhere (*8*, *15*). The column is 6 ft. long with eleven sample taps equally spaced along the length of the column (Figure 2). The inside or cold wall temperature is maintained by circulating cooling water from a large constant temperature reservoir through the inner cylinder. The outside or hot wall temperature is maintained by an electrical heating element wrapped around the outer cylinder.

Under normal operating conditions the entire annulus is filled with solution being separated, and samples can be withdrawn from any ten of the eleven sample taps. In order to replenish the material withdrawn as samples a feed reservoir located slightly above the upper sample tap is connected to the sample tap located nearest $y = 0$, that is at the point in the column where the concentration does not change [Equation (3*b*)]. For equimolar feeds this corresponds to the center tap. The feed apparatus was modified for purposes of this investigation so that the 6-ft. column could be operated at lesser effective column lengths. The column length was varied by adjusting the feed reservoir so that the solution level in the annulus corresponded to the desired height. In all cases the feed tap was relocated to the effective center of the column for each run requiring a different column length. Figure 2 shows the column arrangement for operation at L_T = 109 cm. in which solution fills the lower 0.6 of the column.

Helium gas is piped to the feed reservoir and to the top sample tap at slightly above atmospheric pressure. Helium is used to fill the annulus because it has a thermal conductivity approximately equal to that of the *n*-heptane-benzene solution being separated (0.0778 vs. 0.086), and therefore marked changes in temperature difference in the region of the interface are avoided.

Temperatures in the column were measured with thermocouples soldered to the hot and cold walls and a self-balancing potentiometer. For this particular investigation four additional thermocouples were attached to the hot wall on the lower one-fifth of the column to obtain accurate hot wall temperature measurements when operating with short column lengths.

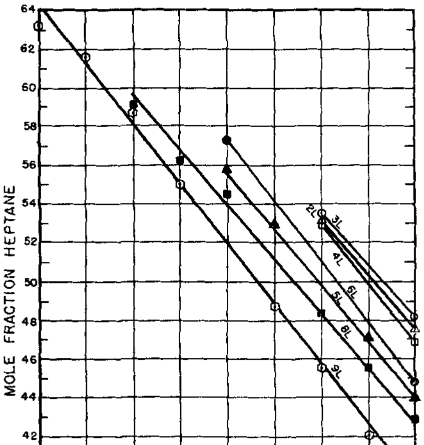

Fig. 4. Concentration profile at steady state in a thermogravitational column.

Procedure

The start-up procedure for transient runs has been described in detail elsewhere (*15*). In brief the column is cleaned and brought to isothermal conditions. It was then flushed with helium gas and filled to the desired level with feed solution from the reservoir. Temperature equilibrium was attained as rapidly as possible (see discussion below) by adjustment of the voltage control on the heating element.

Samples were taken during the transient period at time intervals such that the sampling procedure did not influence the essentially batch nature of the process (*19*). In order to facilitate comparison with theory, samples were taken in pairs at taps located symmetrically around the feed tap. With reference to Figure 2 sample tap pairs for that particular effective length are 5-11, 6-10, and 7-9.

In accordance with theory the relaxation time of a thermogravitational column without reservoirs is approximately proportional to L^2_T. The effective length was varied by a factor of five in this investigation, and in order to obtain data in reasonable times with the longer columns it was necessary to operate under conditions such that the shorter columns came to equilibrium rather rapidly. Under such conditions the time required for the column to attain temperature equilibrium proved to be important. A series of experiments was conducted to determine the approximate time required to attain temperature equilibrium. The results of one such experiment are shown in Figure 3. On the basis of such data it was decided to consider that $t = 0$ corresponded to 1 min. after the cooling water flow and electrical power were started to the column. (A negative ΔT is noted for time $<$ 25 sec. in Figure 3. This results from the fact that the cooling water was at a temperature higher than room temperature.)

After the separation in the column reached steady state conditions, samples were withdrawn at each available tap. Both transient and steady state samples were of approximately 0.1-cc. volume and were analyzed with a refractometer which had been previously calibrated with the same reagents (*14*).

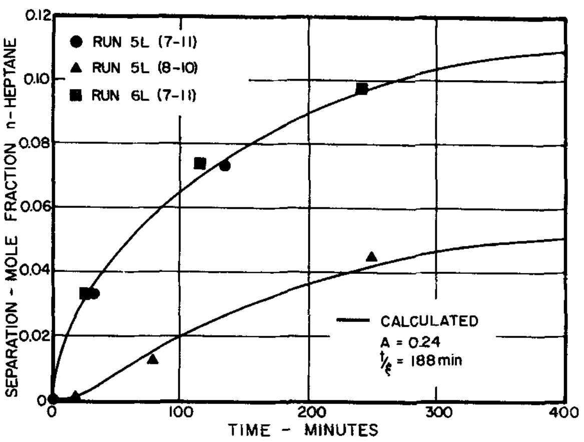

Fig. 6. Comparison of experimental data with values calculated from an average t/ξ value.

Reagents

The feed solution was equimolal *n*-heptane-benzene. The benzene was 0.4°C. boiling range. The *n*-heptane was pure grade.

RESULTS

Experimental results are presented in Table 1 and Figure 4. Transient data are presented in Table 1 as the difference in concentration at sample tap pairs corresponding to the time at which the samples were taken. The listed values of time have been corrected for the time necessary to attain temperature equilibrium as noted above. In most cases samples were withdrawn from the extreme sample taps only. In Run 5L data were obtained not only at the end taps (7-11) but also at the pair (8-10). Runs 10L and 12L represent similar data for a longer column.

An attempt was made to obtain the same temperature difference for each run, but considerable deviation is noted in the values presented in Table 1. It was decided that it would be better to compensate for temperature differences in treatment of the data rather than attempt to adjust the temperature once a run had been under way long enough to establish a temperature difference.

COMPARISON WITH THEORY

Analysis of Steady State Data

It was noted previously that the dimensionless grouping A could be determined from steady state data by application of Equation (4). The maximum separation of the equimolal composition feed was less than 0.3, and under these conditions $C(1-C) \cong 0.25$. With this simplification Equation (4) reduces to

$$C = C_0 + (A/2)(y/L_T) \qquad (7)$$

Values of A were determined from the slopes of straight lines drawn through the data as shown on Figure 4. It is felt that such agreement with the predicted straight-line relation offers strong support of the theoretical developments. Other values of A as determined from steady state data are included in Table 1.

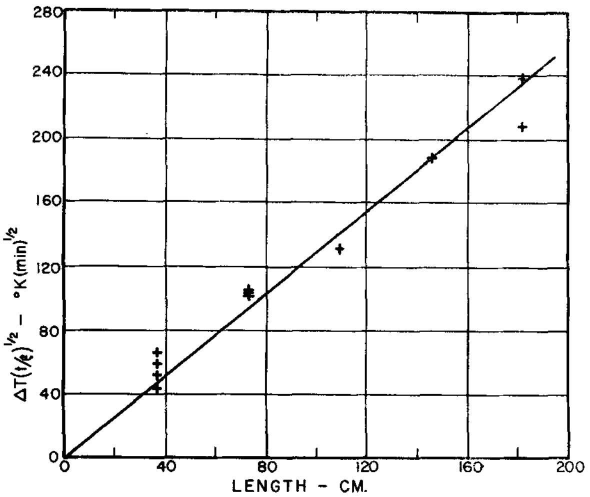

Fig. 7. Linearity of the grouping $\Delta T(t/\xi)^{1/2}$ as a function of column length.

In accordance with Equation (5) A should be a linear function of total column length. Figure 5 indicates remarkable agreement between theory and experiment in respect to the predicted effect of length on steady state separation.

TABLE 1. EXPERIMENTAL DATA

Run no.	Sample tap pair	ΔT, °C.	L_T, cm.	t, min.	ΔC, mole fraction	t/ξ		A
						Individual, min.	Average, min.	
2L	(9-11)	7.8	36.5	0	0.000	—	43.6	0.113
				2.5	0.013	27		
				7.5	0.017	42		
				34	0.033	51		
3L	(9-11)	5.8	36.5	0	0.000	—	53.5	0.106
				2.5	0.008	63		
				17	0.022	55		
				59	0.039	51		
4L	(9-11)	7.0	36.5	0	0.003	—	70.7	0.123
				7.5	0.013	90		
				34	0.033	63		
5L	(7-11)	7.5	73.0	0	0.000	—	188	0.230
				33	0.028	220		
				135	0.063	173		
	(8-10)			17	0.001	164	192	—
				79	0.013	217		
				250	0.045	173		
6L	(7-11)	7.6	73.0	0	−0.001	—	177	0.252
				24	0.033	179		
				114	0.074	164		
				241	0.097	186		
8L	(5-11)	6.4	109.6	0	−0.003	—	418	0.342
				62	0.044	496		
				285	0.104	407		
				542	0.136	402		
9L	(3-11)	6.7	146.2	0	0.003	—	780	0.520
				95	0.063	825		
				485	0.146	808		
				970	0.204	746		
10L	(1-11)	7.1	182.5	0	−0.001	—	1,120	0.614*
				99	0.050	1,900		
				396	0.138	1,040		
				839	0.201	990		
12L	(2-10)	7.2	182.5	0	0.000	—	835	0.601*
				179	0.052	853		
				420	0.102	840		
				910	0.165	828		
13L	(9-11)	8.5	36.5	5	0.007	179	58.7	
				19	0.026	45		
				45	0.039	46		

* Determined from previous measurements made on the same column at the same ΔT (*15*).

Analysis of Transient Data

The transient data were analyzed in a manner described previously (*15*). This method of analysis yields a value of (t/ξ) for each transient data point, and these values are listed in Table 1. The previously published solutions in graphical form apply only at sample taps located every one-fifth of the distance from the mid-point to the end of the column, and therefore it was necessary to interpolate between graphs in interpreting some data.

The values of t/ξ should be the same for all data taken during any one run, and the scatter of the values of t/ξ listed in Table 1 attests to the severity of this test of the theory and data. A weighted average value of t/ξ was determined for each run (*15*). The manner in which a single average value of t/ξ in combination with the previously determined value of A serves to represent the data is illustrated in Figure 6 which includes all data from runs 5L and 6L corresponding to a column length of 75 cm. (lower 0.4 of column filled with solution).

In accordance with Equation (6) $(t/\xi)^{1/2}$ should be directly proportional to column length if the group (m/Π^2K) is constant. As noted previously the ΔT for all runs were not identical. For the conditions of these experiments $K_c >> K_d$, and therefore K is proportional to $(\Delta T)^2$. In order to incorporate this factor into the correlation Equation (6) was rearranged to

$$\Delta T(t/\xi)^{1/2} = \frac{\mu(9\,!\,D)^{1/2}}{\Pi\,\beta_T g(2\omega)^3} L_T \quad (8)$$

Figure 7 demonstrates the extent to which the experimental results and the theory as represented by Equation (8) are in agreement. The analysis of the transient data serves as a stringent test of both the theory and the data, and it is felt that the results summarized in Figure 7 represent good agreement. Further comparison with fundamental theory gives additional support to this conclusion.

Comparison with Fundamental Theory

Not only does the application of the transport equation predict the effect of length on the transient and steady state separation but it also predicts the slopes of the straight lines on Figures 5 and 7 in terms of physical properties, column dimensions, and operating variables. Comparison of the values of the slopes determined empirically with values predicted from basic data therefore provides an additional test of the assumptions made in the development of the transport equation.

In this manner the slope of the line on Figure 7 was compared with the value calculated from Equation (8) with values of physical properties previously summarized for the *n*-heptane-benzene system (*13*) and a value of $2\omega = 0.07466$ cm. as determined experimentally for the column used. The two values were found to be in remarkable agreement.

Experimental slope
$10.0°K.(sec.)^{1/2}$/cm.
Theoretical slope
$10.2°K.(sec.)^{1/2}$/cm.

In accordance with Equation (5) the slope of the plot of A vs. L is equal to $(H/2K)$. The grouping H contains the thermal diffusion constant α which was determined to be 1.02 from the slope of the line presented on Figure 5. This agrees within 10% of values for α for the same system obtained by other investigators using thermogravitational columns operated under a variety of conditions (*12, 17*).

SUMMARY

Transient and steady state data obtained in a batch thermogravitational column whose effective length was varied from 36.5 to 182.7 cm. show good agreement with the theoretically predicted effect of column length and yield results in remarkable agreement with fundamental theory and previous investigations.

ACKNOWLEDGMENT

The support of the National Science Foundation is gratefully acknowledged.

NOTATION

A = $HL_T/2K$
B = width of the column (mean circumference of annular space)
C = fraction of component 1 in a binary solution
C_0 = fraction of component 1 in material charged into the column
D = ordinary diffusion coefficient
g = acceleration due to gravity
H = $\dfrac{\alpha\beta_T\rho g(2\omega)^3 B(\Delta T)^2}{6\,!\,\mu\,\overline{T}}$
K = $K_c + K_d$
K_c = $\dfrac{\beta_T{}^2\rho g^2(2\omega)^7 B(\Delta T)^2}{9\,!\,D\mu^2}$
K_d = $2\omega DB\rho$
L_T = total effective column length
m = amount of solution per unit column length
t = actual time
T = absolute temperature
$\overline{T}$ = arithmetic average of the hot and cold wall temperatures
y = axis parallel to walls in the direction of normal convective flow

Greek Letters

α = thermal diffusion constant
β_T = $(\partial\rho)/(\partial T)$
ΔC = difference in concentration at $\pm\, y$
ΔT = temperature difference between hot and cold walls
μ = coefficient of viscosity
ξ = dimensionless time, Equation (6)
ρ = density
τ = amount of component one passing through a cross section of the column normal to the walls
ω = one-half the distance between the plates of a thermogravitational column

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