The Effect of Rate of Sampling on the Transient Behavior of Thermogravitational Thermal Diffusion Columns Without Reservoirs

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In experimental investigations of the transient behavior of batch thermogravitational thermal diffusion columns it is expedient to obtain more than one sample from the column during a single run. Such sampling modifies the true batch nature of the column and thereby influences the experimental measurements to some degree. A combined theoretical and experimental investigation was carried out to determine the extent of the influence of sampling rate and thereby provide a means of predetermining a suitable sampling rate.

The theoretical analysis was made by approximating the intermittent sampling as a continuous flow through the column. The transport equation of Furry, Jones, and Onsager was applied in the analysis, and an analytical solution was obtained for small separations of equicomposition binary solutions. The series solution is presented in the form of a graph. Experimental data were obtained in two thermogravitational columns with different plate spacings to test the theory. The effect of sampling rate was investigated, and theory and experiments were found to be in good agreement. It is concluded that the theory is entirely adequate to permit the prediction of sampling rates which will yield the maximum number of samples without disturbing the true batch behavior of the column.

When a uniform mixture is subjected to a temperature gradient, the mixture becomes nonuniform in composition. This general phenomenon is called "thermal diffusion." The separation obtained is small and was of little practical interest until Clusius and Dickel introduced the thermogravitational thermal diffusion column in 1938 (*1*). These columns multiply the separation achieved by thermal diffusion by utilizing convection currents to produce a cascading effect.

The separation obtained in thermogravitational thermal diffusion columns is greatly influenced by column dimensions and operating variables. Several phenomenological theories have been proposed to aid in proper design; the development of Furry, Jones, and Onsager (*3*) is perhaps the most widely accepted. Only relatively recently have experimental results been published which tend to confirm the theory (*2, 5* to *8*). One of the more critical and at the same time convenient tests of column theory is provided by investigation of the transient behavior of batch columns (*5, 7*). In experiments of this type it is expedient to obtain more than one sample during a single run. These samples are withdrawn from the solution that is in the annulus of the column. The first sample withdrawn from the column is the only one representing the true behavior of a batch column because sampling effectively introduces a bulk flow through the column. The influence of the small bulk flow introduced by intermittent sampling on the rate of approach to steady state is amenable to mathematical analysis, and therefore a combined theoretical and experimental investigation was undertaken. The results of such an investigation would aid in the selection of optimum sampling rates in future investigations.

THEORY

The process of sampling introduces a bulk flow in the column. Although sampling is done at short intervals and introduces an intermittent bulk flow, the effect of sampling can be approximated by assuming the presence of a small continuous flow through the column, σ. Jones and Furry (*4*) have modified the original transport equation of Furry, Jones, and Onsager (*3*) to account for bulk flow through a thermal diffusion column:

$$\tau_1 = HC_1C_2 - K\frac{\partial C_1}{\partial y} + \sigma C_1 \qquad (1)$$

Equation (1) in combination with the continuity conditions yields

$$\frac{m}{K}\frac{\partial C_1}{\partial \theta} = \frac{\partial^2 C_1}{\partial y^2} - \frac{\sigma}{K}\frac{\partial C_1}{\partial y} - \frac{H}{K}\frac{\partial [C_1C_2]}{\partial y} \qquad (2)$$

The nonlinear term in Equation (2) makes it difficult to obtain an analytical solution. However for an initial value of $C_1 = C_0$ equal to 0.5 and for small separations the product C_1C_2 can be considered equal to a constant value of 0.25 for $0.3 \leq C \leq 0.7$. Incorporation of this assumption reduces Equation (2) to

$$\frac{m}{K}\frac{\partial C_1}{\partial \theta} = \frac{\partial^2 C_1}{\partial y^2} - \frac{\sigma}{K}\frac{\partial C_1}{\partial y} \qquad (3)$$

It is convenient to present Equation (3) in dimensionless form by defining a dimensionless length, a dimensionless flow, and a dimensionless time. The resulting partial differential equation in dimensionless form is

$$\frac{\partial C}{\partial t} = \frac{\partial^2 C}{\partial X^2} - P\frac{\partial C}{\partial X} \qquad (4)$$

where the subscript 1 on C has been dropped.

In eliminating the nonlinear term in Equation (2) to obtain Equation (3) the solution was restricted to $C_0 = 0.5$ and $0.3 \leq C_1 \leq 0.7$. Under such conditions it is reasonable as well as convenient to assume symmetry around the vertical center of the column ($X = 0$). Accordingly a solution is found for $0 \leq X \leq 1$ subject to the following boundary conditions:

$$C(X, 0) = C_0 \qquad (5)$$

$$C(0, t) = C_0 \qquad (6)$$

$$\frac{\partial C}{\partial X}(+1, t) = \frac{HL}{4K} \equiv \frac{A}{4} \qquad (7)$$

The solution can be obtained by using the method of separation of variables and is given by Equations (8) and (9):

$$\frac{\Delta C}{\Delta_0 C} = \frac{2[C(X,t) - C_0]}{\Delta_0 C} = \frac{e^{-P}}{P}\left[(e^{PX} - 1) - \frac{4Pe^{PX/2}}{(1 - e^{-P})}\psi\right] \qquad (8)$$

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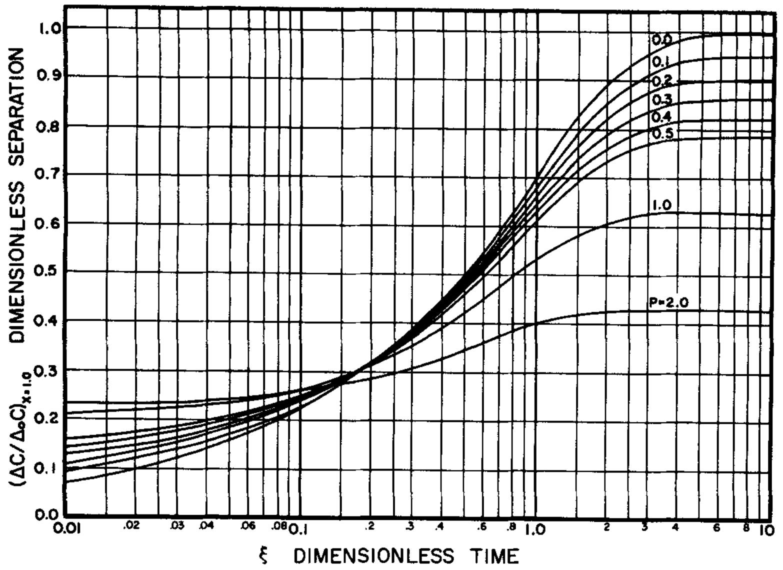

Fig. 1. Dimensionless separation at the ends of the column as a function of dimensionless time (ξ) and dimensionless sampling rate (P).

$$\psi \equiv \sum_{1}^{\infty} \frac{P^2 - \lambda_n^2 \cos \alpha_n e^{-3P^2}}{\alpha_n (2P^2 + \lambda_n^2)} \sin(\alpha_n X)\, e^{-\lambda_n^2 t} \qquad (9)$$

From Equations (8) and (9) $\Delta C/\Delta_o C$ can be computed as a function of t with P as parameter. To facilitate comparison with theoretical and experimental results previously published (5) it is convenient to plot the results of such computations as a function of ξ rather than t:

$$\xi \equiv \frac{\pi^2}{4} t \qquad (10)$$

The results of computations for $X = 1.0$ (ΔC = concentration difference between the ends of the column) are presented in Figure 1.* In solving Equations (8) and (9) the first twenty values of α_n were obtained for various values of P (9), and these values were used in Equations (8) and (9). A medium speed digital computer was used for these computations. Values of $(\Delta C/\Delta_o C)$ as a function of ξ for $P = 0$ (true batch case) were obtained from the literature (5).

EXPERIMENTAL

The equipment used consisted of two concentric-cylinder batch thermogravitational thermal-diffusion columns without reservoirs of standard design. These columns are 6 ft. in length and differed mainly in annular spacing (0.0752 and 0.1143 cm.). The equipment has been described in detail by Powers (7).

The system studied was a 50 mole % n-heptane and benzene mixture. The physical properties for the system are available in the literature (5). The samples were analyzed by measuring the index of refraction at 25°C. with a refractometer.

Powers (7) has described in detail how both transient data and steady state data are obtained with these columns. In order to obtain meaningful transient data for this investigation samples of measured volume were withdrawn simultaneously from the two end taps at equal time intervals. Sample size was maintained constant for any one run, but the sampling rate was varied in different runs both by changing the sample size and frequency. The mean temperature was approximately 100°F. for all experiments, and temperature difference was not varied in either column. Table 1 contains typical data obtained for one of the six transient runs.

COMPARISON OF THEORETICAL AND EXPERIMENTAL RESULTS

In comparing the experimental results with the series solution it was convenient to convert the experimental data to the corresponding dimensionless values. Values of $(\Delta C/\Delta_o C)_{\exp}$ were calculated by dividing the experimental ΔC values obtained under transient conditions by the measured steady state batch separation $\Delta_o C$. Real time values θ were converted to dimensionless time ξ by applying the required definitions with published data for the physical properties of the solution (5). Typical plots of experimental data treated in this manner are presented in Figure 2.

In order to compare the experimental results with the theoretical calculations a value of the dimensionless flow P was computed as follows. The total amount of sample withdrawn from one sample tap was divided by the total time of the run to obtain an average volumetric flow rate. The volumetric flow rate was converted to mass flow rate by the use of a mean value of the density of the solution. From σ, P is computed from the defining equation. For this value of P the theoretical values of $(\Delta C/\Delta_o C)$ are computed as a function of ξ, with the general computer program used, and plotted as solid lines for comparison with the experimental data. To emphasize the effect of sampling on the transient behavior in each case the theoretical curve for $P = 0$ (true batch case) is also plotted.

As can be seen from Figure 2 the experimental results are in remarkably good agreement with the theory at lower values of P, but at higher values of P the actual separation obtained is observed to be lower than that predicted by theory. The four other sets of data obtained at values of P = 0.175, 0.194, 0.207, and 0.305 show similar agreement (9). These observa-

TABLE 1. TYPICAL TRANSIENT DATA*

Run number: 2
Column number: II
Average cold wall temperature: 85°F.
Average hot wall temperature: 115° F.
Temperature difference: 30° F.
Calculated dimensionless flow: 0.207

Time, min.	Mole fraction of n-Heptane at Top tap	Mole fraction of n-Heptane at Bottom tap	Sample volume, cc.	ΔC	ξ	$\frac{\Delta C}{\Delta_o C}$
0	0.5007	0.5007	1.0	0.0000	0.000	0.000
240	0.5814	0.4513	1.0	0.1301	0.448	0.451
480	0.6015	0.4258	1.0	0.1757	0.896	0.609
720	0.6195	0.4143	1.0	0.2052	1.344	0.710
960	0.6241	0.4082	1.0	0.2159	1.792	0.748
1,200	0.6287	0.4004	1.0	0.2283	2.240	0.793
1,680	0.6346	0.3927	1.0	0.2419	3.136	0.838
3,120	0.6346	0.3927	1.0	0.2419	5.824	0.838

* The majority of the data obtained during this run have been omitted. Complete data for this and five other runs are available (9).

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* A full-size version of Figure 1 will be furnished, on request, by J. E. Powers.

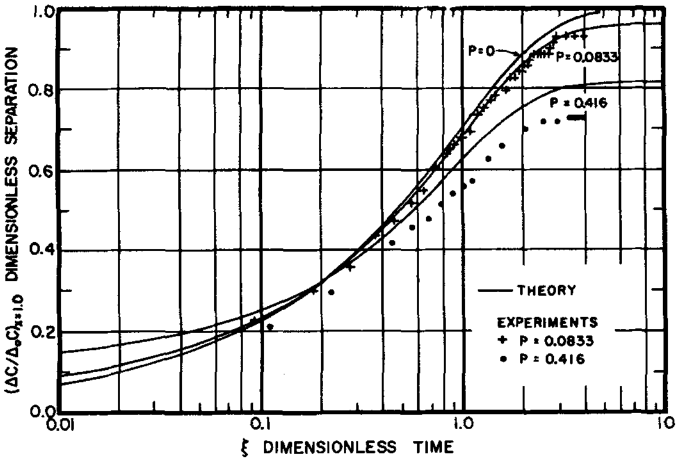

Fig. 2. Comparison of the experimentally observed effect of sampling rate on separation with theoretically predicted results for both a small sampling rate (P = 0.0833) and a large sampling rate (P = 0.416).

tions are similar to those of a previous investigation of the effect of flow rate on separation in continuous-flow columns operated under steady state conditions (*8*).

CHOICE OF PROPER SAMPLING RATE

The two columns used in the investigation were specially made and have an annular spacing quite a bit larger than the majority of such columns currently in use. The standard column of this type has an annular spacing of about 0.0309 cm. (0.012 in.), and it is of interest to determine a reasonable sampling rate for such a column. The following data apply to such a column separating a 50 mole % *n*-heptane-benzene mixture at a mean temperature of 100°F.

2ω = 0.0309 cm.
L_T = 182.7 cm.
B = 4.590 cm.
ΔT = 31.3°C.
ρ = 0.7407 g./cc.
β_T = 0.951×10^{-3} g./cc. °C.
D = 0.315×10^{-4} sq.cm./sec.
μ = 0.367 centipoise

Using these data together with the definition of K one obtains

$$K = 6.299 \times 10^{-4} \text{ g. cm./sec.}$$

From Figure 1 it can be concluded that the column behavior will be disturbed only slightly if P = 0.05. When one uses this value for P together with $L = L_T/2$ and K as listed above, an average mass flow rate is calculated from the definition of P:

$$\sigma = \frac{PK}{L} = 3.53 \times 10^{-7} \text{ g./sec.}$$

For purposes of analysis by index of refraction a sample size of 0.1 cc. is sufficient, and therefore samples should be drawn no more frequently than once every 53 hr.

Under the conditions specified above the column will be very nearly at steady state in 55 days (*7*). Therefore $P = 0.05$, about twenty-five samples could be obtained.

For the column described above essentially pure *n*-heptane will be obtained at the top of the column and pure benzene at the bottom. Therefore the restriction $0.3 < C_1 < 0.7$ is not satisfied. In order to allow for this discrepancy the sampling rate should probably be reduced to once a week. Seven samples are more than adequate to properly define an experimental curve.

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NOTATION

A = HL/K
B = width of the column (mean circumference of annular space)
C = fraction of component 1
C_1, C_2 = fractions of component 1, 2 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
$H = \dfrac{\alpha\beta_T\rho g(2\omega)^3 B(\Delta T)^2}{6!\mu\overline{T}}$
$K = \dfrac{\beta_T^2\rho g^2(2\omega)^7 B(\Delta T)^2}{9!D\mu^2} + 2\omega DB\rho$
L = linear distance from $y = 0$ to the end of the column
L_T = total column length = $2L$
m = amount of solution per unit column length
P = dimensionless flow ≡ $\sigma L/K$
t = dimensionless time ≡ $K\theta/(mL^2)$
T = absolute temperature
$\overline{T}$ = arithmetic average of the hot and cold wall temperatures
X = y/L, dimensionless length
y = axis parallel to walls in the direction of normal convective flow

Greek Letters

α = thermal diffusion constant
α_n = one of the roots of the equation $\tan\alpha = -(2/P)\alpha$
β_T = $-\partial\rho/\partial T$
ΔC = difference in concentration at $\pm X$
$\Delta_0 C$ = difference in concentration at the ends of the column under steady state, batch ($P = 0$) conditions
ΔT = temperature difference between hot and cold walls
μ = coefficient of viscosity
ξ = dimensionless time, Equation (10)
ρ = density
σ = average mass flow (sampling rate) from one sample tap
τ_1 = 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
θ = real time
λ_n = $\alpha_n^2 + (P/2)^2$
ψ = as defined by Equation (9)

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