Thermal Diffusion in a Packed Column

ALDEN H. EMERY, JR., and MAURICE LORENZ

Purdue University, Lafayette, Indiana

In the past a number of investigators (*1* to *6*) have shown interest in the use of the thermal-diffusion column to make specialized separations. The customary thermal-diffusion column presents construction difficulties because the distance between the hot and cold walls must be very small, on the order of 0.02 in., to obtain reasonable separations. Large plate spacing may be tolerated, however, if an obstruction to flow is placed in the space between the walls. A number of investigators have experimented with baffles; Washall and Melpolder (*7*) recently did work on a spiral-wrapped column. The first packed column was reported in 1948 by Debye and Bueche (*8*), and the only work on the effects of operating variables on separations in packed columns done to date was reported by Sullivan et al. in 1957 (*9*).

In a previous paper (*10*), the transport equation for the packed thermal-diffusion column was developed by modifying the differential equation basic to the convective velocity distribution. This equation contains one term representative of the driving force for convection, namely gravity and the horizontal density gradient, one term for the transmission of drag force through the fluid by viscous shear, and one term for the drag of the packing on the fluid. The first two terms are the starting point for the column without packing.

The same kind of transport equation resulted for the packed column as for the column without packing, but the coefficients H and K vary in a different manner with plate spacing, and a new variable, the packing permeability, is involved. In the work reported here these transport equations were tested in batch operation by varying these parameters.

EXPERIMENTAL WORK

The thermal-diffusion column used consisted of parallel-vertical plates, the working space of which was about 2 ft. high by 4 in. wide (*11*). Heat was supplied by a steam jacket on the hot plate and removed by cold water flowing in a jacket on the cold plate. The plates included three large ports to fill and drain, two pressure taps in the center portion to measure permeabilities, five hypodermic needles for withdrawing samples, and nine thermocouples. The plates were spaced by a solid steel plate, the center of which was removed to form the working space. Plastic tape formed the gasket between the spacer and the plates.

Three packing materials were used: steel wool, coarse glass wool of about 20-μ diam., and fine glass wool of about 2-μ diam., the variety usually found in laboratories. The permeability of each packing could be varied by changing the density of packing. This was limited at the low-permeability end by the maximum amount that could be compressed into the working space without warping the plates and at the high-permeability end by the amount that would maintain its shape in the working space without forming channels. In addition, these three materials cover different ranges of permeability. The total permeability range covered was from 2×10^6 to 36×10^6 sq. cm., as shown in Table 1.

The parallel-plate column was convenient for work with packed columns, because at the end of a series of runs the column could be dismantled without disturbing the packing and whether or not the packing had shifted or formed channels could be determined by visual inspection. Several series of runs were rejected because the packing was not uniform after the runs. On the other hand, the parallel-plate column was inconvenient because of a serious edge effect. It was difficult to put packing into the working space up to the spacer so that it would not interfere with the gasket. Spaces at this point as small as 1/64 in. may cause large errors. This problem was solved by coating the edge of the packing with plaster of paris so that the plaster and not the spacer formed the confines of the working space. Straggling fibers then were filed off before the column was assembled.

After the column was assembled, it was filled with liquid, 50 mole % cumene (isopropylbenzene) in cetane (n-hexadecane), and closed off. Samples were withdrawn periodically from the upper and lower hypodermic taps during the run. At the end of the run, samples were withdrawn from all hypodermic taps and analyzed by refractive index. Then the column was flushed with feed, and a new run was started. The maxi-

Maurice Lorenz is with the Esso Research and Engineering Company, Linden, New Jersey.

TABLE 1. EXPERIMENTAL RESULTS

Series	Packing	$2w$ cm.	$100(1-\epsilon)$	$10^6 k$ sq.cm.	$10^{-6} V_1$	$10^{-7} V_2$	Δ_∞ mole %	s_{Δ_∞}	τ hr.	s_τ
4	s*	0.181	3.2	35.7	3.95	2.01	7.09	0.081	1.110	0.052
7	s	0.179	8.9	12.6	10.70	14.24	16.1	1.2	7.9	1.6
8	s	0.179	4.8	20.8	6.59	5.68	10.64	0.24	2.38	0.20
9	s	0.343	6.2	16.6	2.14	1.83	3.21	0.10	0.534	0.085
12	20*	0.333	6.2	17.3	2.20	2.45	3.56	0.10	0.677	0.080
16	20	0.343		10.8	3.29	5.04	5.29	0.10	1.135	0.081
17	20	0.338	8.7	9.80	3.79	6.44	6.53	0.10	1.65	0.11
18	20	0.351	11.1	5.10	6.62	22.1	10.02	0.31	6.00	0.35
19	20	0.343	13.4	4.27	8.20	31.6	10.24	0.11	8.37	0.30
20	20	0.343	8.0	11.9	3.01	4.16	4.557	0.080	1.225	0.081
21	20	0.186	7.9	8.96	13.9	32.0	21.7	1.1	13.4	1.7
23	20	0.498	8.0	7.90	2.11	3.87	3.322	0.080	0.952	0.071
27	20	0.683	9.8	5.70	1.553	3.35	2.300	0.069	1.00	0.10
28	2*	0.686	6.1	1.80	4.69	37.3	7.535	0.070	9.57	0.43

* Packing material: s = steel wool, 20 = 20 μ glass wool, 2 = 2 μ glass wool.

mum separation encountered was 21 mole %; the longest run was about 60 hours.

After a series of such runs was made, the column was cleaned with a solvent, the solvent was evaporated, and the permeability was measured by passage of a heavy oil of known viscosity through the column at room temperature. The column then was opened and the packing inspected for flaws.

PHENOMENOLOGY

The equation applicable to batch operation of this thermal-diffusion column is *(11)*

$$\Delta = \Delta_\infty [1 - 0.94 \exp(-t/\tau)] \quad (1)$$

in which Δ is the difference in concentration between the upper and lower sample taps, and Δ_∞ and τ are constants for a given series of runs. The coefficient 0.94 is determined by the sample tap distance and column length of the apparatus. The constants Δ_∞ and τ and their standard errors were determined by regression on Equation (1) with the standard error in Δ, s_Δ, assumed constant for one series. The results are shown in Table 1. The basic data are contained in Lorenz's thesis *(11)*.

The data fit the exponential curve well as shown in Figure 1 for two series. Thus it is apparently safe to use the exponential equation developed from the theory as a simple phenomenological equation.

EFFECTS OF PLATE SPACING AND PERMEABILITY

According to the theory

$$\Delta_\infty = HL_\Delta/4K \quad (2)$$

for mole fractions near 0.5 in which L_Δ is the distance between sample taps (20 in.), and

$$\tau = 2\,w\,B\,\rho\epsilon\,L^2/\pi^2\,K \quad (3)$$

in which $2w$ is the plate spacing, L is the total length of the column (23¾ in.), and

$$H = gB\beta\rho\alpha\epsilon(\Delta T)^2 w^3 H(Y)/6\eta T \quad (4)$$

$$K = g^2 B\beta^2 \rho\epsilon(\Delta T)^2 w^7 K(Y)/15\eta^2 D \quad (5)$$

$$H(Y) = \left[1 - \frac{3}{Y^2}(Y \operatorname{ctnh} Y - 1)\right]/Y^2 \quad (6)$$

$$K(Y) = \left[1 - \frac{5}{Y}\operatorname{ctnh} Y - \frac{15}{Y^4} - \frac{15}{4Y^2} + \frac{15}{4Y^3}\operatorname{ctnh} Y + \frac{45}{4Y^2}\operatorname{ctnh}^2 Y\right]/Y^4 \quad (7)$$

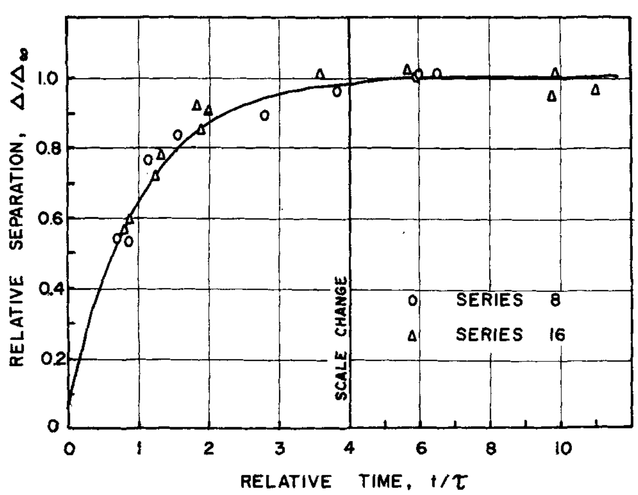

Fig. 1. Sample results showing the fit of the date to the regression curve. Series 8, steel wool in a plate spacing of 1/16 in. Series 16, 20 μ glass wool in a plate spacing of ⅛ in.

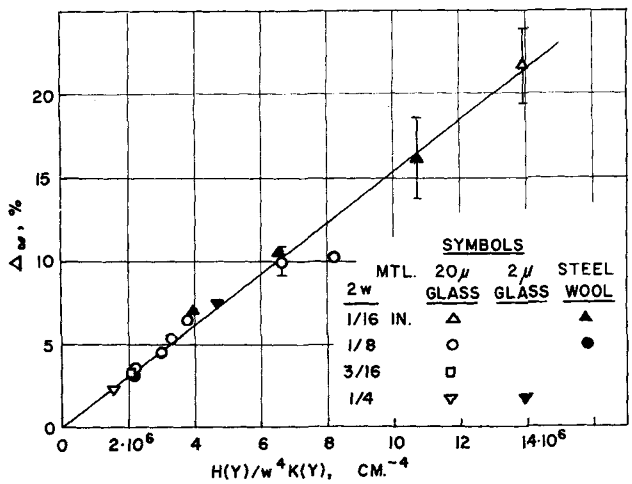

Fig. 2. Correlation of ultimate separation, Δ_∞, with the theoretical group V_1.

$$Y = w/\sqrt{k} \quad (8)$$

By substitution

$$\Delta_\infty = \frac{5L_\Delta}{8g} P_1 V_1 \quad (9)$$

in which P_1 is a function of properties of the fluid

$$P_1 = \frac{\alpha}{\beta}\left(\frac{D\eta}{T}\right) \quad (10)$$

and V_1 is a function only of the variables plate spacing and permeability

$$V_1 = \frac{H(Y)}{w^4\,K(Y)} \quad (11)$$

In Figure 2, Δ_∞ is plotted against V_1. The vertical range shown for each point is $\pm\ 2s_{\Delta_\infty}$. Since the points on this straight line include data from three different packing materials at various densities and four different plate spacings, the theory evidently gives the correct effect of plate spacing and permeability on Δ_∞.

The scatter of the points from the straight line indicates a source of random error in addition to that associated with one series. The s_{Δ_∞} used in Figure 2 is obtained during the regression on Equation (1) and represents, therefore, those sources of error contributing to the scatter of the points in a given series (that is, at one packing density and plate spacing). It includes neither errors in the measurement of plate spacing and permeability nor the effect of inhomogeneities in the packing. If the $\pm\ 2s_{\Delta_\infty}$ range of 95% of the points had included the best straight line, it could have been concluded that the scatter from the regression curve in a given series represented most of the error. However, only about two-thirds of the points include the straight line. Since the measurement errors of plate spacing and permeability contribute to a variation in the abscissa of slightly over 1%, it is clear that inhomogeneities in the packing contribute significantly to the scatter between series.

In a similar manner

$$\tau = \frac{30L^2}{\pi^2 g^2} P_2 V_2 \quad (12)$$

where P_2 is a function of the properties of the fluid

$$P_2 = \eta^2 D/\beta^2 \quad (13)$$

and V_2 is a function of the plate spacing and permeabilty

$$V_2 = 1/w^6\,K(Y)\,(\Delta T)^2 \quad (14)$$

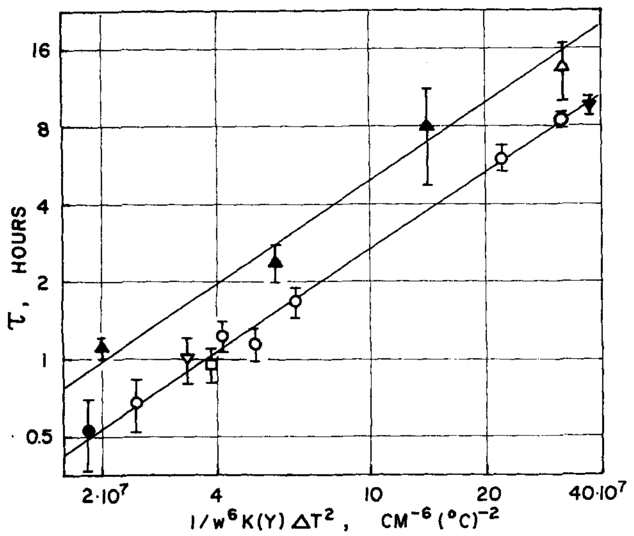

Fig. 3. Correlation of relaxation time, τ, with the theoretical group V_2.

The temperature difference between the plates, ΔT, is included in the variable because it varies slightly from run to run. The average value was 80°.

Figure 3 shows τ plotted against V_2, and the $\pm\ 2s_\tau$ range. The points for all packing materials, plate spacings, and different densities fall on one straight line with the exception of the data taken with a plate spacing of 1/16 in. This line, the best straight line through these points, is shown in Figure 3. The four points from the plate spacing of 1/16 in., however, are significantly removed from this line, and another straight line through the origin must be drawn to fit them. It thus may be concluded that the theory accounts satisfactorily for the effect of permeability on τ and for the effect of plate spacing at ⅛ in. and above, but that the data at the lowest plate spacing do not follow the other data.

The natural explanation for this discrepancy is to suppose that it is an imperfection of the column associated with the wall, a wall effect, which becomes more important as the vicinity of the wall becomes a greater proportion of the total bed. Undoubtedly the packing density is altered close to the wall. This may be rationalized. If the bed is more dense in the vicinity of the wall than in the middle of the column, the flow pattern during thermal diffusion is vastly different than during the permeability measurement. During thermal diffusion, the greatest flow occurs adjacent to the walls and tapers off to zero in the center of the column. During the permeability measurement, however, a more uniform plug-like flow occurs across the entire column. Thus the permeability measured is an average across the whole bed, whereas the proper permeability should weight more those portions of the bed close to the walls. If the bed is more dense close to the wall, the permeability actually measured will be too high. The abscissa of Figure 3 varies approximately with the reciprocal square of the permeability. Thus, if the proper lower permeability had been used in the abscissa for the 1/16 in. points, they would have been shifted to the right and would have agreed more closely with those of the other plate spacings.

ABSOLUTE VALUES OF THE CONSTANTS

Equations (9) and (12) purport to give not only the effects of the variables, but also the absolute magnitude of the phenomenological constants. To check this, P_1 and P_2 were calculated and compared to values obtained from separate measurements of the individual properties. The results are shown in Table 2 with $\pm\ 2s$ limits. The experimental results were obtained from the slopes of the straight lines in Figures 2 and 3, which in turn were determined by weighted regression. The theoretical values were obtained from Equations (10) and (13) and independent measurements of the properties of the liquid used (unpublished data taken in this laboratory). Two values of P_2 are listed corresponding to the two straight lines in Figure 3.

Table 2. Comparison of Absolute Magnitudes

Group	Experimental	Theoretical
P_1	$(4.75 \pm 0.06)\ 10^{-7}$	$(3.5 \pm 0.7)10^{-7}$
P_2, $2w$ = 1/16 in.	$(15 \pm 1)10^{-3}$	$(2.0 \pm 0.3)10^{-3}$
P_2, other	$(8.2 \pm 0.4)10^{-3}$	$(2.0 \pm 0.3)10^{-3}$

In all cases, the theoretical values are significantly different from the experimental. The P_1 values are tantalizingly close, but the P_2 values are off by a factor of four. One must conclude that the theory does not give the correct values of the phenomenological coefficients. In this respect the packed-column theory is not unlike that for the open column for which experimental and theoretical coefficients have sometimes been close (*12*) and have sometimes differed by large factors (*13*), with perhaps a factor of two being characteristic.

CONCLUSIONS

The theory correctly gives the effects of plate spacing and permeability on the behavior of the batch thermal-diffusion column, with the exception of the effect of plate spacing on transient behavior at the lowest plate spacing. The theory does not give the correct absolute values of the phenomenological coefficients of the operating equations. Thus the packed column theory is in about the same position as that for the open column.

NOTATION

B = width of the column parallel to the heat transfer surfaces
D = diffusion coefficient
g = acceleration of gravity
H = coefficient defined by Equation (4)
k = permeability of the packing
K = coefficient defined by Equation (5)
L = total column height
L_Δ = column height between sample taps
P_1, P_2 = arbitrary combinations of fluid properties, defined by Equations (10) and (13)
s = standard error
t = time
T = absolute temperature
V_1, V_2 = arbitrary combinations of apparatus parameters, defined by Equations (11) and (14)
w = half-width of the column perpendicular to the heat transfer surfaces
Y = dimensionless distance defined by Equation (8)

Greek Letters

α = thermal-diffusion constant
β = $-\ \partial\rho/\partial T$
Δ = difference in concentration between two points in the column
Δ_∞ = Δ at infinite time
ϵ = void fraction in the packing
η = viscosity
ρ = density
τ = relaxation time

LITERATURE CITED

1. Jones, A. L., *Ind. Eng. Chem.*, 47, 212 (1955).
2. ———, *Petrol. Process.*, 6, 132 (1951).
3. ———, and R. W. Foreman, *Ind. Eng. Chem.*, 44, 2249 (1952).
4. Sellbach, C. W., and R. W. Quackenbush, *J. Am. Oil Chemists' Soc.*, 34, 603 (1957).
5. ———, *Ind. Eng. Chem.*, 50, 353 (1958).
6. Anon., *Chem. Eng. News*, 39, 69 (April 3, 1961).
7. Washall, T. A., and F. W. Melpolder, *Ind. Eng. Chem., Process Design Dev.*, 1, 26 (1962).
8. Debye, Peter, and A. M. Bueche, "High Polymer Physics," H. A. Robinson, ed., p. 497, Chemical Publishing, Brooklyn, New York (1948).
9. Sullivan, L. J., T. C., Ruppel, and C. B. Willingham, *Ind. Eng. Chem.*, 49, 110 (1957).
10. Lorenz, Maurice, and A. H. Emery, Jr., *Chem. Eng. Sci.*, 11, 16 (1959).
11. Lorenz, Maurice, Ph.D. thesis, Purdue Univ., Lafayette, Ind. (1960).
12. Crownover, C. F., and J. E. Powers, *A.I.Ch.E. Journal*, 8, 166 (1962).
13 Powers, J. E., and C. R. Wilke, *ibid.*, 3, 213 (1957).

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The Interrelation of Geometry, Orientation, and Acceleration in the Peak Heat Flux Problem

C. P. COSTELLO and J. M. ADAMS

University of Washington, Seattle, Washington

Boiling heat transfer is widely employed in high-performance systems owing to the fact that extremely high energy transfer rates per unit area (that is, heat fluxes) may be obtained with relatively low surface to fluid temperature differences. At a certain heat flux, a vapor film is able to stabilize on the heater surface, partially insulating it and causing it to overheat. The unit energy transfer rate at which this condition occurs will be called the *peak heat flux* in this paper.

Certain analytic and semianalytic correlations [that is, (*1, 2, 3*)] have been proposed to enable prediction of the peak heat flux with varying degrees of success. More extensive study of the problem is required to ascertain the correct picture of the physical situation at the peak heat flux condition.

Studies of the effects of high accelerations on the peak heat flux are desirable from at least two standpoints:

1. Certain systems employ boiling heat transfer in various acceleration fields.
2. Most important, when accelerations are imposed on systems there is a means of appraising the realism of physical models which have been used to devise various peak heat flux correlations.

For these reasons, some attention has been given to studies of the effects of acceleration on peak heat flux. Gambill and his co-workers, (*4, 5*) studied spiral flows of water in channels where centripetal accelerations were obtained owing to the path of the fluid. Gambill and Greene (*4*) indicated that the peak heat flux, $(q/A)_p$, appeared to be related to the acceleration divided by local gravitational acceleration, (a/g), as follows:

$$(q/A)_p \propto (a/g)^{0.43-0.48} \qquad (1)$$

But since the fluid was below its saturation temperature and flowing at high velocity, Gambill and Greene were reluctant to ascribe all of the increases in $(q/A)_p$ to acceleration effects.

To eliminate these confounding factors, Costello and Adams (*6*) ran pool boiling tests wherein the pool was rotated to produce accelerations up to $a/g = 40$. For values of a/g up to 10 the data showed

$$(q/A)_p \propto (a/g)^{0.15} \qquad (2)$$

while for $a/g > 10$

$$(q/A)_p \propto (a/g)^{0.25} \qquad (3)$$

Equation (3) shows the behavior that the analytic correlations of Zuber et al. (*2*), Borishanskii (*3*), and others have predicted. No correlations predict the behavior of Equation (2), however.

Choi (*7*) imposed magnetically produced accelerations on a system in which Freon-113 was pool boiled. When he plotted his data in terms of an equivalent acceleration, they bore striking similarity to those of Costello and Adams (*6*) in that for lower accelerations the data behaved according to Equation (2) while at high accelerations Equation (3) characterized the data. Ivey (*9*) conducted tests using stainless steel cylinders 0.048-in. O.D. and 1.25 in. long. These were rotated in a centrifuge and Ivey found that Equation (2) held over the range $1 \leq a/g \leq 160$. However, it was necessary to correct for substantial pressure buildups and subcoolings in the centrifuge employed by Ivey, and this required the use of techniques which may not be valid for $a/g > 1$. At any rate, few data were taken in the range $1 \leq a/g \leq 10$.

Usiskin and Siegel (*8*) obtained some data on the effects of accelerations less than that of normal gravity $(a/g < 1)$ by means of drop tests. Since the existence of steady state was uncertain, the data are questionable to some extent, but they appear to behave in the manner