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An Experimental Study of Gas Chromatography in the Turbulent Flow Region in Open Tubular Columns

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Summary

The decrease in the plate height with increasing Reynolds number, predicted by theory, has been verified for gas chromatography in open tubular columns. It has been shown that this decrease is most pronounced when the mass distribution coefficient $k = 0$ and considerably lessened for $k > 0$. The Golay equation has been found to break down at relatively low flow velocities, viz., Re $\sim$ 200.

INTRODUCTION

The experimental test of the most important characteristics of the plate height in the turbulent flow region predicted by a previous theoretical study (*1*) is the object of the present investigation. In particular the decrease of the plate height with increasing flow velocity (or Reynolds number) and the "anomolous" increase of the plate height with increasing mass distribution coefficient in the turbulent flow region appear to be the most crucial aspects of the predicted plate-height behavior.

A meaningful test of the theoretical expressions derived above for the contributions to the plate height originating in the gas phase can at best be made by employing a method whereby the mobile and stationary phase contribution to *H* can be measured separately. Several methods for doing this have been proposed (2–9). A technique similar to that employed by van Berge et al. (9) will be used in this study.

Rearrangement of the plate-height expression derived previously (*1*) yields

$$\frac{H}{f_m} = h_M(x)r_t + C_s\frac{\bar{u}_of_s}{f_m} \tag{1}$$

where

$$h_M(x) = I_1\mathrm{ReSc} \tag{2}$$

and I_1 is an integral previously evaluated (*1*). Since

$$\mathrm{Re} = \frac{2\bar{u}_o\rho_o'r_t}{\eta_o} = \frac{2\bar{u}(x)\rho'(x)r_t}{\eta(x)} \tag{3}$$

$$\mathrm{Sc} = \frac{\eta_o}{D_{mo}\rho_o'} = \frac{\eta(x)}{D_m(x)\rho'(x)} \tag{4}$$

and

$$\eta_o = \eta(x) \tag{5}$$

and assuming ideal gas behavior, $h_M(x)$ does not change along the column length. C_s is also independent of x. Straight-line analysis of Eq. (1) by varying the quantities H/f_m and $\bar{u}_of_s/f_m$ will yield, under suitable circumstances, the quantities $h_M(x)$ and C_s which can be found from the abscises and the gradients of the resulting straight lines, respectively. This analysis will be valid only if $h_M(x)r_t$ and C_s do not vary during the course of an experiment in which data for such a straight-line plot are obtained. $\mathrm{h}_M(x)$ evidently remains constant as long as Re, Sc, and k remain constant. This implies that such an experiment must be carried out at a constant value of Re. This constraint also fixes Sc. k will remain constant as long as the solute-mobile phase gas mixture can be regarded as ideal (*10,11*). C_s depends on k, D_{so}, and d_f in the case of gas-liquid chromatography. None of these quantities depend on $\bar{u}_of_s/f_m$ if ideal gas behavior is assumed.

It is instructive to measure the change in the friction factor f with Reynolds number. From such information the point where turbulence sets in may be obtained under suitable conditions. This can at best be done by measuring experimentally (*12*)

$$f = \frac{2(P_i^2 - P_o^2)r_t^3\rho_o'}{P_o\eta^2L\mathrm{Re}^2} \tag{6}$$

It has been shown that

$$f = \frac{16}{\mathrm{Re}} \tag{7}$$

for laminar flow. In the turbulent flow region the Blasius formula gives the value of f for Re values up to 10^5 (*12*) as

$$f=\frac{0.0791}{\mathrm{Re}} \tag{8}$$

An increase in the slope of ln f versus ln Re may thus be an indication of the onset of turbulence (*12*).

EXPERIMENTAL

Since the experiments are almost entirely concerned with the turbulent flow region, a number of problems arise which would not be encountered in conventional open-tubular chromatography. Because of the high linear flow rates involved, it has been necessary to employ a detector with a sufficiently low time constant; as discussed below, the flame ionization detector has been found satisfactory. For the same reason it has been necessary to devise an inlet system which can operate at high pressures and would also not cause undue spreading of the inlet band. A schematic diagram of the apparatus is shown in Fig. 1.

The inlet system shown in Fig. 2 is similar to that described by Peterson and Lundberg (*13*). The essential difference is a triggered spring device for moving the gaseous sample very rapidly into the column circuit. The reproducibility of the inlet system was determined by repetitive injection of vapor and was found to be reproducible to within 1%. The sample volume as determined from the dimensions of the sample hole in the inlet shaft was 7.46 μl. The gaseous sample used during the experiment consisted of a

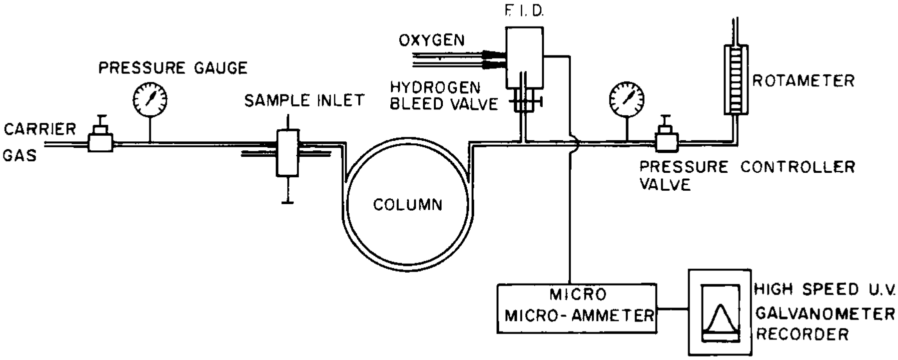

FIG. 1. Schematic diagram of apparatus.

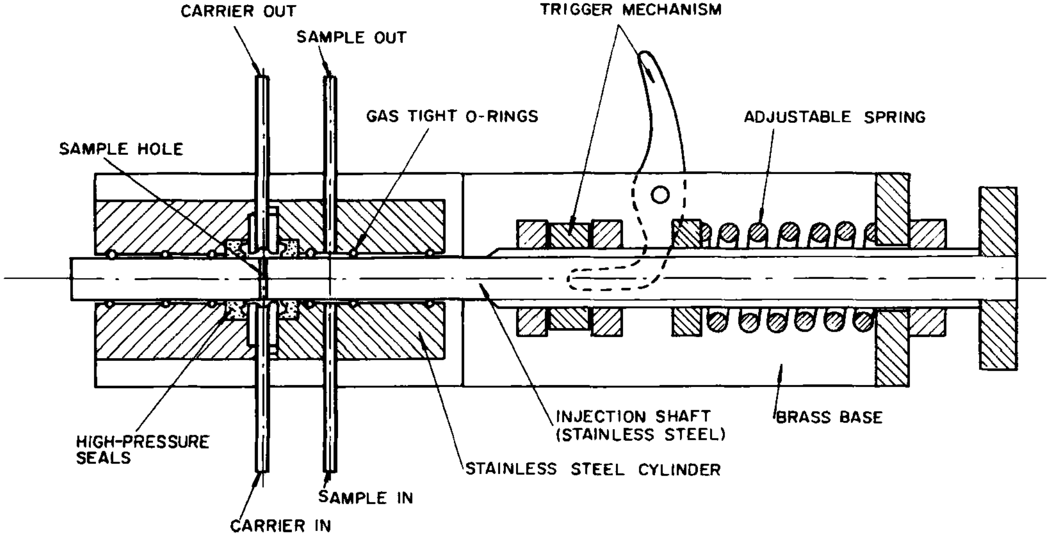

FIG. 2. Sample introduction system.

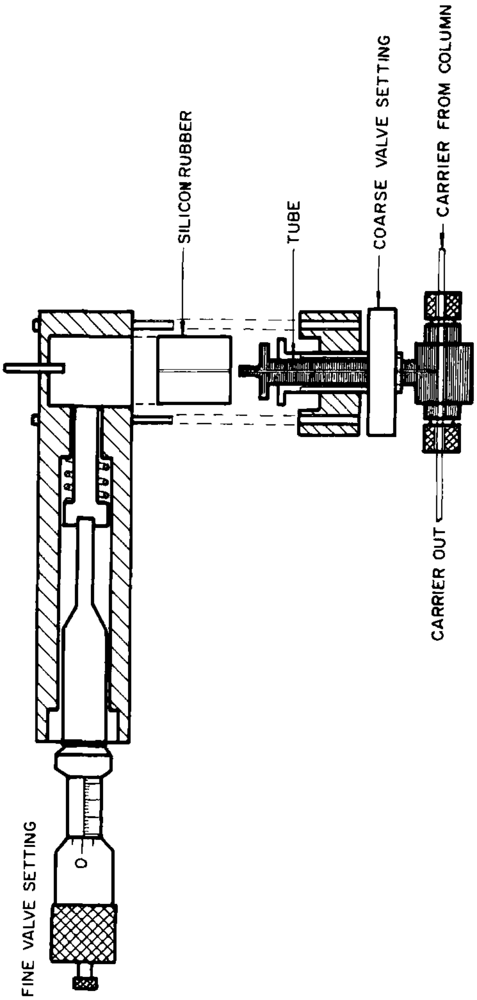

FIG. 3. Eluate control valve.

mixture of hydrocarbons, i.e., acetylene, *n*-butane, *n*-pentane, and *n*-hexane. It was stored in a small steel cylinder together with an excess of nitrogen at relatively low pressures (2–3 atm).

A conventional flame ionization detector (Beckman Instruments), modified as shown in Fig. 3, was used. Because of the very large-volume flow rates of the carrier gas encountered in the course of the experiments, a simple valve was used to control the amount of eluate bled through the detector. The valve provided extremely satisfactory operation up to pressures of 100 atm. The signal from the detector was fed to a Keithley Micromicroammeter model 415 (frequency response better than 10^{-3} sec^{-1}) on a Visigraph FR-201 galvanometric recorder (frequency response of galvanometer better than 10^{-2} sec^{-1}).

All experiments were carried out using a 500-ft copper column with an inside diameter of 0.14 cm. The column was cleaned and the inner walls were coated with a 10% squalane solution in petroleum ether (bp, 30–40°C) by means of the dynamic coating method described by Dijkstra and de Goey (*14*). Nitrogen was used as carrier gas and the column was operated at room temperature (25°C). The pressures at the column inlet and outlet were measured on Bourdon pressure gauges. Measurements of carrier gas flow rates were made with a rotameter at the column outlet and for $P_0 = 0.87$ atm.

The suitability of the high-speed gas chromatograph depends mainly on the extent to which extracolumn effects, i.e., inlet, detector, and electronic effects, contribute to the measured band width at the column outlet. By connecting the inlet to the detector with a tube 3 cm in length and of the same diameter as the column and by measuring the recorded band width at half-height, σ_{teo}^2 was determined over a wide range of linear flow velocities. Similar data obtained with the column itself and over the same range of flow velocities ($100 < \text{Re} < 20{,}000$) indicated that $\sigma_{\text{teo}}^2 \leqslant 10^{-4} \sigma_{\text{tTo}}^2$.

The apparatus described above was used to vary $\bar{u}_0 f_s/f_m$ at a fixed Reynolds number. This was done in practice by adjusting the inlet and outlet pressures at a constant value of $\bar{u}_0 P_0$. The quantity H/f_m was determined for each of the solutes injected at a variety of $\bar{u}_0 f_s/f_m$ values. The whole procedure was repeated for different Reynolds numbers in the range $500 < \text{Re} < 15{,}000$. The pressure drop across the column was also measured at various flow rates. The plate height was obtained in the usual way (*15*) by measuring the width of the peaks at half-height. The reproducibility of these measurements was determined at a number of operating conditions. Nowhere was the random error larger than 5% for 95% confidence limits.

RESULTS AND DISCUSSION

It is essential for the subsequent discussion of the results to determine to what extent the assumption of ideal gas behavior implicitly assumed in this experimental work holds. The data compiled in Table 1 give an indication of the pressure ranges that were employed during the various runs at both the column inlet and outlet. Ideal behavior is assumed in a number of instances. In the carrier ideality is assumed in Eqs. (1) and (5).

$$P(x)U(x) = P_o U_o \tag{9}$$

Equation (9) holds to within 2% for nitrogen at 20°C over the pressure range (1–100 atm) employed in the experimental work (*16*). This degree of accuracy appears to be sufficient where used in Eqs. (3) and (4). Equation (9) has, furthermore, been used in the calculation of the compressibility corrections f_m and f_s. A recalculation of f_s while taking deviations from ideality into account by using the methods proposed by Martire and Locke (*17*) indicates that f_s thus obtained differs by less than 1% from the value obtained by assuming Eq. (9) to hold over the pressure range used during the

TABLE 1

Typical Pressure Ranges Employed at Both the Column Inlet and Outlet

	P_i, atm		P_o, atm	
Re	Minimum	Maximum	Minimum	Maximum
484	3.64	11.27	1.24	10.74
645	3.97	8.27	1.11	7.54
1250	4.51	11.71	1.14	10.74
1976	6.97	11.34	1.14	9.31
3589	11.67	14.77	1.06	9.84
6532	19.11	28.31	1.29	20.84
10485	29.17	58.31	1.51	41.77
10372	43.51	60.31	10.51	46.84

course of the experiment. The assumption of a pressure independent value of the carrier gas viscosity coefficient [Eq. (5)] holds to within 8% (*16*) over the pressure range 1–100 atm. The implication of this variation is discussed below. The assumption of ideal behavior of the solute vapor dissolved in the carrier gas involves two variables, viz., the diffusion coefficient of the solute in the mobile phase D_m and the mass distribution coefficient k. According to methods proposed by Reid and Sherwood (*16*), $D_m\rho'$ is smaller by about 7% at 100 atm than it is at atm than it is at atmospheric pressure. Evidently this deviation, together with the observed pressure dependence of the viscosity of the mobile carrier, implies that the Schmidt number [Eq. (4)] may vary by as much as 16% along the column length for the maximum pressure drop across the column (100 atm) employed in this study. This deviation need not, however, affect the usefulness of Eq. (1), since clearly, as can be easily verified from Eqs. (2–4), $h_M(x)$ does not depend explicitly on the viscosity coefficient of the carrier gas. Furthermore, the pressure dependences of $\bar{u}(x)\rho'(x)$ and $D_m(x)\rho'(x)$ in the group ScRe = $2u(x)\rho'(x)r_t/D_m(x)\rho'(x)$ tend to counteract each other. $h_M(x)$ can therefore be expected to remain constant along the column length to within 7% for a pressure drop of 100 atm across the column. Nonideality affects the mass distribution coefficient k significantly. Desty et al. (*10*) and others (*18*) have shown that ln k decreases linearly with the average column pressure $\bar{P}$ where

$$\bar{P} = \frac{\int_0^L p(x)\,dx}{\int_0^L dx} = P_o f_s \qquad (10)$$

In the present investigation a pressure dependence of k of this type was indeed observed. This dependence of k on $\bar{P}$ affects the results in two ways. On the one hand k was found to vary during the course of an experimental run at fixed Reynolds number because of the dependence of $\bar{P}$ on f_s. This effect had the unfortuante result that both C_s and $h_M(x)$ may change during such a run because of their dependence on k. This phenomenon could not be corrected for in the present study, but the range of variation in k has been carefully reported. On the other hand the dependence of k on $\bar{P}$ manifested itself in a variation of k for a given solute with

Reynolds number. This implies that the variation of $h_M(x)$ with Reynolds number, at a fixed value of k, cannot be established.

It is evident from the data listed in Table 1 that the pressure ranges employed are, in fact, in most cases much smaller than those considered in the discussion above. The implication of the assumption of ideality will therefore be even less drastic than was pointed out for the 1–100-atm range.

The data relevant to the carrier gas are shown in Table 2. The values shown have either been obtained directly from Reid and Sherwood (*16*) or calculated by the methods recommended there.

Experimentally determined values of $h_M(x)$ for various values of Re for acetylene ($k = 0$) are shown in Fig. 4. These values have been obtained from the experimentally measured values at the column outlet and

$$h_M(x) = \frac{h_M}{f_m}$$

Curve a is a linear extrapolation of the data obtained at low Reynolds numbers (Re < 100) to the higher Reynolds number region (Re ~ 1000) which is usually still laminar. Curve b has been obtained from the Golay equation with $C_s = 0$ and Sc = 1.0, a value typical of acetylene in N_2 (see Table 2). The experimental values of $h_M(x)$ for Re > 500 fall below both curves a and b and tend to flatten off before they finally start to decrease for Re > 2000. The premature change in the slope of the experimental values can be attributed to a deviation from streamline flow at those values of Re. Evidence in support of this supposition can be found in Fig. 5, where the variation of the Fanning friction factor f with Reynolds number is depicted logarithmically. f has been calculated according to Eq. (6). The solid lines have been obtained from Eqs. (7) and (8). An

TABLE 2

Data Relevant to the Carrier Gas[a]

Solute	D_mP, cm² atm sec⁻¹	Sc
Acetylene	0.179	1.17
n-Butane	0.096	1.57
n-Pentane	0.085	1.79
n-Hexane	0.075	2.00

[a] Nitrogen viscosity = 0.019 cP.

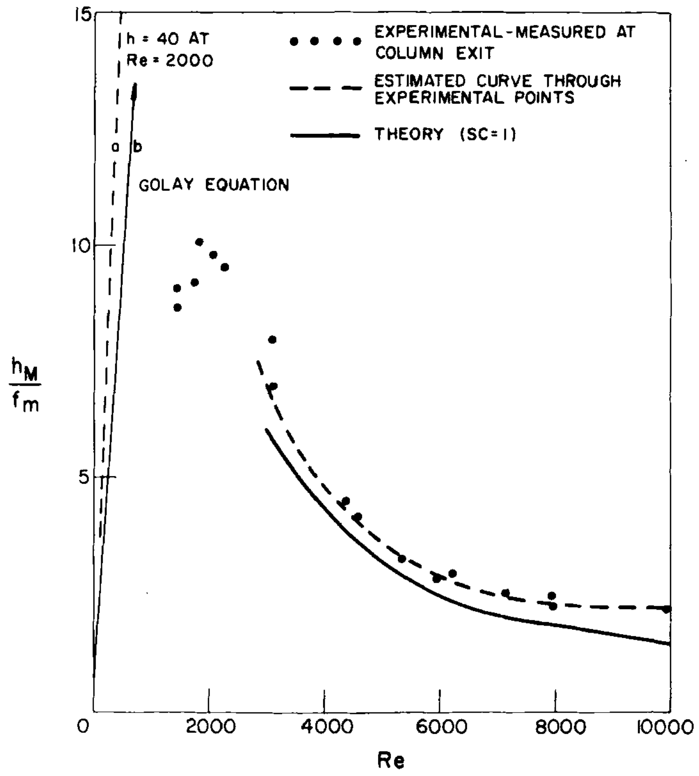

FIG. 4. Variation of $h_M(x)$ with Re for $k = 0$ obtained both experimentally and theoretically.

increase in the slope of the experimentally determined curve above the slope of the theoretical line at Re $\simeq$ 500 also indicates a deviation from laminar flow at this Reynolds number. Such deviations need not, and probably do not, however, imply that the flow dynamics has become turbulent in the sense that the flow is unstable in this region. Deviations from laminar flow in the flow region below the critical Reynolds number may occur (*19*) but the system will tend to damp them out; i.e., the flow dynamics is stable. Only in the flow region above the critical Reynolds number are small perturbations increased spontaneously and can the flow dynamics become truly turbulent. The onset of this unstable region is clearly demonstrated by the decrease of h_M/f_m for Reynolds numbers $\geqslant$ 2000, shown in Fig. 4. The corresponding variation predicted by the theory is also shown. The agreement between theory and experiment in this flow region is, if anything, too good. Finally, therefore, it can be concluded from the data shown in Fig. 4 that the Golay equation breaks down in the flow region $500 \leq \text{Re} \leq 2000$. Discrepancies can therefore, in normal practice, be expected between theory and experiment in this region. It will, however, be virtually impossible, from a fundamental view point, to obtain a suitable expression for the plate height for this flow region.

The experimental data for the retarded solutes were analyzed by obtaining the linear regression line between the variables H/f_m and $\bar{u}_0 f_s/f_m$ for each value of the Reynolds number and for the various solutes. The value of $h_M(x)$ could be obtained from the intercept of the regression line on the H/f_m axis (and $r_t = 0.07$ cm) and C_s from

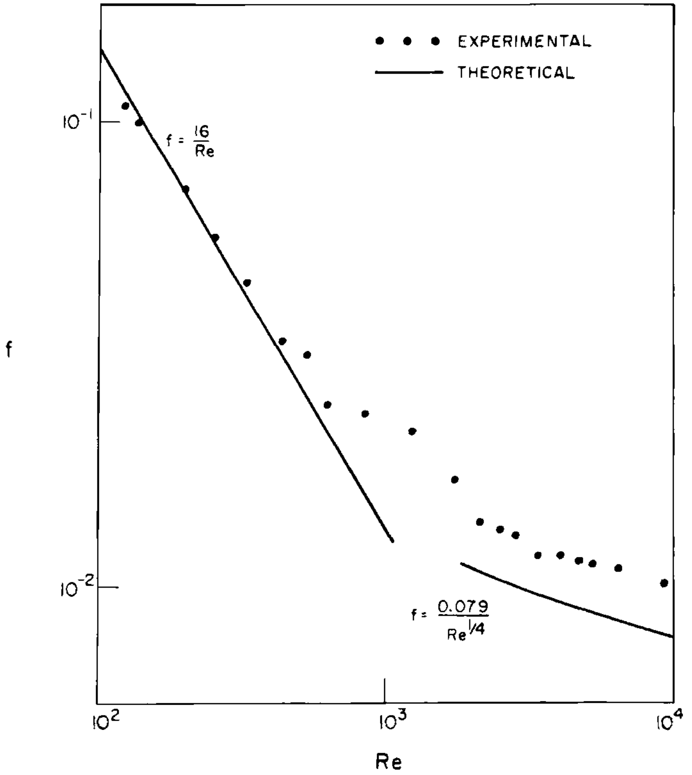

FIG. 5. Variation of friction factor with Reynolds number.

TABLE 3

Results of Linear Regression Analysis of Experimental Data for the Various Solutes

Re	k range	$C_m \times 10^4$ sec	$C_s \times 10^2$ sec	$h_M(x)$
		n-Butane		
484	0.13–0.16	27 ± 2.0	1.8 ± 0.2	24.90 ± 1.8
645	0.14–0.15	17 ± 2.0	1.7 ± 0.4	19.20 ± 1.1
1250	0.09–0.13	9.5 ± 1.8	0.9 ± 0.5	22.70 ± 4.3
1976	0.08–0.10	7.5 ± 0.4	0.5 ± 0.2	28.60 ± 1.5
3589	0.12–0.13	4.6 ± 0.2	0.6 ± 0.2	31.70 ± 1.4
6550	0.11–0.13	3.1 ± 0.2	0.6 ± 0.2	38.40 ± 2.5
10485	0.08–0.11	0.24 ± 0.09	1.0 ± 0.2	4.84 ± 1.8
16372	0.08–0.10	0.50 ± 0.01	0.7 ± 0.3	15.60 ± 0.3
		n-Pentane		
484	0.44–0.53	67 ± 5	4.5 ± 0.6	62.60 ± 4.8
645	0.47–0.51	54 ± 8	3.6 ± 1.4	67.40 ± 9.9
1250	0.47–0.58	24 ± 4	3.8 ± 1.0	57.20 ± 9.9
1976	0.46–0.51	20 ± 2	2.6 ± 0.6	76.20 ± 7.6
3589	0.43–0.45	19 ± 1	1.1 ± 1.0	126.60 ± 6.7
6550	0.36–0.43	7.9 ± 0.3	1.7 ± 0.3	99.40 ± 3.4
10485	0.26–0.38	1.3 ± 0.3	3.0 ± 0.4	25.60 ± 6.0
16372	0.26–0.34	0.78 ± 0.6	2.7 ± 1.8	24.60 ± 19.0
		n-Hexane		
484	1.38–1.70	170 ± 10	7.6 ± 1.5	159.6 ± 9.5
645	1.50–1.65	100 ± 20	7.1 ± 4.0	124.6 ± 25.0
1250	1.59–1.85	93 ± 8	4.3 ± 1.9	222.6 ± 19.0
1976	1.50–1.70	69 ± 2	3.0 ± 0.8	258.8 ± 6.6
3589	1.33–1.39	36 ± 1	3.4 ± 1.5	250.0 ± 9.0
6550	1.10–1.32	26 ± 3	3.0 ± 3.4	329.0 ± 38.0
10485	0.77–1.15	8.5 ± 0.7	5.4 ± 0.8	169.6 ± 14.0
16372	0.75–0.98	4.8 ± 1.5	5.6 ± 4.0	148.4 ± 48.0

its slope. Furthermore, C_m, as given by

$$H_M(x = L) = C_m \bar{u}_0 \tag{11}$$

was obtained at a fixed pressure at the column outlet of 0.87 atm. The data thus obtained are given in Table 3. The limits indicated for $h_M(x)$, C_m, and C_s indicate the region of 95% confidence. A general characteristic of the data as a whole is the large margin of error in the values shown. Furthermore, it is evident that the margin of error increases with increasing Reynolds number. This can probably be attributed to two factors. The first is that at the higher Reynolds number the large flow velocities involved may result in an increased scatter in the experimental results. The second, and probably the most important, is the accentuated deviations from ideality brought about by higher pressure drops across the column (see also Table 1). For *n*-hexane at Re $\simeq$ 16,000, the deviation of *k* during a run was ~25%. This data appears, however, to be good enough to support the broad tendencies predicted by the theory.

It is instructive to note that C_s remains roughly constant with changing Reynolds number, as is to be expected. A decrease in the value of C_m of two orders of magnitude over the Re range listed is

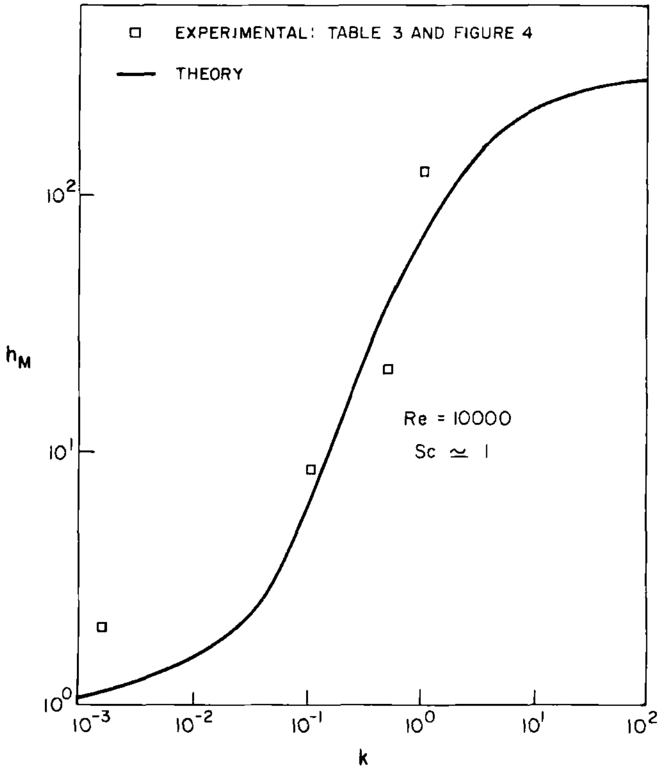

FIG. 6. Comparison of the variation of h_M with *k* found experimentally and that predicted by theory.

observed. Since C_m is expected to be constant in the laminar flow region, the decrease of C_m in the flow region $400 \leqslant \mathrm{Re} \leqslant 2000$ can again be attributed to deviations from streamline flow in this region. In the flow region $\mathrm{Re} \geqslant 2000$, $h_M(x)$ does not decrease as dramatically with Re for the larger k values than for $k = 0$ (see Fig. 4). Instead it remains fairly constant over the Reynolds number range reported. This experimental result has, of course, been anticipated by the theory as can be seen from the previous publication (*1*) (Fig. 6). Furthermore, it would appear that $h_M(x)$ increases by a factor 80 when k changes from $k \simeq 0$ to $k \simeq 1$ at $\mathrm{Re} \simeq 10{,}000$ (the value of $h_M(x)$ for $k = 0$ is obtained from the broken line in Fig. 4 at $\mathrm{Re} = 10{,}000$).

The broad qualitative trends pointed out above, except those effects peculiar to the flow region $400 \leqslant \mathrm{Re} \leqslant 2000$, are incorporated in the proposed plate-height equations for the turbulent flow region. A quantitative test of the $h_M(x) \sim \mathrm{Re}$ behavior predicted by Eq. (39) of a previous paper (*1*) against the experimental data shown in Table 3 is not possible because of the variation of k with Re. An important check of the quantitative correctness of the theoretical predictions would be to compare the agreement between $h_M(x) \sim k$ trends at a fixed value of Re. For this purpose the experimentally determined values of $h_M(x)$ for the various values of k and $\mathrm{Re} = 10{,}485$ are shown in Fig. 6. The agreement appears to be reasonable.

List of Symbols[*]

C_s	convenient parameter, related to band broadening mechanism residing in the stationary phase, defined by $H_s = C_s\bar{u}$ (T)
D_m	molecular diffusion coefficient in the mobile phase (L^2T^{-1})
D_{mo}	value of D_m measured at the column outlet (L^2T^{-1})
D_s	molecular diffusion coefficient in the stationary phase (L^2T^{-1})
D_{so}	value of D_s measured at the column outlet (L^2T^{-1})
d_f	thickness of a formally uniform layer of stationary phase (L)

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[*] Dimensions are given where applicable in terms of mass (M), length (L), and time (T).

f	Fanning friction factor defined by Eq. (6)
f_s	correction for compressibility of the mobile phase given by $f_s = (3/2)\ [(p^2)^{-1}/(p^3)^{-1}]$
f_m	correction for compressibility of the mobile phase given by $f_m = [9(p^4)^{-1}(p^2)^{-1}]/8[(p^3)^{-1}]^2$
H	plate height measured at the column outlet (L)
H_s	contribution to H of mechanisms residing in the stationary phase (L)
$h_M = H_M/r_t$	H_M measured in units of r_t
I_1	constant
k	mass distribution coefficient; ratio of the solute mass in the stationary phase to the solute mass in the mobile phase at equilibrium
L	column length (L)
$\bar{P}$	average column pressure ($ML^{-1}T^{-2}$)
P_i	value of P measured at the column inlet ($ML^{-1}T^{-2}$)
P_o	value of P measured at the column outlet ($ML^{-1}T^{-2}$)
$p = P_i/P_o$	ratio of the inlet to the outlet pressure
Re	Reynolds number; $\mathrm{Re} = 2r_t\bar{u}(x)/\nu(x)$
r_t	radius of open tubular column (L)
$\mathrm{Sc} = \nu/D_m$	Schmidt number
$\bar{u}$	radial average of u (LT^{-1})
$\bar{u}_o$	value of $\bar{u}$ measured at the column outlet (LT^{-1})
x	axial column coordinate with the sample inlet point chosen as the origin (L)
η	viscosity in the mobile phase ($ML^{-1}T^{-1}$)
η_o	value of η measured at the column outlet ($ML^{-1}T^{-1}$)
ρ'	density of mobile phase (ML^{-3})
ρ'_o	value of ρ' measured at the column outlet (ML^{-3})
σ_{teo}	standard deviation of the solute concentration distribution resulting from extracolumn effects in units of time and measured at the column outlet (T)
σ_{tTo}	total standard deviation of the solute concentration distribution in units of time, measured at the column outlet (T)

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