Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Theoretical and Experimental Study on the Use of Gas Chromatography in Turbulent Flow Conditions

Francois Doue[a]; Georges Guiochon[a]
[a] ECOLE POLYTECHNIQUE, PARIS 5ème, france

To cite this Article Doue, Francois and Guiochon, Georges(1970) 'Theoretical and Experimental Study on the Use of Gas Chromatography in Turbulent Flow Conditions', Separation Science and Technology, 5: 3, 197 — 218

To link to this Article: DOI: 10.1080/01496397008080027

URL: http://dx.doi.org/10.1080/01496397008080027

SEPARATION SCIENCE, 5(3), pp. 197–218, June, 1970

Theoretical and Experimental Study on the Use of Gas Chromatography in Turbulent Flow Conditions

FRANCOIS DOUE and GEORGES GUIOCHON
ECOLE POLYTECHNIQUE
PARIS 5ÈME, FRANCE

Summary

It is relatively easy to carry out gas chromatographic analysis under conditions where the carrier gas flow is turbulent if open tube columns are used. This speeds up the mass transfer in the mobile gas phase. Conditions necessary to reach the turbulent flow region are given and equipment is described.

It is shown theoretically that in the fully turbulent flow of gas the retention times of all compounds should be independent of inlet pressure and of the carrier gas flow rate to the extent that the partition coefficients are themselves pressure independent, and the carrier gas ideal. Also, the HETP should be constant for all compounds, and for inert peak equal to about 5 times the column radius.

Experimental data fully support these theoretical results. When the flow velocity is larger than the critical Reynolds number, the retention time decreases only slightly with increasing column inlet pressure, and the HETP decreases smoothly towards a limiting value equal to about $6r_0$. The efficiency for retained peaks is, however, much smaller due to the effects of resistance to mass transfer in the liquid phase, and the analytical results are not as good as expected.

The possibility of carrying out gas chromatography under conditions where the carrier gas flow is turbulent was suggested many years ago (*1*), and the advantages of this type of flow have been discussed by various authors (*1–5*). Giddings (*1*) pointed out that mass transfer is very fast in turbulent flow and that the adverse effects on peak broadening of the local, random, and/or systematic variations of carrier gas flow rate across the column could be reduced. This suggestion, however, has not been explored in detail up to now in spite of some theoretical (*2*, *3*) and experimental (*4*, *5*) studies in gas (*4*) and liquid (*5*) chromatography.

Because the influence of mass transfer in the mobile phase on the efficiency of the columns and the effect of flow on mass transfer are much better understood in gas chromatography, we shall not discuss the problem of turbulent flow in liquid chromatography.

Gas chromatography is carried out using either packed or capillary columns. Although it is possible to use turbulent flow in packed columns, this would obviously need very high inlet pressure and, consequently, special equipment. With large bore capillary columns, conventional equipment allows easy experimental work.

From the theoretical point of view, high pressure makes the phenomena in the column more complex. Furthermore, analysis of the various processes on which the column efficiency depends is much more complex for packed columns than for capillary columns. This work is thus restricted to capillary columns for which most problems can be solved and for which retention times as well as the predicted efficiency is in substantial agreement with experimental results.

THEORETICAL SECTION

The theoretical problems which should be solved in chromatography are predictions of retention time and peak width or efficiency. The first problem deals with the flow velocity of the carrier gas, the nature of flow, and the conditions of its transformation from laminar viscous flow to turbulent flow. The second problem is related to mass transfer in the mobile and stationary phases. Before discussing these problems, however, it is important to be precise about what we consider as turbulent flow.

I. Laminar and Turbulent Flows

In laminar flow (*6*) the flow rate at any point is well defined at any time. In most cases it is constant, but sometimes it fluctuates continuously around an average value. In the latter case the mathematical solution is said to be unstable. Consequently, the trajectory of an infinitely small volume of fluid can be calculated from its initial position and starting time. Furthermore, the molecules which are initially in this volume will be separated from one another by molecular diffusion only. The stream lines can be calculated in either case using the Navier-Stokes equation. In other words, the laminar flow is described by the Navier-Stokes equation. This is the type of flow which is encountered in normal chromatographic practice (*6*). It should be pointed out that this is in full agreement with the appearance of eddies in packed columns (*7*) or even in open tubes (*8*) and with a relative instability of these eddies. In the simple case of a stationary, spherical body in an infinite flow, the Navier-Stokes equation predicts such eddies down-stream from the sphere and their instability (*9*). Because of the complexity of the Navier-Stokes equation and because numerical analysis is not yet advanced enough, the flow in packed columns cannot be fully described. On the other hand, the flow in a straight, open tube, where the streamlines are straight lines parallel to the tube axis, can be described.

In turbulent flow there is no such continuity. The flow rate at any point fluctuates at random in a very broad range, so only time-average velocities can be used. There is no correlation between the flow rates at two different points at the same time, although there is a relationship between the time-average velocities (*10*). There are no streamlines. The molecules which are together in a small volume at a given time may be separated at any later time and their trajectories will not be related. Such a flow cannot be described by analytical equations, but only by statistical analysis. Turbulent flow is different in nature from laminar flow as encountered in normal gas chromatography, in spite of the innumerable eddies which appear between packing particles.

II. Transition Between Laminar and Turbulent Flow Rates

The nature of flow depends on the value of the Reynolds number:

$$\mathrm{Re} = \frac{ud\rho}{\eta} \qquad (1)$$

It is usually assumed that the critical value of Re above which the flow becomes turbulent in straight open tubes is about 1800. This value is approximative for several reasons. The flow does not become suddenly turbulent when Re becomes larger than 1800. Flow becomes unstable, eddies appear in various places and become more and more numerous, and consequently the critical value of Re depends on end effects, on the smoothness of the tube wall, etc. Furthermore, because of the Poiseuille flow profile, the flow rate is larger on the tube axis and the flow becomes turbulent in the center of the tube first, then progressively a larger and larger part of the flow becomes turbulent. The critical value may be quite different for coiled tubes (*11*, *12*).

In packed tubes, the Reynolds number is usually calculated by using the particle diameter instead of the tube diameter (*6*).

Table 1 gives the values of the dynamic viscosity η, the NTP density ρ, and the NTP kinematic viscosity η/ρ for the main possible carrier gases. Carbon dioxide has the smallest kinematic viscosity after SF_6.

TABLE 1

Viscosities of the Main Possible Carrier Gases

	η[a] (micropoise)	ρ[a] (10^{-4} g/cm^3)	η/ρ[a]	$10^6 \times \eta^2/\rho$[a]	η/ρ[b]	$10^6 \times \eta^2/\rho$[b]
Hydrogen	84	0.893	0.941	79	1.58	162
Helium	186	1.786	1.041	194	1.75	402
Nitrogen	166	12.502	0.133	22.1	0.227	47.6
Argon	212	17.86	0.119	25.1	0.207	56.0
Carbon dioxide	138	19.65	0.0702	9.69	0.129	23.8
Methane	103	7.144	0.144	14.8	0.275	39.6
Sulfur hexafluoride	180[c]	65.19	0.027[c]			

[a] NTP.

[b] 100°C, atmospheric pressure.

[c] 21.1°C.

Solving Eq. (1) for u allows us to calculate the carrier gas velocity above which the flow becomes turbulent, or the critical flow velocity:

$$u_c = 900 \frac{1}{r_0} \frac{\eta}{\rho} \tag{2}$$

Figure 1 shows the variations of the critical flow velocity with column diameter for several carrier gases. Carbon dioxide allows us to obtain turbulent flow with the smallest velocity and thus will be the most convenient to carry out experimental work in this field.

III. The Critical Value of the Column Inlet Pressure

To study the behavior of peaks eluted by a turbulent flow of carrier gas, we need to work with gas velocities at least several times larger than the critical flow rate, i.e., at Reynolds numbers larger than about 5000. Because of experimental problems, it is very important to know the relationship between pressure and flow rate.

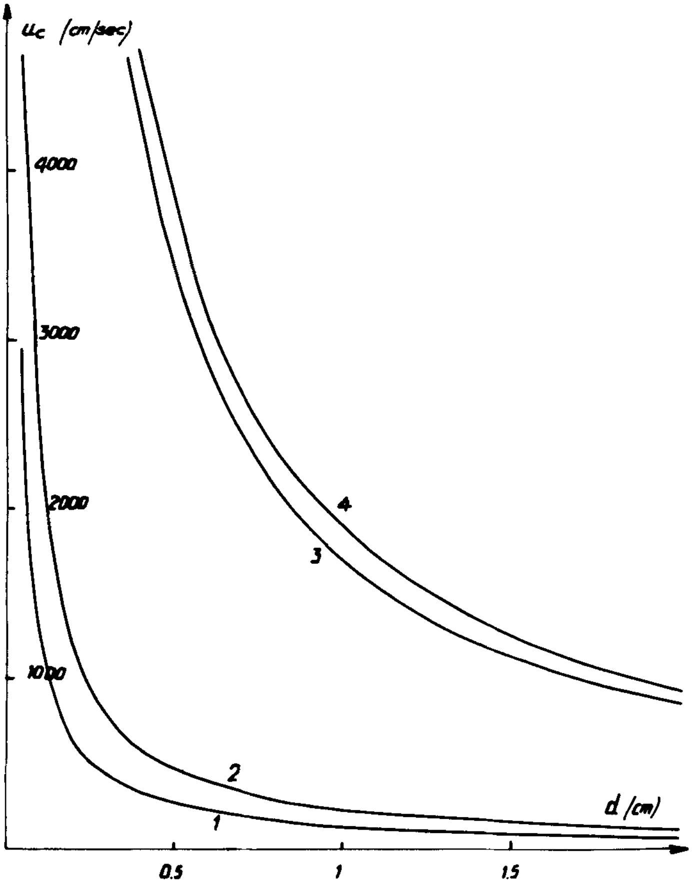

FIG. 1. Variation of the critical outlet velocity of the carrier gas with the column inner diameter (Eq. 2). Temperature, 0°C. 1: Carbon dioxide. 2: Nitrogen. 3: Hydrogen. 4: Helium.

In the laminar flow range the outlet carrier gas velocity for an open tube is given by Poiseuille's law:

$$u_s = \frac{r_0^2 p_s}{16\eta L}(P^2 - 1) \tag{3}$$

with $d = 2r_0$ and $P = p_e/p_s$. The critical value of the inlet to outlet pressure ratio is obtained by combining Eqs. (2) and (3) and solving for P:

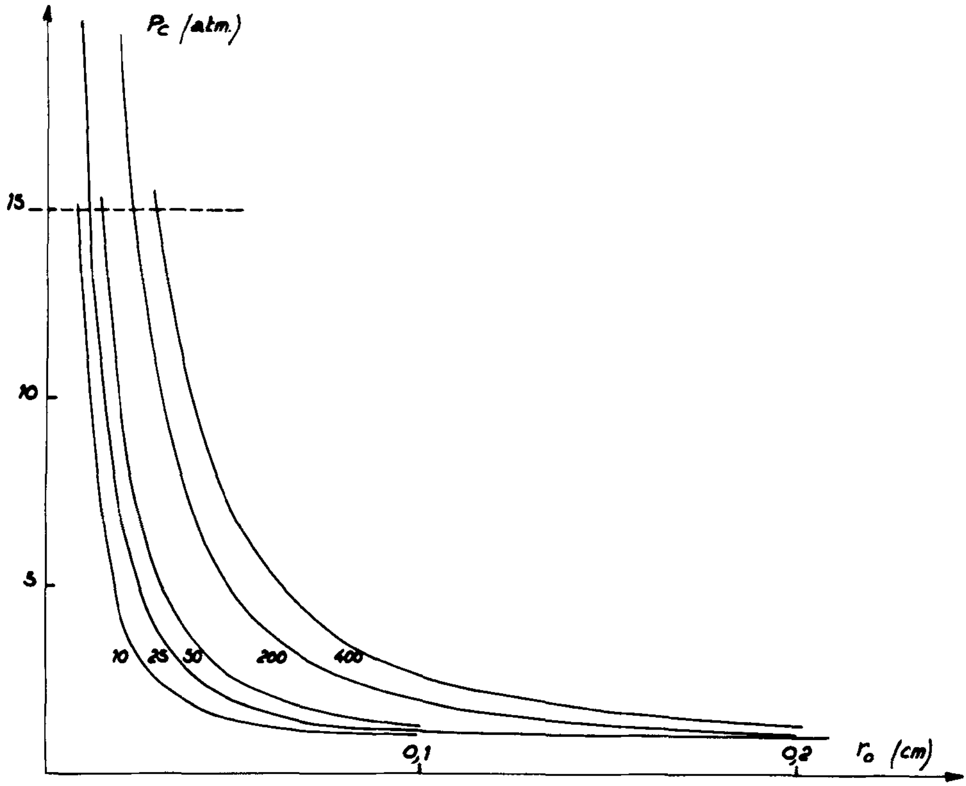

FIG. 2. Variation of the critical value of the inlet pressure with the column inner diameter. The number given for each curve is the corresponding value of $10^6 \times \eta^2/\rho$ (Eq. 4). Column length, 10 m.

$$P_c = \left[1 + \frac{14400\eta^2 L}{r_0^3 p_s \rho_s}\right]^{1/2} \tag{4}$$

If the outlet pressure is atmospheric, Eq. (4) also gives the critical value of the absolute inlet pressure in atmospheres, but p_s as well as the other parameters in Eq. (4), should be in related units (baryes in the cgs system). Figure 2 shows the variations of P_c with r_0 for several carrier gases in open tube columns 10 m in length.

A similar equation is obtained from Darcy's law (*6*):

$$P_c = \left[1 + \frac{3600\eta^2 L}{k d_p p_s \rho_s}\right]^{1/2} \tag{5}$$

Equation (5), however, is much more approximate than Eq. (4). Whereas Poiseuille's law is rigorous for straight tubes, Darcy's law is only an approximation valid at low flow rates (*6*). The inlet pressure necessary to obtain a given outlet velocity is larger at high velocity than indicated by the analog of Eq. (3) (for packed columns $u_s = kp_s/2\eta L(P^2 - 1)$. Consequently, the critical value of the inlet to outlet pressure ratio may be considerably larger than given by Eq. (5). This equation, however, shows that large inlet pressures are necessary to reach turbulent flow in packed columns. For example, for a 1-m long column packed with coarse particles between 0.315 and 0.40 mm and carbon dioxide as carrier gas at 0°C, Eq. (5) gives $P_c = 24$ atm. Most probably an inlet pressure of between 30 and 40 atm would be required. However, the efficiency to be expected from such a column is rather small, and any practical work would need longer columns and still higher pressures (*4*).

By contrast, Eq. (4) leads to moderate values of P_c, well in the range of most pressure regulators used in conventional gas chromatography. Thus, the use of turbulent flow is practically limited to open tube columns. Furthermore, Figs. 1 and 2 show that the carrier gas should be nitrogen, argon or better, carbon dioxide. The smaller the column diameter the better its efficiency, but the larger the critical inlet pressure. Thus the use of a carrier gas with a low kinematic viscosity permits the use of smaller diameter columns.

IV. The Flow Velocity in Turbulent Flow

The relationship between the outlet flow velocity, the inlet and outlet pressures, and the column parameters may be calculated for turbulent flow in much the same way as for laminar flow (*6*). Equilibrium in an infinitely thin column section is between the hydrostatic force and the shear stress exerted by the flow on the tube wall (*13*). The shear force is given by:

$$F = -AKf \tag{6}$$

whatever the flow type. Parameter A is the inner surface of the tube wall ($2\pi r_0\, dl$), K is the time-average kinetic energy of the unit volume of fluid ($\frac{1}{2}\rho\bar{u}_t^2$), and f the friction factor (*13*). Hence:

$$F = -\pi r_0 \rho \bar{u}_t^2 f\, dl \tag{7}$$

where $\bar{u}_t$ is the time-average flow velocity along the tube axis. In laminar flow the friction factor is shown to be equal to 16/Re (*13*). In turbulent flow this factor is strongly dependent on the wall roughness and varies only slightly with the Reynolds number. For very smooth tubes, f is given by Blasius' formula (*13*):

$$f = \frac{0.0791}{\mathrm{Re}^{1/4}} \tag{8}$$

if the Reynolds number is less than 10^5. If the tube wall is rough, the friction factor is larger and varies more slowly with Re. For example, if the ratio of the average height of wall protuberances to the tube diameter is 4×10^{-3}, the friction factor is proportional to $\mathrm{Re}^{-1/6}$. It is most probable that the open tubes currently in use in gas chromatography are still more rough (for 1 mm i.d. tubes this means irregularities of 4 μ for average height only). We may thus assume that in the range of flow velocities investigated in this work ($2 \times 10^3 < \mathrm{Re} < 10^4$) the friction factor is constant and equal to 0.12 (*13*).

The equilibrium between the shear stress and the hydrostatic pressure force in a column section of thickness dl and abscissa l is:

$$\pi r_0^2 d_p = -\pi r_0 \rho \bar{u}_t^2 f\, dl \tag{9}$$

If the carrier gas is ideal:

$$\rho = \frac{Mp}{RT} \quad \text{and} \quad \bar{u}_t = \frac{p_s u_s}{p} \tag{10}$$

combining Eqs. (9) and (10) gives:

$$p\, d_p = -\frac{M p_s^2 u_s^2}{RT r_0} f\, dl \tag{11}$$

Integrating Eq. (11) between column inlet and outlet and solving for u_s gives:

$$u_s = \sqrt{\frac{r_0 RT}{2fLM}(P^2 - 1)} \tag{12}$$

where u_s is the time-average, cross-section average carrier gas velocity.

In laminar flow where f is equal to 16/Re (*13*), Eq. (12) is equivalent to Eq. (3). For turbulent flow in rough tubes we have:

$$u_s = \sqrt{\frac{r_0 RT}{0.24LM}(P^2 - 1)} \tag{13}$$

V. The Retention Time in Turbulent Flow

As we have shown above, the turbulent flow is obtained only for relatively large values of the inlet pressure, so in Eq. (13) unity is small compared to P^2 and may be neglected. Under such conditions u_s is proportional to the inlet to outlet pressure ratio and not to its square as it is in laminar flow.

The derivation of the relationship between the time-average velocity and the outlet velocity (*14*) is independent of the nature of the flow. The only assumption made is that the carrier gas behaves ideally. Then:

$$\bar{u} = ju_s = \frac{3}{2}\frac{P^2 - 1}{P^3 - 1}u_s \simeq \frac{3}{2P}u_s \tag{14}$$

From Eq. (13) it follows that in turbulent flow:

$$\bar{u} = \sqrt{\frac{9r_0RT}{8fLM}} = 9310\sqrt{\frac{r_0T}{LM}}\ \text{cm/sec}^* \tag{15}$$

The time-average velocity is constant, *independent of the inlet pressure,* and depends only on the nature of the carrier gas (M) and the column radius and length. Consequently, the retention time is also independent of the inlet pressure:

$$t_R = \frac{L}{\bar{u}}(1 + k') = (1 + k')\sqrt{\frac{8fL^3M}{9r_0RT}} \tag{16}$$

This result is approximative and some slight variation of t_R with P may take place if one of the assumptions made in the derivation of Eq. (15) is not completely valid, i.e., if: (a) turbulent flow has not developed in practically all the tube section (there is always a layer of fluid in laminar motion along the tube wall); (b) the wall is not rough enough and f decreases slightly with increasing flow rate; (c) the carrier gas is not ideal [its compressibility increases with increasing average pressure whereas the partition coefficient k' decreases (*15*)]; and (d) the column is not a straight, open tube. Such a column would be difficult to use. If open tubular columns are coiled, the centrifugal force which acts on any elementary volume of fluid is perpendicular to the tube axis and can be equilibrated only by a shear force acting on the same direction. A secondary circulation should then take place, leading to two major effects (*12*): first, the critical Reynolds number would be larger and the transition region broadened; and second, for a given flow velocity, the pressure drop would be larger.

The effects of deviations from the first two assumptions are not important and will lead to only a slight variation of the retention time with inlet pressure. The first effect smoothes the retention time varia-

---

* r_0, L, and M in cgs units; T in °K.

tion when the flow velocity is increased above the critical one. The two effects of carrier gas nonideality are small even with carbon dioxide, as will be shown later. Furthermore, these two effects are in opposite direction and partially compensate for each other.

A secondary circulation does exist in any coiled tube (*8, 12, 16*) but its effect in turbulent flow is very difficult to account for and will be neglected here since the coil-to-tube diameter ratio of the column used is 700. It will make the carrier gas flow velocity increase more slowly with the inlet pressure than predicted by Eqs. (12) and (15), which could also be understood as either a decrease in column permeability or an increase in its apparent length. This could lead to an increase of the retention time with increasing inlet pressure.

This rather paradoxical effect of the practical independence of the retention time on the inlet pressure is easily explained. In turbulent flow when the inlet pressure is increased, an increasing fraction of the mechanical energy of the fluid is degraded into heat by the turbulence. The flow rate increases less than it would do in laminar flow. In the latter case, because of the compressibility of gases, the average flow velocity increases roughly in proportion to P whereas the outlet flow rate is proportional to $P^2 - 1$. In turbulent flow the compressibility of gases plays a similar role and the average flow velocity is constant whereas the average pressure and the mass flow rate increase only in proportion to P. With an incompressible fluid, as in liquid chromatography, the average velocity would be proportional to $\Delta p^{1/2}$.

VI. Mass Transfer in Turbulent Flow

Sir Geoffrey Taylor has studied a problem very similar to that of mass transfer of inert compounds in turbulent flow (*17*). A plate height equation may be derived from his results in much the same way as the Taylor-Golay equation for HETP of inert peaks in open tube columns may be calculated in laminar flow (*18, 19*).

The diffusion coefficient in turbulent flow is given by (*17*):

$$D = 10.06 r_0 v^* \qquad (17)$$

where v^* is the characteristic flow velocity defined by:

$$v^* = \sqrt{\frac{\tau_0}{\rho}}$$

τ_0 is the shear of the turbulent fluid on the unit surface of tube wall (*13*).

As shown above after Eq. (6):

$$\tau_0 = \tfrac{1}{2}\rho\bar{u}_t^2 f \tag{19}$$

Hence:

$$D = 10.06\sqrt{\frac{f}{2}}\, r_0\bar{u}_t \tag{20}$$

f in Eq. (21) may be taken as equal to 0.12, as shown above.

Taylor has also shown that the concentration profile obtained when an inert plug is injected in a turbulent flow is practically Gaussian after the zone traveled downstream about 100 column diameters. This is always the case in gas chromatography. Furthermore, the dispersion of this zone, which results from both axial diffusion and resistance to mass transfer in the radial direction, may be accounted for by assuming that only diffusion, with a virtual diffusion coefficient:

$$D^* = 10.1\sqrt{\frac{f}{2}}\, r_0\bar{u}_t = 2.47 r_0\bar{u}_t \tag{21}$$

is acting on this zone. The difference, 0.04, accounts for axial diffusion.

VII. Plate Height Equation

In conventional gas chromatographic terms, this means that the plate height for an inert peak is given by:

$$H = 4.94 r_0 \tag{22}$$

The plate height, as well as the retention time, is constant and independent of the carrier gas outlet flow rate. The reduced plate height (*4*) is constant and equal to 2.47. These two results are in agreement with the experimental results of Giddings et al. (*4*).

In laminar flow the plate height for an inert gas is given by the Taylor-Golay equation (*18, 19*):

$$H = \frac{2D_g}{u_s} + \frac{r_0^2}{24D_g}u_s \tag{23}$$

The first term is negligible at high flow velocities (if combined with Eq. 20, Eq. 23 yields Eq. 22). At the critical velocities (Eq. 2) if the flow is laminar:

$$H_c = \frac{r_0^2}{24D_g}u_c = \frac{75\eta}{2\rho D_g}r_0 \tag{24}$$

If the flow is turbulent $H_c = 4.94r_0$. Carbon dioxide has the smallest value of η/ρ:0.07. The corresponding value of D_g is about 0.1 (CH_4

in CO_2) and H_c (laminar) $= 26.5r_0$. With hydrogen, $H_c = 60r_0$. A very important decrease of H should be expected when the flow becomes turbulent, as was found by Giddings (*4*). This decrease, however, will not be abrupt. Because of the radial velocity profile, a layer where the flow is laminar exists along the tube wall. The thickness of this layer decreases with increasing flow rate; the HETP also decreases, progressively.

These results are valid only for inert peaks but may be extended to retained peaks, because Eq. (17) is valid in the gas phase, whether the peak is retained or not. The plate height equation may be written:

$$H = C_g r_0 + C_l \bar{u} \tag{25}$$

The pressure correction coefficient for the resistance to mass transfer in the liquid phase was derived by Giddings in a calculation which is independent of the type of flow but assumes only that the carrier gas is ideal (*20*). According to Eq. (25), H, C_g, and C_l depend on k', and it is not possible to use the functions derived by Golay (*19*) for them since the velocity profile is not the same in laminar and turbulent flow. Furthermore, the existence of a boundary layer, which can be only crossed by molecular diffusion, makes the problem still more complicated. Most probably, however, because these profiles have similar shapes, C_g will greatly increase with k' whereas C_l will reach a maximum for a k' value of 1 or a few units. If we take the usual value of C_l in conventional gas chromatography (typically 10^{-3} to 10^{-4} sec) and the value of $\bar{u}$ given by Eq. (15), the second term of Eq. (25) will be small compared to the first one. (For CO_2 carrier gas and a 10-m long, 1 mm i.d. column, $\bar{u} = 485$ cm/sec).

In theory these results are also valid only for straight tubes. Taylor (*17*) has observed that the widths of the bands eluted through water or crude pipes are larger than expected from his calculations. He suggested that this effect should be attributed to the curvature of pipes although this has not been clearly demonstrated and is not in agreement with more recent experimental work (*12*). A variation of H with the flow rate could also come from the same origin.

VIII. Optimization of Experimental Parameters

The number of theoretical plates necessary to achieve a given separation is given by Purnell's equation (*21*):

$$n = 16R^2 \left(\frac{\alpha}{\alpha - 1}\right)^2 \left(\frac{1 + k'}{k'}\right)^2 \tag{26}$$

The necessary column length is:

$$L = nH = 16R^2\left(\frac{\alpha}{\alpha - 1}\right)^2\left(\frac{1 + k'}{k'}\right)^2 \tag{27}$$

The analysis time is the retention time of the second solute of the pair on a column of length L.

Combination of Eq. (16) and (27) yields:

$$t_R = \frac{128}{3}R^3\left(\frac{\alpha}{\alpha - 1}\right)^3\frac{(1 + k')^4}{k'^3}\sqrt{\frac{2fMH^3}{9r_0RT}} \tag{28}$$

This equation is very similar to the one obtained in conventional gas chromatography (*22*). It shows that the analysis time increases in proportion to the cube of both the resolution of the two peaks and the inverse of $\alpha - 1$. By definition of the relative retention (*23*):

$$\alpha = \frac{t'_{R_2}}{t'_{R_1}} = \frac{k'_2}{k'_1} = \frac{K_2}{K_1} = e^{\Delta(\Delta G^\circ)/RT} \tag{29}$$

If α is near unity, as for difficult analysis:

$$\frac{\alpha - 1}{\alpha} \simeq \frac{\Delta(\Delta G^\circ)}{RT} \tag{30}$$

The retention time is accordingly inversely proportional to the cube of the difference in free enthalpy of vaporization of the two solutes from the stationary phase.

The column capacity factor should not be chosen larger than a few units, especially because H probably increases fast with increasing k'. Since H increases linearly with r_0, the column diameter should be chosen as small as possible. Finally, the nature of the carrier gas is difficult to choose because its influence on H is not known. The proportionality of t_R to the square root of the molecular weight of the carrier gas would not lead to a choice of heavy gases such as SF_6 or perfluorobutane, but it will favor light gases. Earlier results by Giddings (*4*) show, however, a strong dependence of H on the nature of the carrier gas, the HETP for pentane in helium being 3.5 times larger than in nitrogen at a Reynolds number of 6000.

EXPERIMENTAL SECTION

We used an apparatus built in this laboratory with conventional equipment for the experiments. Special care was taken to solve the problems which arise from the use of unusual flow rates and from the small retention times obtained.

I. Pneumatic System

The inlet pressure was controlled by a conventional flow controller (Dubé, Paris) to any value between 1 and 16 atm (absolute pressure). The fluctuations of the inlet pressure were about 1%. Their effects on the results discussed hereafter were negligible.

The carrier gas was carbon dioxide. The columns were 1 mm i.d. copper tubes between 10 and 100 m in length. The coil diameter was 70 cm. The experiments on inert peaks were made with empty tubes. Analyses were carried out on columns coated with a thin layer of squalane or of graphitized carbon black Sterling MT (Cabot).

Only gas samples were used, either pure methane or methane saturated in hydrocarbons vapors at various temperatures. They were injected with a sliding gas sampling valve actuated with compressed air (Microtek, Techmation, Paris). The sample size was 10 μl. The valve was leakproof for pressures less than 12 atm. The sampling time was a few hundreths of a second (*24*). An electrical switch actuated at the same time as the valve, permitted the injection time to be recorded.

II. Detector

Because of the very large flow rate and the small column efficiency, the performance of a concentration sensitive detector, such as the cross-section detector, is not satisfactory. We used a flame ionization detector which, as a mass-flow detector, gives a very good response. The detector itself was conventional. The burner tip had an i.d. of 0.8 mm, larger than usual. However, the carrier gas flow-rate of about 900 cm^3/min, which corresponds to a velocity of 20 m/sec, was much too large and would have blown out the flame. A coaxial splitter was used at the outlet of the column. A valve, downstream from the splitter on the main line, permitted us to adjust the splitting ratio.

III. Amplifier and Recorder

The amplifier was an Atlas DC 60 which is very sensitive and very fast. With a sensitivity of 10^{-13} A the response time is 10 msec. The chromatograms were recorded on a photographic UV recorder (Southern). The galvanometer used had a frequency response of 50 Hz and a sensitivity of 10 cm/mV.

IV. Behavior of Carbon Dioxide

In the pressure range investigated here, carbon dioxide is somewhat more compressible than an ideal gas. The experimental conditions were not very different from the critical conditions ($T_c = 304.2°K$, $P_c = 72.9$ atm). However, Martire (*25*) has shown that the effect of this compressibility on the retention times is negligible when the inlet pressure is smaller than 5 atm and remains small under 15 atm. Thus, it was not necessary to use the method derived by Cruickshank (*26*) for nonideal gases, and Eq. (14) was used throughout this work.

The carrier gas viscosity remains constant in the pressure and temperature ranges investigated. For example, the variation in viscosity at 0°C is less than a few per cent when the pressure increases from 1 to 15 atm (*27*).

The Reynolds number is proportional to the product $u \times \rho$, i.e., the mass flow rate, which is constant all along the column in steady-state flow. Hence, the Reynolds number is the same all along the column.

Thus the most important effect of the carrier gas nonideality is the variation of the partition coefficient with the average pressure. From results described by Desty, the decrease in the column capacity factor may be estimated to 2–3% for an increase of 1 atm in the average pressure of carbon dioxide (*5*).

EXPERIMENTAL RESULTS

We have determined the variations of the retention time of an inert peak and of the efficiency of the column in the velocity range corresponding to a Reynolds number between 1500 and 7000. The results observed at Reynolds number below 1500, in laminar flow, will be reported elsewhere.

The feasibility of some simple analysis has also been investigated.

I. Variation of the Flow Rate with the Inlet Pressure

Figure 3 shows the variations of the average flow velocity with the square of the inlet pressure. According to Eqs. (3), (4), and (15), $\bar{u}$ should be proportional to $(P^2 - 1)^2/P^3 - 1$ in laminar flow and constant in turbulent flow. The experimental results show a slight increase of the average flow velocity with the inlet pressure. The experimental values are between 20 and 45% larger than those predicted by theory. This can be accounted for either by the small curvature of the columns or by a progressive development of a fully turbulent flow. In any case,

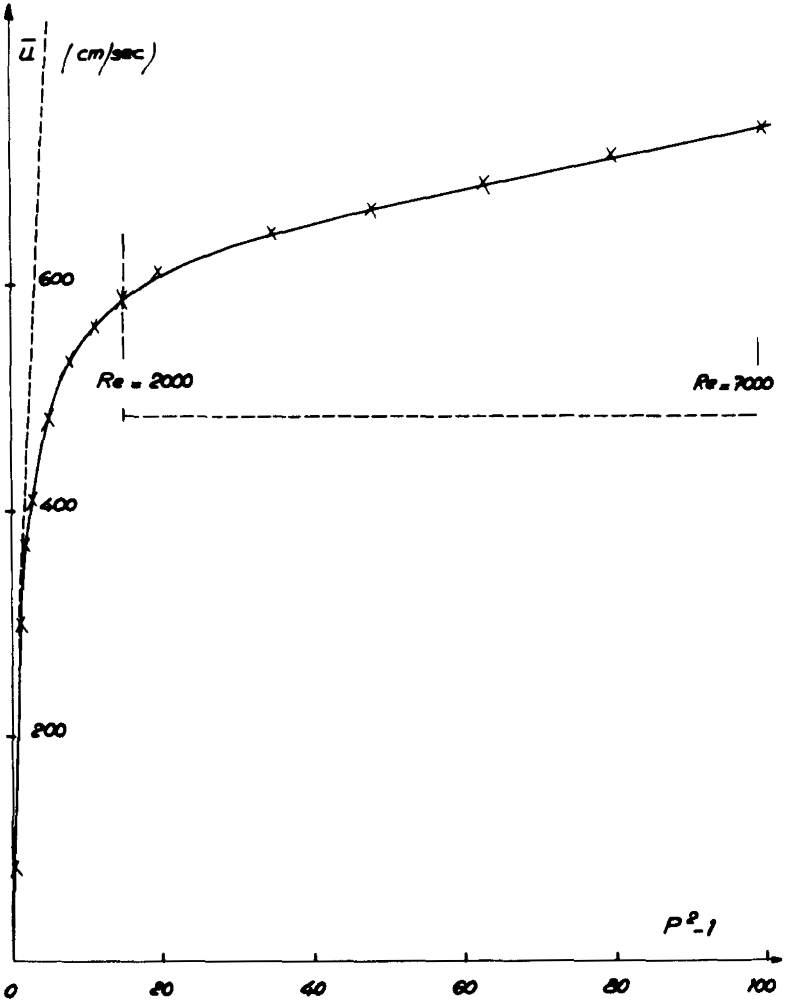

FIG. 3. Variation of the average carrier gas velocity $\bar{u}$ with the absolute inlet pressure (abscissa $P^2 - 1 = P_e^2 - 1$). Column length, 10 m; i.d., 1 mm. Carrier gas: carbon dioxide, 0°C. The dashed lines are theoretical lines derived from the Poiseuille equation for laminar flow in open tubes and from Eq. (15).

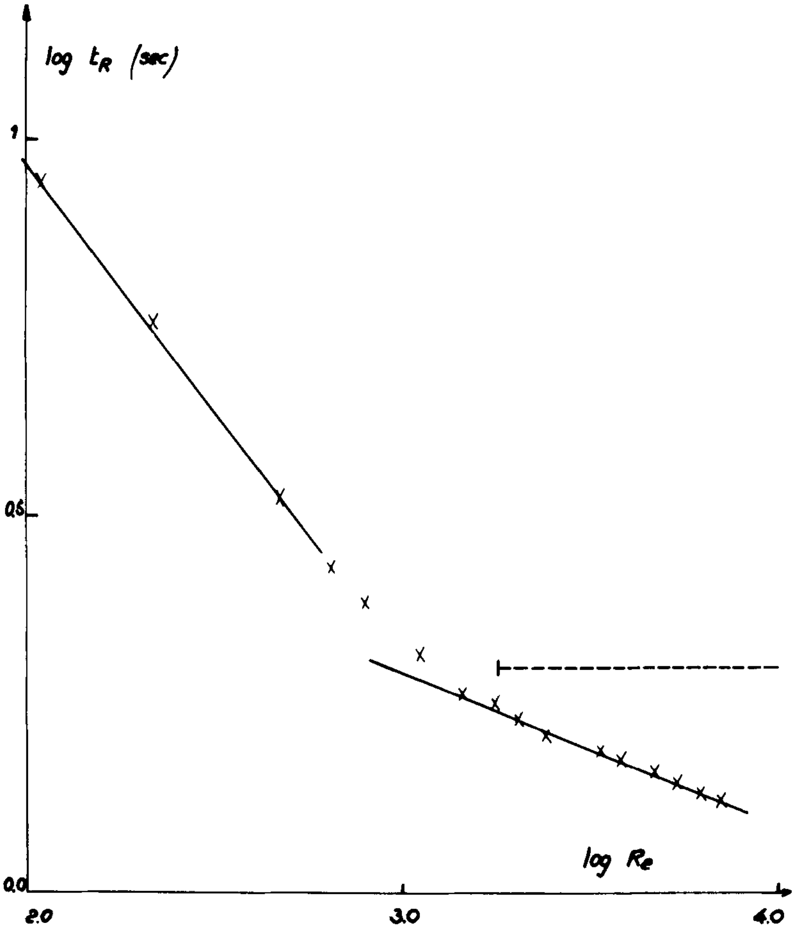

FIG. 4. Variation of the retention time of an inert compound with the Reynolds' number. Same column and conditions as for Fig. 3. The dashed line is derived from Eq. (16).

the variation in $\bar{u}$ is small, less than 20% for an increase in inlet pressure from 5 to 10 atm.

II. Variation of the Retention Time with the Inlet Pressure

Figure 4 shows the variation of the retention time of methane peaks with the Reynolds number. The retention time decreases slowly with increasing flow rate, but the variation is not important: the retention time is approximately proportional to $\mathrm{Re}^{-1/5}$. The value derived from Eq. 16 is 2.04 sec, i.e., only 1.5 time larger than the smallest value measured experimentally.

In spite of a residual variation of the average flow velocity and the retention time which is not negligible, there is substantial agreement between the experimental results and the theoretical predictions derived from approximative equations. The disagreement can most probably be accounted for by a slight dependence of the friction factor on the Reynolds number, i.e., a wall roughness smaller than expected.

Of special importance is the fact that, once the turbulent flow is fully developed in the open-tube column, there is no reason to increase the inlet pressure since no appreciable gain in retention time will result.

III. Variation of the Efficiency with the Flow Velocity

Figure 5 shows the variation of HETP for methane peaks with the Reynolds number. When the turbulent flow occurs in the column the HETP decreases rapidly, then more smoothly, and reaches an apparent limit which is approximately equal to $6r_0$ (3 mm). This value is in excellent agreement with the theoretical prediction which results from Eqs. (17) and (22). This agreement is remarkable in view of the approximation made in deriving these equations and of the less satisfactory agreement observed for retention times.

These results are also in agreement with those obtained by Giddings (*4*) who used experimental conditions which are quite different from ours. With small diameter columns, high pressure drops, and helium as carrier gas, he observed that the efficiency for methane is constant in turbulent flow. From his published data, this constant plate height is about $10r_0$. This difference from our results and with theory might well come from the fact that a layer of alumina coated on the wall of an open-tube column might give some retention of methane at 0°C. We shall show later that the efficiency falls sharply with increasing retention.

IV. Analytical Results

Figures 6 and 7 show the analysis of a mixture of *n*-pentane, *n*-hexane, and *n*-heptane on two different columns, both with a turbulent flow of carbon dioxide. Columns characteristics and performances are summarized on Table 2.

The first analysis was made using a conventional open-tube column

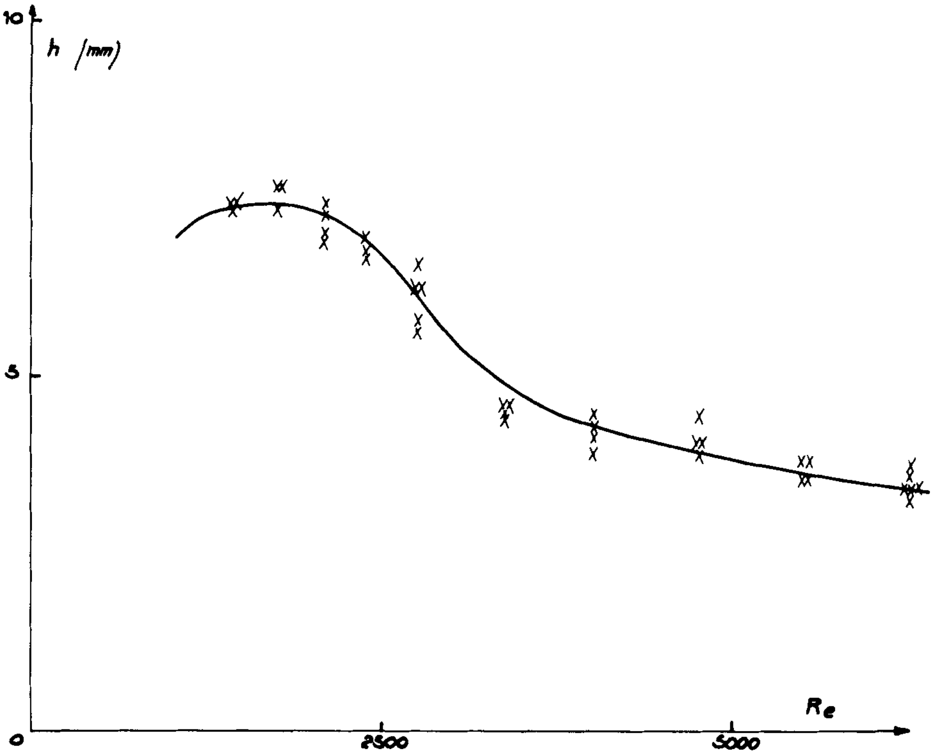

FIG. 5. Variation of HETP with the Reynolds' number for an inert compound. Same column and conditions as for Fig. 3 ($u_0 = 700$ cm/sec corresponds to Re of 1000).

TABLE 2

Performance of Two Capillary Columns in Turbulent Flow

	Figure 6			Figure 7		
	n-C_5	n-C_6	n-C_7	n-C_5	n-C_6	n-C_7
k'	0.64	1.21	2.3	0.12	0.31	0.80
n	240	235	90	2980	1230	325
N	36	70	42	58	70	66
N/t_R	29	42	17	19	20	13
R	1.16	1.16		1.7	1.84	
$R/t_R^{1/2}$	0.97	0.45		1.12	1.08	

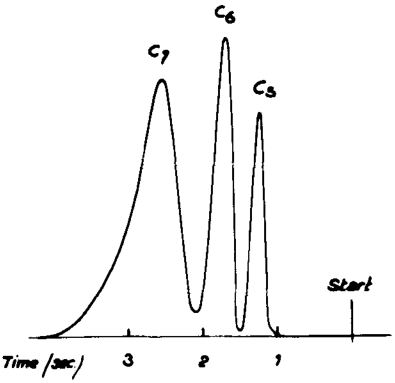

FIG. 6. Analysis of a mixture of *n*-pentane (C_5). *n*-hexane (C_6), and *n*-heptane (C_7). Column length, 10 m; i.d., 1 mm. Liquid phase, squalane. Temperature, 30°C. $P_e = 4.6$ atm (absolute). $R_e = 6300$. Carrier gas: CO_2.

coated with a thin layer of squalane (average film thickness 0.6 μ). Although the column capacity factor is about 1.2 for *n*-hexane, the peaks are relatively large, much larger than for methane. The efficiency decreases steadily with increasing k'. The ratio of the resolution of two successive *n*-alkanes to the cubic root of retention time (*22*) is 0.97 for pentane–hexane and 0.45 for hexane–heptane. This is well within the range of performances obtained with good, conventional open-tube columns.

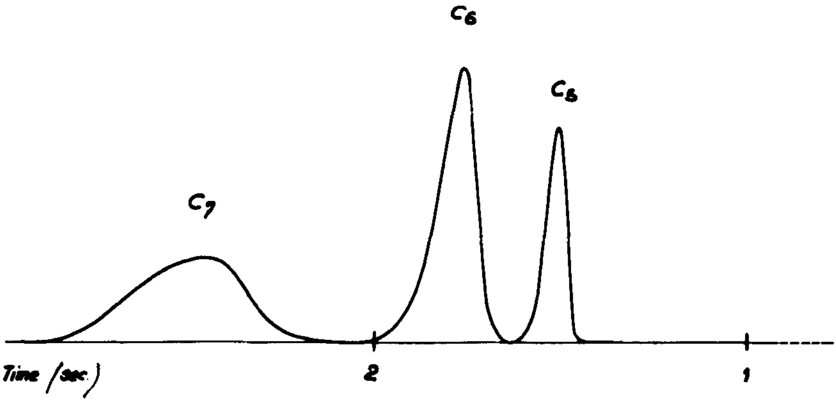

FIG. 7. Analysis of the same mixture as in Fig. 7. Column length, 10 m; i.d., 1 mm, thin layer of graphitized carbon black Sterling MT. Temperature, 100°C. $P_e = 5.1$ atm. Carrier gas, CO_2.

Because the contribution of the resistance to mass transfer in the stationary phase to the overall HETP could be important, we also made some analyses using open-tube columns, the wall of which were coated with a porous layer of graphitized carbon black (PLOT columns) (*28*). The kinetics of desorption of alkanes is very fast and, accordingly, the corresponding term in the plate height equation should be negligible. In spite of this improvement the peak width was quite large and the performances were not appreciably better. The ratio of the resolution of two successive *n*-alkanes to the cubic root of retention time (*22*) was 1.12 for pentane–hexane and 1.08 for hexane–heptane. The efficiency was better but the larger resolution was partly a result of the larger relative retention of *n*-alkanes on carbon black (2.6 instead of 2). These results are also in agreement with those reported by Giddings (*4*).

CONCLUSION

Although these results are extremely interesting from a theoretical point of view their practical value is limited. Because the performances in analytical applications are not much better than those obtained under conventional experimental conditions, it does not seem worthwhile to undertake the solution of the many technological problems associated with the use of high inlet pressure and very large flow rates.

In order to obtain the number of theoretical plates necessary to solve the many analytical problems, it would be necessary to use very long columns, narrower than those used in this work. This would mean that the inlet pressure should be between 150 and 200 atm, such as Giddings used (*4*), and the analysis times will not be much shorter than those obtained under more conventional conditions.

Gas chromatography, however, is a very useful tool to solve many problems. It will be of special interest to study problems in connection with turbulent flow and mass transfer in turbulent flow.

Acknowledgment

This work was done under grant NATO No. SA. 5-2-05 B (244).

REFERENCES

1. J. C. Giddings and R. A. Robison, *Anal. Chem.*, **34**, 885 (1962).
2. J. C. Sternberg and R. E. Poulson, *Anal. Chem.*, **36**, 1492 (1964).
3. V. Pretorius and T. W. Smuts, *Anal. Chem.*, **38**, 274 (1966).
4. J. C. Giddings, W. A. Manwaring, and M. M. Myers, *Science*, **154**, 346 (1966).
5. J. H. Knox, *Anal. Chem.*, **38**, 253 (1966).

6. G. Guiochon, *Chromatogr. Rev.*, **8**, 1 (1967).

7. J. C. Giddings, *Dynamics of Chromatography,* Dekker, New York, 1964, Chap. 8.

8. I. Halasz and P. Walkling, *Ber. Bunsenges. Phys. Chem.*, **74**, 66 (1970).

9. J. E. From and F. H. Harlow, *Phys. Fluids*, **6**, 975 (1963).

10. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena,* Wiley, London, 1960, Chap. 5.

11. K. E. B. Anderson, *Trans. Roy. Inst. Technol. Stockholm,* 1963, p. 201.

12. J. A. Koutsky and R. J. Adler, *Can. J. Chem. Eng.*, **42**, 239 (1964).

13. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena,* Wiley, London, 1960, Chap. 6.

14. A. T. James and A. J. P. Martin, *Biochem. J.*, **50**, 679 (1952).

15. D. H. Desty, A. Goldup, G. R. Luckhurst, and W. T. Swanton, in *Gas Chromatography 1962* (M. Van Swaay, ed.), Butterworths, London, 1962, p. 67.

16. W. R. Dean, *Phil. Mag.*, **4**, 208 (1927).

17. Sir Geoffrey Taylor, *Proc. Roy. Soc.*, **A223**, 446 (1954).

18. Sir Geoffrey Taylor, *Proc. Roy. Soc.*, **A219**, 186 (1953).

19. M. J. E. Golay, in *Gas Chromatography 1958* (D. H. Desty, ed.), Butterworths, London, 1958, p. 35.

20. J. C. Giddings, S. L. Seager, L. R. Stucki, and S. H. Stewart, *Anal. Chem.* **32**, 867 (1960).

21. J. H. Purnell, *J. Chem. Soc.*, **1960**, 1268.

22. G. Guiochon, in *Advances in Chromatography* (J. C. Giddings and R. A. Keller, eds.), Dekker, New York, 1969, p. 179.

23. B. Karger, *Anal. Chem.*, **39**(8), 24A (1967).

24. G. Guiochon and G. Preau, *J. Gas Chromatogr.*, **4**, 343 (1966).

25. D. E. Martire, *Anal. Chem.*, **37**, 144 (1965).

26. A. J. B. Cruickshank, B. W. Ganey, and C. L. Young, in *Gas Chromatography, 1968* (C. L. A. Harboun, ed.), The Institute of Petroleum, London, 1969, p. 76.

27. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena,* Wiley, London, 1960, p. 17.

28. I. Halasz, K. Hartman, and E. Heine, in *Gas Chromatography, 1964* (A. Goldup, ed.), The Institute of Petroleum, London, 1965, p. 38.

Received by editor December 4, 1969