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Ultra-High-Pressure Gas Chromatography in Micro Columns to 2000 Atmospheres*

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Summary

A gas-chromatographic system working at inlet pressures to 2000 atm has been constructed. Data acquired on micro columns packed with 13-μ adsorptive particles are described. Results, although rather erratic at present, show efficiencies as high as 4000 plates/ft, or roughly 40,000 plates for a 3-m column. In addition, equilibrium migration rates show a strong dependence on pressure, with variations up to the fourfold level. The relationship of the present work to previous work; the experimental system; and the role of gas nonidealities are all discussed.

Gas and liquid chromatography are tools having many experimental dimensions—temperature, pressure, physical size, nature of stationary and mobile phases, and others. One of the least-explored dimensions—a dimension for which we can conceive enormous range and influence—is pressure.

Normal operating pressures in chromatography are the order of 1 atm. From there we can go down a slight degree toward zero, or up essentially without limit. It is the uncharted upper pressure region that forms the basis for the present study. We wish to enquire if the enormous forces involved can be used, as theory suggests, to control column efficiency and speed, and to shift equilibrium (perhaps surprisingly) as much as temperature or polarity have previously done.

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To carry out the present initial phase of this study, we have constructed a gas-chromatography (GC) apparatus operating to pressures (inlet) of 2000 atm (about 30,000 psi). Our work at various pressures up to this level has provided a glimpse of the potential of this ignored dimension. Not only is an analytical potential apparent, but the type of apparatus used may provide a unique tool for studying some of the hard-to-measure equilbriums and transport properties of very dense gases.

Experimental difficulties, although not prohibitive, are partially responsible for the slow beginning of this field. However, the exploration of high inlet pressures in GC—with the outlet ordinarily of 1 atm—has mainly been discouraged by one of the cardinal but now outdated rules of good GC technique. High inlet-to-outlet pressure ratios have been almost universally shunned because of the belief that the nonconstant flow rate caused by high compressibility would take the column too far from optimum over too much of its length. Detailed theory emphatically disagrees (*1*). With this encouragement—and the promise of other advantages —experimental work was started in 1964. We have already seen a hint of possible advantages. A record 4000 plates/ft (1000 plates/ft is considered to be very good) and speeds in excess of 5000 plates/sec (to be detailed later as an aspect of turbulent-flow GC) have been realized. The surface has barely been scratched as far as optimization goes. It is now clear that the longstanding rule against using large pressure drops has neither a theoretical nor a practical basis.

The potential value of high-pressure (20 to 200 atm) and ultra-high-pressure (>200 atm, above normal tank pressures) GC has been adequately outlined elsewhere (2–5). This paper describes the first experimental results for the ultra-high-pressure case. Some of the specific properties of ultra-high-pressure systems and the problems and characteristics associated with experimental procedures are discussed. Specifically, we wish to report the details regarding operation of a GC system at pressures to 2000 atm. The previous maximum operating pressure, also reported from this laboratory (5), was 170 atm.

A pressure of 1000 or 2000 is not, of course, an ultra-high pressure by the standards of normal research on static, condensed chemical systems. One can easily go much higher if, as usual, one has a nonflow, nongaseous system, without the necessity for the strict requirements of sample injection into the stream, and finally detection of that sample. However, without these simplifications a few thousand atmospheres is presently rather extreme.

With the current pressure level, the high-inlet-pressure micro-column (HIPMC) system, reported earlier, has its equivalent in the ultra-high-inlet-pressure micro-column (UHIPMC) system. The use of micro columns, in which both tube and particle diameter have been reduced by roughly one order of magnitude below normal values, shows many practical and theoretical advantages (*6*).

RELEVANT PROPERTIES OF THE HIGH-PRESSURE GASES USED

Working at gas pressures to 2000 atm quite naturally makes it necessary to consider gas nonideality and its effect on GC performance. Gas nonideality, of course, has advantages and disadvantages. The favorable induction or enhancement of migration through the solution forces that exist in high-pressure carrier gases is related to nonideality. Unfavorable effects are the increases in viscosity and decreases in diffusivity with increasing pressure. In practice one can select a gas for which the respective advantages of ideality and nonideality are balanced to optimize the separation.

For a given high pressure, the degree of nonideality depends most strongly on the reduced temperature, $T_r = T/T_c$, of the carrier gas. Critical temperatures of common carrier gases range from −268°C for helium to 31°C for CO_2. At 25°C, T_r values for the most important carriers are: He, 60; H_2, 9.0; N_2, 2.3; A, 2.0; CO_2, 0.98. The properties of the most ideal of these—He—do not depart greatly from ideality, as can be seen from Table 1. The other two gases used here, N_2 and A, show larger deviations. The effect of nonideality would, of course, be measurable for He at our experimental pressures, but it would cause no gross changes in chromatographic characteristics. Furthermore, unlike N_2 and A, He pressure has little effect on chromatographic migration. This will be demonstrated later.

In a given experimental run the local column pressure varies all the way from 1 atm to the inlet pressure—near 2000 atm in some cases. Thus a single pressure (with its associated level of nonideality) does not characterize the gas in the column. However, the column's observable parameters—notably retention time and plate height—can be formulated in terms of averages (*5,14*). The

TABLE 1

Departures from Ideality of Gases Used in this Study at 1000 and 2000 Atm Pressure and 25°C[a]

	He		N_2		A	
	1000	2000	1000	2000	1000	2000
$z = pV/\mathscr{R}T$	1.4[b]		2.1[b]	3.1[c]	1.8[b]	2.7[b]
η/η_0	1.15[d]	1.3[d,e]	3.2[f]	4.0[d,e]	3.4[g]	4.0[d,e]
$D_g/D_{g(\text{ideal})}$	0.68[e,h]		0.53[e,h]	0.46[e,h]	0.55[e,h]	0.49[e,h]
$j/j_{(\text{ideal})}$			1.85[i]	2.74[i]	1.56[i]	2.38[i]

[a] Compressibility factor, viscosity, diffusivity, and James-Martin correction factor are relative to ideal-gas case.

[b] From Hamrin and Thodos (*8*).

[c] From Byrne and Thodos (*7*).

[d] From a generalized table in Ross and Brown (*9*).

[e] Considerable uncertainty in values.

[f] From Michels and Gibson (*11*).

[g] From Michels et al. (*10*).

[h] Calculated from Enskög equation (*12*).

[i] From Schettler and Giddings (*13*).

exact evaluation of the integrals involved is hindered by numerical complexity and the lack of knowledge concerning the pressure dependence of diffusivities, migration rates, and even viscosities and compressibilities (*13*). Thus although no fundamental problems exist, little progress has yet been made relating chromatographic performance to the unique properties of high-pressure gases.

One of the most useful averages in GC is described by the James-Martin factor j. This may be generally defined as $j = \bar{\nu}/\nu_0$, the ratio of the peak's mean migration velocity over its outlet velocity (just prior to elution). By considering the compressibility of an ideal gas, James and Martin derived an expression that reduces to $j = 3p_0/2p_i$ when the outlet pressure p_0 is small compared to the inlet pressure p_i. At high pressure, the j factor is modified by nonideal departures in the compressibility factor ($pV/\mathscr{R}T$), viscosity, and migration rate. These departures have been accounted for generally (*13*); in addition, specific calculations have been made for N_2, H_2 and A; using experimental compressibility and viscosity data but ignoring the as yet little-understood variations in migration rate. These calculated departures are indicated in Table 1 in terms of $j/j_{(\text{ideal})}$.

The theory of James and Martin, which provides ideal j values,

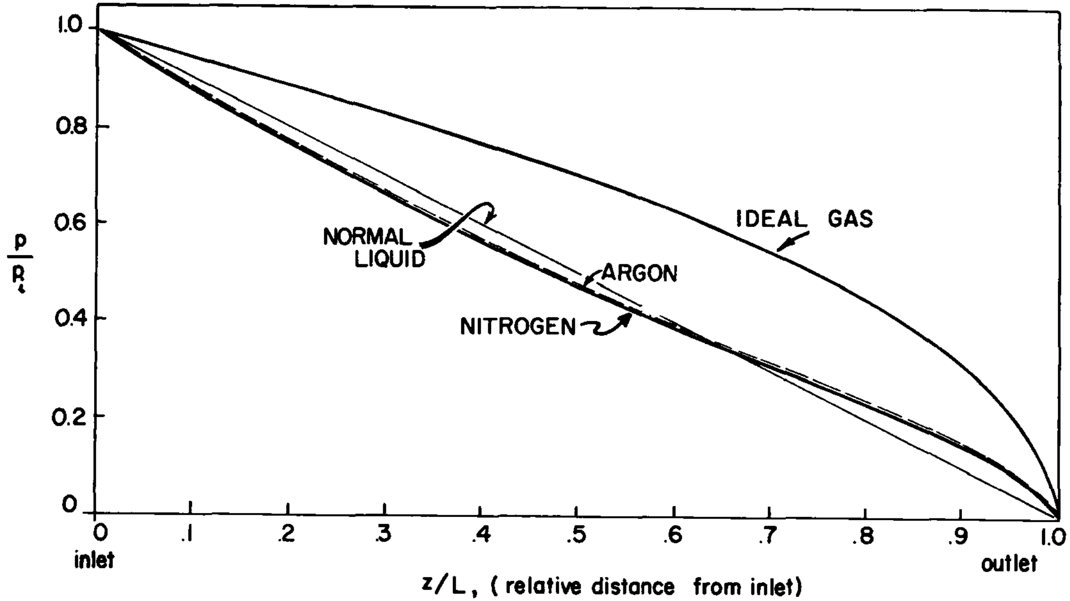

FIG. 1. Calculated pressure profiles (relative to the inlet value) for an inlet pressure of 1960 atm and an outlet pressure of 1 atm. The linear "normal" liquid profile assumes an incompressible isoviscous fluid. Temperature assumed for N_2 and A, 25°C.

also leads to ideal pressure profiles for the column. The pressure-distance plots are characteristically concave down, as shown in Fig. 1. The profiles for nonideal gases can be calculated for comparison using the general equation (1), where z is the distance from the

$$1-\frac{z}{L}=\int_{p_o}^{p}\frac{p\,dp}{\eta(pv)}\Big/\int_{p_o}^{p_i}\frac{p\,dp}{\eta(pv)} \tag{1}$$

column inlet and L is column length. Integral evaluation for N_2 and A were obtained from the previous work. The resulting profiles at $p_i = 1960$ atm and $p_o = 1$ atm are also shown in Fig. 1. These two profiles depart considerably from the ideal-gas case; in fact they approach the linear profile characteristic of normal liquids much more closely than they do the ideal-gas profiles. (At these pressures the liquid profile would also be distorted, owing to finite compressibility and changes in viscosity.) As these gases compress an enormous amount in reaching 2000 atm, the explanation for the liquid-like profile clearly involves factors in addition to compressibility. Viscosity is the other element involved in Eq. (1); its role is intuitively clear. As shown in Table 1, viscosity increases with pressure. Thus the higher viscosity near the inlet requires an unusually high pressure gradient to maintain flow. The profile consequently dips below its normal value a short distance down from the inlet (compressibility departures also contribute to this dip by causing a relative increase in velocity and thus in pressure gradient). Near the outlet the profile again assumes its general ideal-gas form (concave down) but starts from a lower point, owing to the original rapid pressure drop.

Of final interest relative to dense-gas properties, it is found that densities approach those of liquids, thus suggesting that intermolecular forces may play an important role in GC performance. For instance, N_2 at 2000 atm and 25°C has a density of 0.73 g/cm^3, which is 91% of the liquid density, 0.808 g/cm^3. At 1000 atm the density is still 69% of the liquid value. Argon's density is 1.2 and 0.93 g/cm^3 at 2000 and 1000 atm, respectively, or 85% and 66% of the liquid's density. The corresponding value for He at 1000 atm is 0.11 g/cm^3, or 76% of liquid density.

EXPERIMENTAL

The experimental system is shown schematically in Fig. 2. The high-pressure compressor is a two-stage air-operated dia-

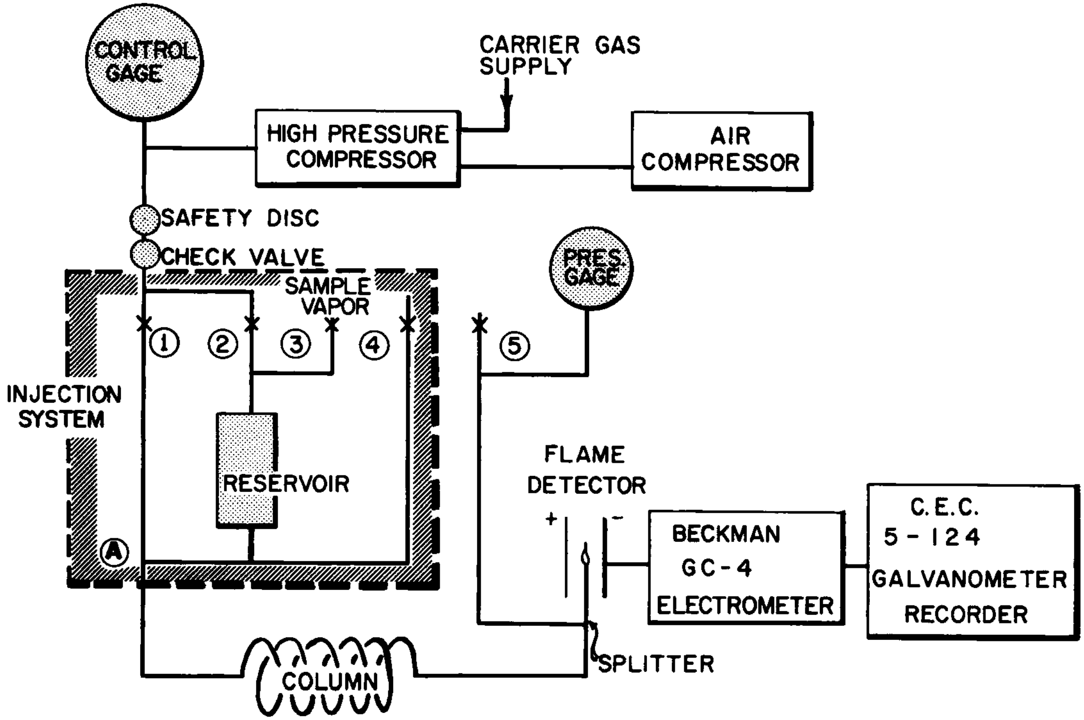

FIG. 2. Schematic illustration of experimental system.

phram-type device (AMINCO No. 46-14021), capable of operating to 30,000 psi. This is driven by air (45 SCFM at 100 psi) from a conventional air compressor. The electrically operated control gauge was used to maintain the desired pressure at the inlet to the column.

The injection system was constructed with the aid of capillary tubing and commercial fittings supplied by High Pressure Equipment Co. (Erie, Pa.). Tee "A" was modified by filling the internal volume with closely machined capillary tubing to eliminate dead space. The sample was introduced into the reservoir at atmospheric pressure by closing valves 1 and 2 and opening valves 3 and 4, thus flushing sample gas through the reservoir. Valves 3 and 4 were then closed, valve 1 opened, and the pressure in the system raised to the desired value. The sample peak was introduced into the column by closing valve 1 momentarily, thus leading to a small, negative, pressure peak at tee "A" and a short injection "surge" from the reservoir. When larger samples were desired, valve 2 was opened for the same short period that valve 1 was closed.

Valve 5 controlled the proportion of the total gas flow that went through the detector.

A safety shield of ¼-in. steel enclosed the high-pressure compressor, the column, and the auxiliary equipment such as the injection system.

The flame-ionization detector, constructed in this laboratory, was connected to a Beckman GC-4 electrometer. A CEC 5-124 galvanometer recorder with a time constant of less than 1 msec was used.

The columns were constructed from ⅛-in. O.D. and 0.020-in. (0.51-mm) I.D. stainless-steel capillary of the type used in the injection system. These were packed with 13-μ particles of neutral WOELM alumina (Alupharm Chemicals, New Orleans, La.) coated with 30 wt % of sodium iodide by Scott's method (*15*). The sizing and packing procedures were essentially as described in a previous report (*6*).

RESULTS AND DISCUSSION

Experimental results were obtained in the pressure range from 250 to 2000 atm. Although the particular columns employed tended toward optimum efficiency at a pressure below 250 atm, this lower pressure range was outside the scope of the present work. It was not deemed necessary to study this range, because some of the most interesting characteristics of a column reveal themselves at velocities above optimum and because the efficiencies are still outstanding.

Three columns were constructed and tried. Two of these were 3 m in length and the other was a 9-m column assembled from 3-m segments. One of the shorter columns demonstrated clear superiority and was thus studied more thoroughly than the others. Our discussion of experimental results will be limited to this column, except as otherwise noted.

The difference between columns can probably be ascribed to variations in packing. The filling of a micro column with sorbent is still very much an empirical procedure which can, no doubt, be improved greatly. It is likely that our best column is still far from optimum with respect to performance characteristics.

The primary object of this study was the evaluation of column characteristics as revealed by the elution properties of single peaks. However, to demonstrate that no fundamental barriers to separation exist at such pressures, a refinery gas mixture was applied to the worst of the short columns at an inlet pressure of 28,000 psi. Propane, isobutane, *n*-butane, and butylene peaks were resolved from the mixture. The propane peak appeared first, at 33 sec; the butylene last, at 65 sec. Resolution was good except for a partial overlap of the last two peaks. As this was the least efficient of our columns (about 3000 plates at best), much better resolving power could be expected in general.

Preliminary column efficiency studies were made using methane peaks. Methane is practically inert as a solute, and its elution characteristics thus reflect the intrinsic merit of the column as a physical-geometrical unit.

Figure 3 shows plate height-pressure curves to 1250 atm inlet for methane in the three carrier gases He, N_2, and A. For comparison, the shaded area represents the performance of good conventional columns; its lower limit (at 0.03 cm, about 1000 plates/ft) represents the best one can normally expect from conventional columns. The micro column studied here compares well, having plate heights as much as three times lower than the above-mentioned limit. This corresponds roughly to 3000 plates/ft. As mentioned earlier, it appears that optimum efficiency (minimum plate

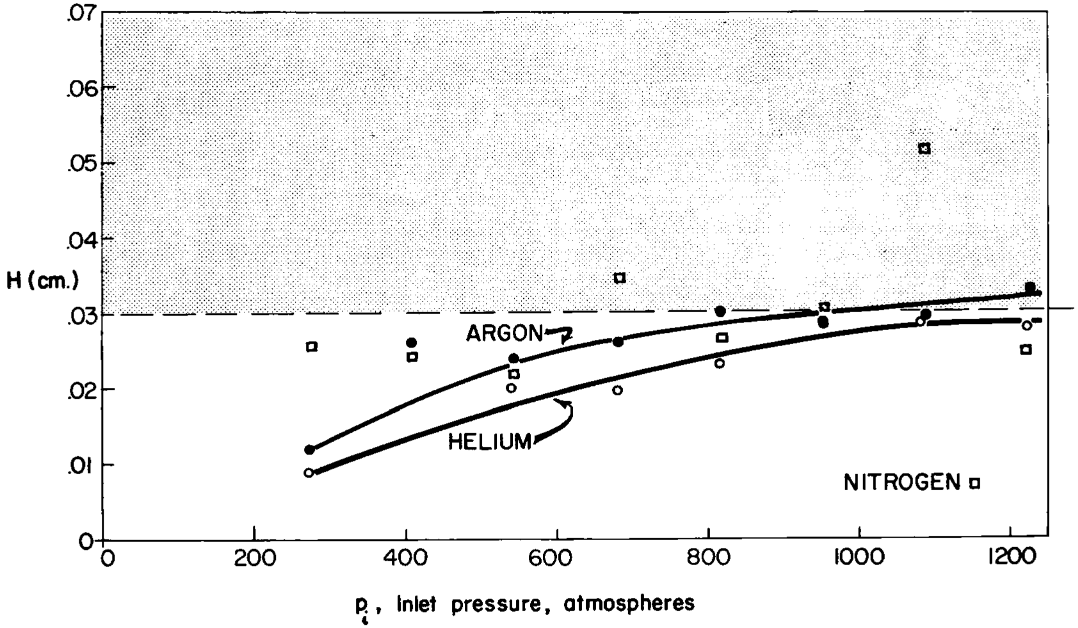

FIG. 3. Plate height-pressure plots for methane in He, N_2, and A at 25°C. Shaded area is efficiency range of good conventional columns.

height) might occur at an even lower pressure. Aside from the low plate heights, these curves also show the concave "downness" or leveling off characteristic of runs at high pressure and high reduced velocity (*16*). This characteristic, owing to coupling or its combination with turbulence, has promising implications for high-speed GC.

Figure 4 shows the corresponding plots for propane, a solute that is retained to a measurable degree by adsorption. (The relative retention parameter R for propane, found by comparison with methane elution times, varied from 0.15 to 0.8.) Column efficiency ranges from good (shaded area) to outstanding. The lowest plate height recorded—0.007 cm or over 4000 plates/ft—is the best so far reported for a GC system. However, it again appears that better values could be obtained at inlet pressures below 250 atm.

Although high-pressure GC phenomena are not perfectly understood, it nonetheless appeared that some of the curves in Fig. 4 showed unusual characteristics. To check this, a second run was made with N_2 over an even broader pressure range. The two curves are indeed quite different, as shown in the figure. The only reasonable explanation is that the injection system or splitter was not working perfectly, thus widening each peak beyond its actual value. If we accept this hypothesis, the "true" plate-height curve for the column would lie at or below the minimum of measured values. As nearly all conceivable distorting mechanisms serve to broaden GC peaks further, this conclusion is quite general (5). Our effort to verify it beyond question was terminated by the accidental loss of packing from the column.

Figures 3 and 4 well illustrate the empirical efficiency of the present UHIPMC system under various conditions. However, they convey little understanding of intrinsic column efficiency. For one thing, inlet pressure, although natural as an independent variable in these plots, is not commonly used. For another, the plots show absolute rather than relative or reduced quantities. A valid alternative is the use of a reduced plot (reduced plate height versus reduced flow velocity), which provides a universal framework for comparing columns (5). We define reduced plate height h as H/d_p, plate height divided by particle diameter. Correspondingly, reduced velocity is defined by $\nu = d_p v/D_g$, particle diameter times gas velocity over diffusivity. The reduced velocity, although constant throughout an ideal-gas column despite gas expansion,

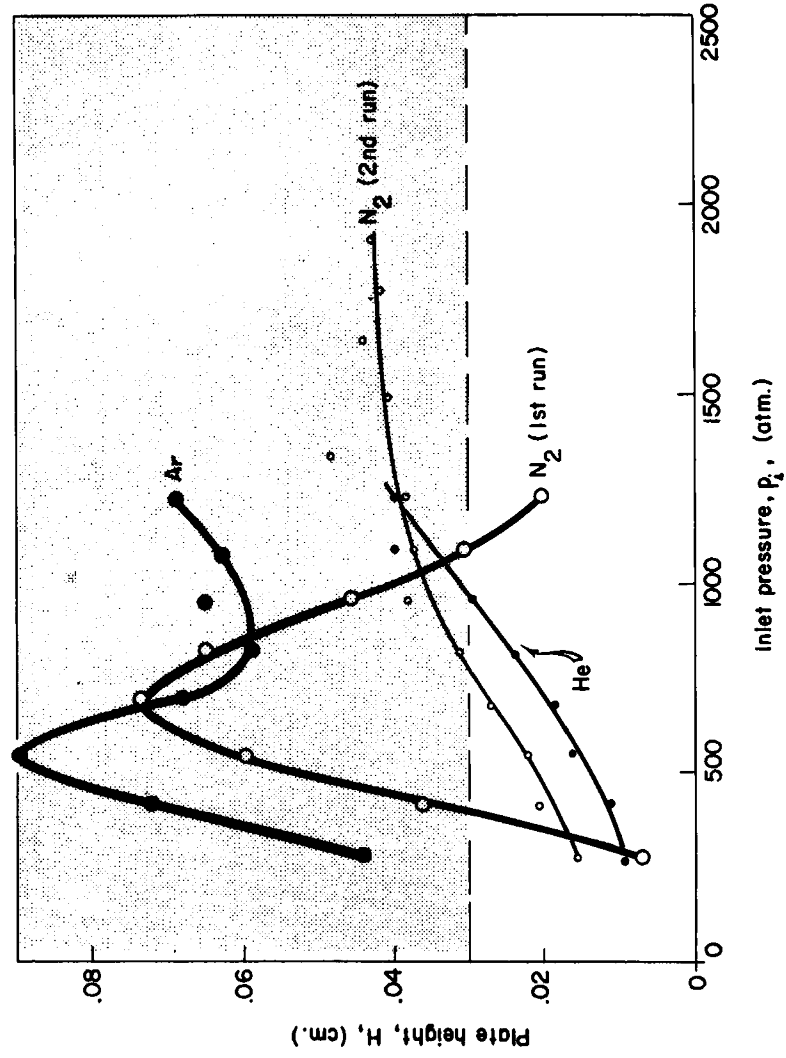

FIG. 4. Plate height-pressure plots for propane in He, N_2, and A at 25°C.

varies somewhat within the present columns. We have therefore used ν_0, the value of ν at the outlet. Mean ν values would be several times higher.

Figure 5 shows several smoothed plots of h versus ν_0. The 9-m column (upper curve), with h in the range 100 to 200, is clearly

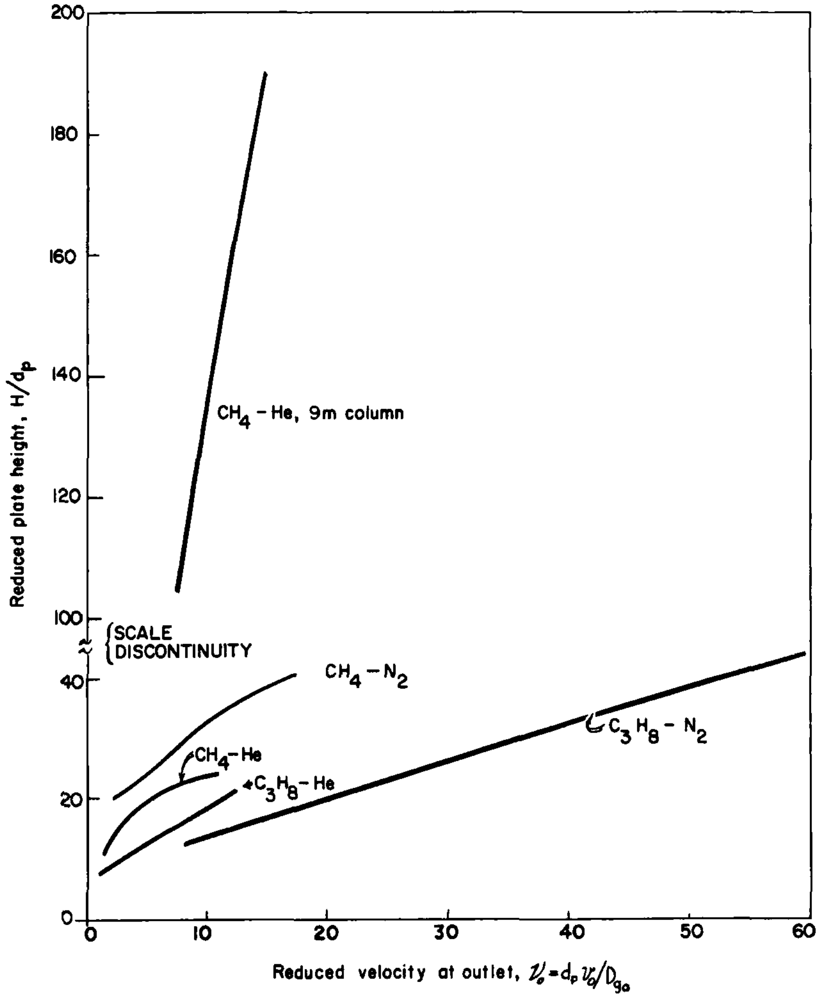

FIG. 5. Reduced plate height versus reduced velocity at the outlet for various solute-gas systems. The upper curve was obtained from the long 9-m column, the other from the regular 3-m column.

unsatisfactory. The most efficient of the 3-m columns (lower four curves) has h values ranging from 8 to 45, although for the best C_3H_8-N_2 curve (not shown here), a minimum h of 5 was reached. These values 5 to 45 vary from average to poor by normal GC standards. At best, we should like to see $h \sim 2$ and, at worst, $h \sim 10$. Admittedly, we have not reached a minimum plate height for the column, an extension that might improve the assessment somewhat. It is likely, however, with the inherent uncertainties and scant experience in packing micro columns that efficiency can be improved several-fold as optimum packing techniques are learned. This conclusion is supported by the high variability in the columns used in this work. It is also possible that the equipment is adding to the measured plate height. This possibility was mentioned earlier and is further supported by the fact that the curves for methane in Fig. 5 lie above those for propane. Normally, we expect the opposite (although the trend is not necessarily a big one). Instrumental perturbations, however, are likely to cause a reversal because the rapidly eluted methane peaks are more easily distorted than those that are slowed by a finite retention.

It was suggested earlier that high pressures might be useful in shifting equilibrium migration rates in GC. The possible magnitude of the effect is indicated in Fig. 6. Here the R value (solute velocity/gas velocity) for propane is plotted as a function of inlet pressure for each of the three carrier gases. There is clearly a strong pressure shift in equilibrium when A and N_2 are used as carriers. Migration rate increases rapidly at several hundred atmospheres and then appears to level off. (The same trend is found with the "inferior" 3-m column as shown by the top curve.) At low pressures these curves would be expected to join that for He; in this case they provide a total fourfold variation in migration rate. By contrast, the He curve remains quite flat with pressure, indicating the relative inertness of He even at high pressures. The pressure-dependence of retention in N_2 and A may be due to "solution" effects in these dense gases, or to competition for adsorptive sites (the leveling off could be due to monolayer formation of the gases). A theoretical treatment of such effects has been given by Locke (*17*).

The strong influence of pressure on migration rate demonstrates the potential for using controlled pressure changes to enhance separation. This potential exists for both gas and liquid forms of chromatography, as shown in a recent article (*18*).

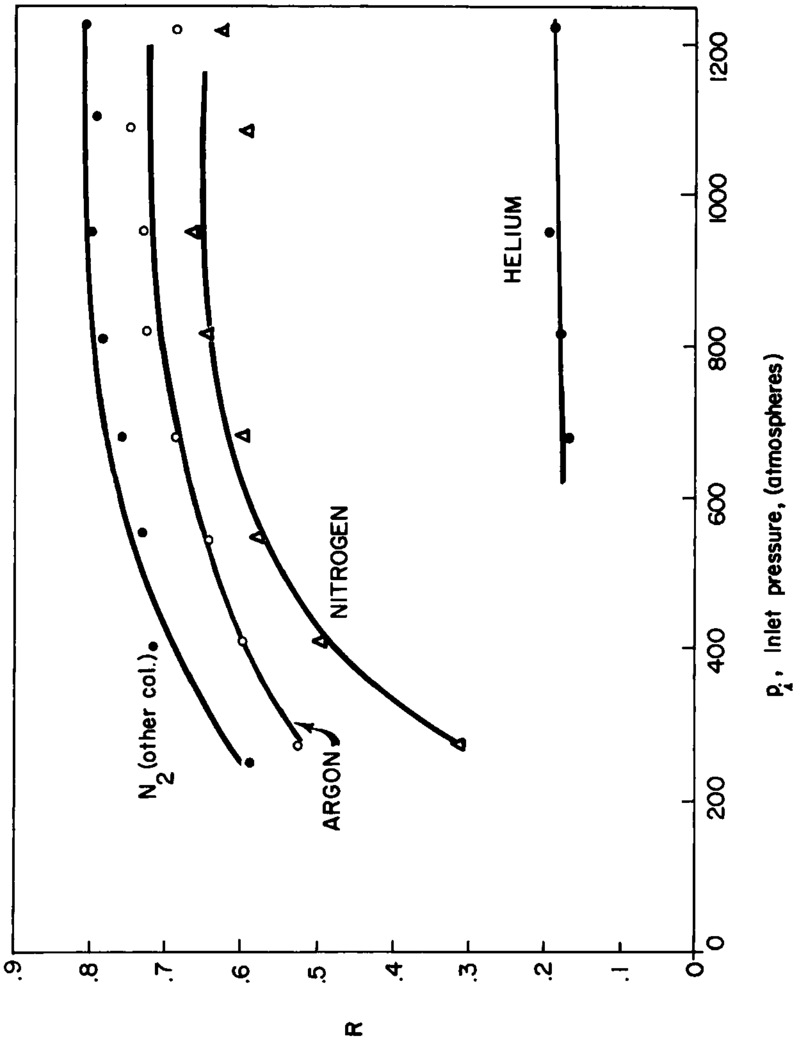

FIG. 6. Dependence of relative migration rate R on pressure. Propane solute at 25°C.

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