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## HIGH-PRESSURE GAS CHROMATOGRAPHY

### I. A PRECISION HIGH-PRESSURE GAS CHROMATOGRAPH FOR ISOBARIC-ISOTHERMAL MEASUREMENTS

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#### SUMMARY

High-pressure gas chromatography can be an important tool for the investigation of the thermodynamic and transport properties of fluids. This series of reports will be devoted to the investigation of a number of hydrocarbon mixtures by means of a new high-pressure gas chromatograph which avoids the difficulties of previous apparatus.

This paper describes the construction of the high-pressure gas chromatograph. The precision of the column pressure was improved by about two orders of magnitude as compared with earlier investigations. Preliminary experiments were carried out on solutes in nitrogen gas at 50°C in the range 1–400 atm. Under these conditions, the experiments cover the whole density region of so-called dilute gas, medium dense gas and dense gas, reaching beyond the critical density of the mobile gas phase.

For the first high-pressure experiments, the solutes were propane, *n*-pentane, *n*-heptane and *n*-nonane. In a later paper, the retention volumes will be discussed in terms of a single equation of state over the whole range of gas densities.

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#### INTRODUCTION

It was recognised at an early stage that high-pressure gas chromatography would offer a new and important tool for studying the behaviour of dense media. For example, it was expected to lead to methods for obtaining data on the equation of state and on the process of diffusion and to a better understanding of intermolecular interactions.

The pressure dependence of gas chromatographic retention was investigated by Sie and co-workers<sup>1,2</sup>, Giddings and co-workers<sup>3,4</sup>, Cruickshank and co-workers<sup>5–7</sup>, Everett and Stoddart<sup>8,9</sup>, Wičar and co-workers<sup>10–12</sup>, Schneider<sup>13</sup> and others. A drawback of the early investigations was that, owing to practical difficulties, there was a large pressure drop over the column. The adverse effect of the pressure drop is most severe at the low end of the pressure range in the reported experiments. The ratio of column inlet pressure to column outlet pressure, *viz.* the ratio  $p_i/p_0$ , reached

the large values:  $p_i/p_0 = 1.5/1$  (Sie *et al.*<sup>1</sup>),  $p_i/p_0 = 2/1$  (Cruickshank *et al.*<sup>5</sup>), and even the extreme value  $p_i/p_0 = 2000/1$  (Schettler *et al.*<sup>4</sup>). Consequently, there was a large uncertainty as to the effective gas pressure in the column. This caused the more subtle pressure effects of the gas chromatographic behaviour to be washed out and, thus, to remain undetected. Thus, Cruickshank *et al.*<sup>7</sup> reported that their results contradicted those of Sie *et al.*<sup>1</sup>. Wičar and co-workers<sup>10-12</sup> reduced the pressure drop over their column to a few tenths of an atmosphere in the pressure range 10–100 atm. Their more accurate results do not support the theoretical approach of Cruickshank *et al.*<sup>6</sup>.

It is clear that in order to obtain more accurate results that can be used for an interpretation by means of statistical thermodynamics, it is necessary to keep the gas close to a predetermined density at all points in the column. Moreover, the precision in the predetermined gas pressure should be improved by at least two orders of magnitude compared with earlier investigations. The present paper is devoted to the description of an isobaric-isothermal high-pressure gas chromatograph, in which the pressure drop over the column is 0.01 atm or less for the pressure range 1–3000 atm, and in which the temperature can be kept constant to within 0.01°C over the range from –200°C to +200°C.

## ISOBARIC-ISOTHERMAL GAS CHROMATOGRAPH

### *General lay-out*

The high-pressure gas chromatograph for isobaric-isothermal precision measurements is shown schematically in Fig. 1. It consists of the following components.

For the high-pressure gas supply system a DP-controlled gas compressor connected to a buffer volume (Fig. 1, 1–12) is used. The pressure range was from 25 to 3000 atm, with a ripple bandwidth of 0.002 atm and a drift stability of 0.0001 atm. In the lower pressure range (1–200 atm), commercial reducing valve pressure regulators are available.

A crucial part of the system is the high-pressure sample injector (Fig. 1, 13–15 and Fig. 2). It can be set to inject sample sizes from 1  $\mu\text{g}$  to 1 g, accurate to within 2%, and it is capable of repeated injections also to within 2%.

The isobaric-isothermal high-pressure gas chromatographic column is housed in a cryostat-thermostat (Fig. 1, 16–18). It is a packed column constructed of a thick-walled copper or stainless-steel tube. The pressure drop between column inlet and column outlet is kept to less than 0.01 atm. The temperature range is from –200°C to +200°C, the ripple bandwidth 0.05°C, and the temperature drift stability 0.01°C.

In the high-pressure gas expansion valve (Fig. 1, 19), the upstream gas pressure, in the range 1–3000 atm, is reduced to a downstream pressure of 1 atm. The gas flow-rate is adjusted by setting this precision valve in the range 0.01–50  $\text{cm}^3/\text{min}$  (NTP), measured at the column outlet. The flow stability is 0.2–1%, and depends on the precision of room temperature (0.02°C) and on the stability of atmospheric pressure.

The hydrogen flame ionisation detector (Fig. 1, 20) is a Carle Model 9000 (Fullerton, CA, U.S.A.). Hydrogen and air (or oxygen) for the flame are supplied by means of two-stage precision pressure regulators (1–4 atm).

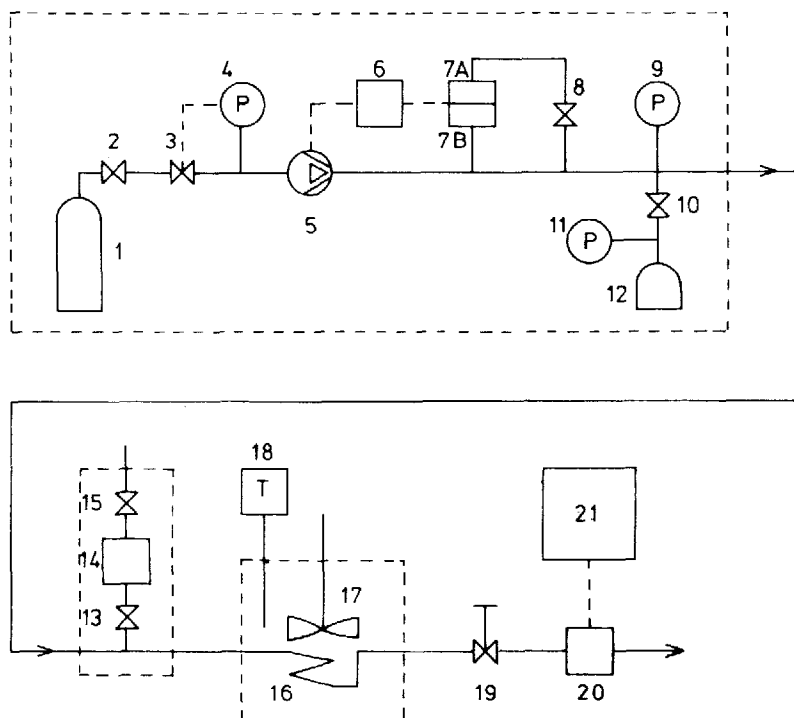


Fig. 1. High-pressure gas chromatograph; 1 12 = high-pressure gas supply; 13 14 = high-pressure sample injector; 16 18 = GC column in cryostat-thermostat. 1 = Gas flask; 2 = stop valve; 3 = pressure regulator, 200 atm; 4 = low-pressure gauge; 5 = gas compressor, 3000 atm; 6 = pulse timer; 7 = differential manometer, 7A upper cavity, 29.5 cm<sup>3</sup>, 7B lower cavity, 0.6 cm<sup>3</sup>; 8 = stop valve; 9 = high-pressure gauge; 10 = stop valve; 11 = high-pressure gauge; 12 = gas buffer volume, 600 cm<sup>3</sup>; 13 = precision miniature valve, injector; 14 = sample chamber, injector; 15 = miniature valve, injector; 16 = GC column; 17 = gas propellor; 18 = temperature controller; 19 = precision miniature valve, high-pressure expansion valve, 3000 → 1 atm; 20 = hydrogen flame ionisation detector; 21 = chart recorder.

The chart recorder (Fig. 1, 21) is a Goertz Electro, Servogor Type RE 511, with a sensitivity of 1 mV full scale (potentiometric), a response time of 1 sec full scale, and a chart speed range of 0.5–600 mm/min.

The workroom is temperature controlled (ripple 0.2°C, drift stability 0.02°C). A detailed description of the various components is given below.

### Components

*High-pressure gas supply system.* The gas compressor is a standard type, air driven, Novaswiss diaphragm-type compressor, for 3000 atm (Nova Werke, Switzerland).

The experimental gas volume capacities for gas chromatography are smaller than the nominal capacities by one to three orders of magnitude. Intermittent operation of the compressor is required in order to reduce its volume capacity. During intermittent operation, however, a difficulty occurs with the reversing valve which stops now and then at some intermediate position where the air drive is incapable of restarting. This practical problem was solved as follows: a small air leak to atmos-

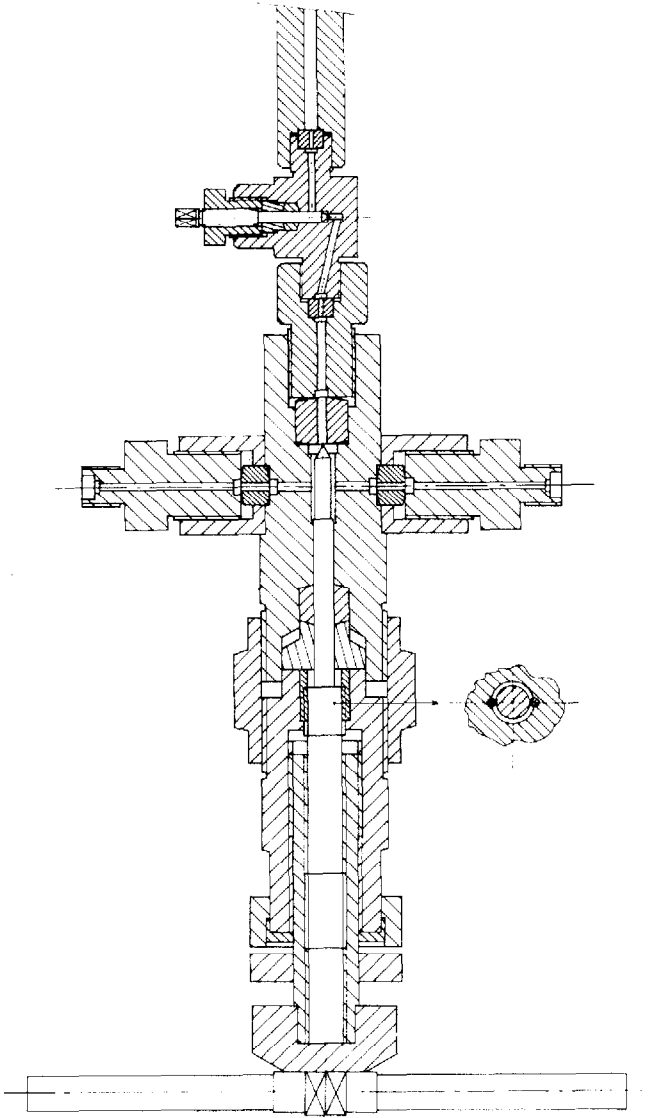


Fig. 2. High-pressure sample injector.

phre was introduced at the plug on one side of the reversing valve. With a suitable combination of air leak and air pressure, the gas compressor becomes self-starting.

In the original compressor, oil leaked from the oil-drive system, passing the gasket ring and the NTH ring (parts No. 42 and 28 of the pneumatic operator No. 552.0018) into the air-drive system, causing this to choke during operation. The gasket ring and NTH ring were therefore replaced by a more effective system: a single Quad-ring No. 4126. This Quad-ring requires a tolerance of only  $2 \times 0.10$  mm between the drive and the housing (parts No. 1 and 9 of pneumatic operator No. 552.0018) instead of the original tolerance of  $2 \times 0.25$  mm. Consequently, a new

drive was made in our workshop with a diameter of 39.80 mm instead of the 39.50 mm of the original factory-supplied drive. At slow driving speeds of *ca.* 1 cycle per sec, and at intermittent operation, it was not necessary to spray oil into the air inlet. This would only have increased the risk of choking the air-drive system. The pressurised air feeding the pneumatic operator is taken directly from the pressure regulator; it does not pass through the lubricator. However, the lubricator oil reservoir is kept connected to the high-pressure air mains of 6 atm, in order to ensure correct oil circulation in the oil-drive system.

A pulse timer controls on-time (0.3–3 sec) and wait-time (5–50 sec), each time cycle with a precision of 1%. Wait-time is the sum of on- and off-time. On- and off-time of the gas compressor are synchronous with the on- and off-time of the pulse timer. However, the pulse timer can be overruled by the differential manometer if the discharge gas pressure exceeds the set value. The gas compressor is then turned off, irrespective of the state of the pulse timer. In the event of line voltage failure, the pulse timer is off. This safety measure prevents the discharge pressure exceeding a safe pressure limit.

The differential manometer is a differential pressure cell, Cat. No. 2417.6, Ruska, Houston, TX, U.S.A. The upper cavity has a volume of 29.5 cm<sup>3</sup>, the lower cavity 0.6 cm<sup>3</sup>. The upper cavity is used as reference pressure gas reservoir and is fed through valve 8 (Fig. 1). The reference pressure is under the valve seat. All-metal connectors and tubings are used in the reference pressure system. Permanent connections are silver soldered.

*High-pressure sample injector.* The small-volume high-pressure sample injector was constructed from two standard miniature high-pressure valves. A sample chamber volume of 20 mm<sup>3</sup> was realised between the seats of the top and bottom valves (15 and 13 in Fig. 1). In valve 13, a combination of M 10 × 1 on the stem and M 18 × 1.5 on the housing resulted in 0.5 mm effective lead of the non-revolving stem for a full turn of the spindle (Fig. 2).

For precision experiments, the sample sizes should be two to four orders of magnitude smaller than the chamber volume of the sample injector. A special technique was adopted to inject such samples down to the microgram range. The sample was prepared as follows. The mixture of hydrocarbons was placed into the sample chamber. Through the top valve 15, the sample chamber was connected to a high-pressure nitrogen gas supply, *i.e.*, 200 atm for experiments in the pressure range 1–150 atm, or 500 atm for the pressure range 150–400 atm. Nitrogen gas was allowed to dissolve in the liquid sample for a few minutes and, subsequently, the top valve was closed. The resulting mixture of nitrogen and hydrocarbon leads to a greater compressibility. A few dozen injections can be made before it becomes necessary to repeat the nitrogen treatment.

A sample is injected directly into the mobile phase by turning the spindle of the bottom valve 13 over *ca.* 90°. The left turn of the spindle for opening the valve, as well as the right turn of the spindle for closing the valve, are limited by a mechanical device (this limiting device is not shown in Fig. 2). The two limit positions, for obtaining a certain sample size, are precisely determined, and then fixed for the repeat injections. Sample sizes of consecutive injections are reproducible to within 2%. The opening and closing positions of the injector may have to be altered slightly after a change of column pressure.

In cases where extremely large samples were needed, a second sample chamber of volume 2 cm<sup>3</sup> was placed in series with the first one of volume 20 mm<sup>3</sup>.

*Isobaric-isothermal high-pressure gas chromatographic column.* The column (Fig. 1, 16) consists of a 0.50 m × 3.0 mm I.D. (8.0 mm O.D.) copper coiled tube. Cone-shaped female connectors, stainless-steel 316, are silver soldered at both ends of the tube. The tube is filled with silicone oil DC 200 (5:95) on Chromosorb PDMCS (100-120 mesh) according to well-known procedures<sup>14</sup>. Column efficiency varies between 15 and 500 theoretical plates in the range 1-400 atm, depending on the nitrogen density. (For experiments at higher pressures, to 3000 atm, a stainless-steel tube column will be used in future.)

Stainless-steel 316 capillary tubing 1 mm I.D., 3 mm O.D. is used to connect the column inlet to the sample injector, and the column outlet to the high-pressure gas expansion valve.

The column packing has a fragile mechanical structure that could be destroyed by large pressure gradients. It is important to avoid abrupt changes of gas pressure during all stages of the experiment. Gas compression and gas decompression are done very slowly.

A practical isobaric column requires that the pressure difference,  $\Delta P$ , between the column inlet and the column outlet is vanishingly small compared with the column gas pressure. According to the method of Chilton and Colburn<sup>15</sup> this is given by eqn. 1.

$$\Delta P = \frac{1700 l}{d_p^2} \cdot u\mu \quad (1)$$

where  $l$  is the length of the column packed bed;  $d_p$  is the diameter of particles composing the bed;  $u$  is the mean flow velocity of fluid; and  $\mu$  is the viscosity of fluid. In our experiments, a small flow velocity of mobile gas phase is chosen, such that  $\Delta P$  is less than 0.01 atm according to eqn. 1.

The temperature in the cryostat-thermostat was kept constant by the following means, depending on the temperature range:

-200 to -60°C, constant cooling baths, e.g., liquid nitrogen at -195.8°C. The precise temperature depends on atmospheric pressure, i.e. 0.0113°C/mTorr for liquid nitrogen.

-60 to 0°C, gas cryostat with propeller; gas is cooled by introducing liquid nitrogen into cryostat, temperature ripple bandwidth 0.2°C, drift stability 0.1°C.

0°C to +40°C, gas cryostat with propeller; gas is cooled by introducing cold nitrogen gas from Dewar. Ripple bandwidth 0.05°C, drift stability 0.01°C.

+40 to +200°C, air thermostat; air is heated by electric heating wires. Ripple bandwidth 0.05°C, drift stability 0.01°C.

*High-pressure gas expansion valve.* The high-pressure expansion valve 19 (Fig. 1) is, essentially, of the same construction as valve 13 (Fig. 1), which is used in the sample injector (Fig. 2). In valve 19, a combination of M10 × 1 on the stem and 3/4 in.-24 UNF on the housing results in 0.058 mm effective lead of the non-revolving stem for a full turn of the spindle.

The realisation of a practical isobaric GC column requires an extremely small and stable gas flow-rate in the presence of a large pressure gradient between stem

and seat of expansion valve 19. A pressure drop of 0.01 atm between inlet and outlet of the column, p.e., corresponds to a flow capacity of only 25 mm<sup>3</sup>/min nitrogen gas at 50°C and 400 atm. A special procedure is adopted in order to obtain such flow-rates. Firstly, a seat is formed *in situ* by forcing the stem down on it until there is no detectable gas flow. By carefully reducing the mechanical tension between stem and seat, a small initial gas leak is then allowed, which is slightly greater than the required gas flow-rate. Finally, the spindle is turned down until the required flow-rate is reached. The gas flow-rate is allowed to stabilise overnight before a GC measurement is made. A newly formed seat may require several days before a stable flow-rate is obtained.

The gas flow-rate is very sensitive to the temperature of the expansion valve. If room temperature cannot be accurately controlled, the expansion valve 19 should be placed in a thermostat.

## EXPERIMENTAL

To test the high-pressure gas chromatograph at working conditions, a mixture of four non-polar solutes, propane, *n*-pentane, *n*-heptane and *n*-nonane was injected into the column, with nitrogen as carrier gas, and silicone oil DC 200 as non-polar stationary liquid phase. Sample sizes were in the range of 1 µg. The preliminary experiments were done at 50°C and at gas pressures in the range 1–400 atm. Under these conditions, the experiments cover the whole density range, from the dilute gas to the medium dense gas and the dense gas, at densities exceeding the critical gas density of the mobile gas phase.

The gas flow-rate is chosen such that  $\Delta P$  is less than 0.01 atm. The retention times ranged from 10 min to 15 h. The column efficiency varied with the nitrogen gas pressure, in the range from 15 to 500 theoretical plates.

The retention volumes measured at the column outlet are converted into retention volumes on-column conditions of pressure and temperature, by the use of *PVT* data of the mobile gas phase, i.e., the *PVT* data of nitrogen<sup>16</sup>. For this conversion, it is thus assumed that the liquid phase does not dissolve in the gas phase, and that the extremely small concentrations of solute would have a vanishingly small effect on the *PVT* data of the mobile gas medium. The GC retention volumes are measured as the expectations of the GC solute peaks.

Since this paper is primarily devoted to the construction of the precision apparatus, the derivation of the equation of state for describing the GC experiments, and a detailed discussion of the experimental results, are deferred. The discussion here is confined to a few technical remarks only.

The experimental GC retention volumes *versus* mobile phase gas pressures are presented in Table I and in Fig. 3. These isotherms, with the present relatively short column, cover the whole range of gas pressures where precision measurements are feasible.

The lower limit of gas pressure was 0.10 atm above atmospheric pressure. The stability of 0.001 atm, of the low pressure regulator in the gas feed, corresponds to an accuracy of *ca.* 1% for the retention volume at 1.10 atm. The upper limit is practically determined by two effects that, in combination, make it difficult to determine the retention volumes for the mixture of four solutes in the dense gas. With

TABLE I

RETENTION VOLUME,  $V_R$ , AS A FUNCTION OF GAS PRESSURE,  $P$ , FOR PROPANE, *n*-PENTANE, *n*-HEPTANE AND *n*-NONANE

Nitrogen gas phase at 50°C and pressure range 1–400 atm. Silicone oil DC 200 stationary liquid phase on Chromosorb PDMCS deactivated support.

$P$ (atm)	$\rho(N_2)$ (amagat)	$V_R$ (cm <sup>3</sup> ) on-column conditions			
		Propane	<i>n</i> -Pentane	<i>n</i> -Heptane	<i>n</i> -Nonane
1.126	0.9512	13.68	18.58	63.65	418.5
1.407	1.188	12.96	17.95	59.48	367.1
1.871	1.581	11.51	16.43	54.22	328.3
2.450	2.070	10.48	15.86	51.83	321.3
3.600	3.042	9.804	15.99	51.38	312.2
5.095	4.305	9.395	14.23	46.29	262.6
9.230	7.798	8.370	12.79	40.12	221.7
13.43	11.35	8.426	12.84	39.32	203.2
20.94	17.68	8.120	12.09	35.16	173.1
29.89	25.22	7.509	11.14	31.16	147.9
42.76	36.03	7.620	10.79	27.80	122.5
58.25	48.94	7.656	10.33	22.83	96.32
85.98	71.72	7.377	9.489	19.58	72.28
141.5	115.4	7.688	9.074	14.64	36.93
205.7	161.5	7.250	8.150	11.12	21.23
292.8	215.6	6.999	7.725	9.284	14.12
393.0	266.6	—	7.589	8.468	11.39

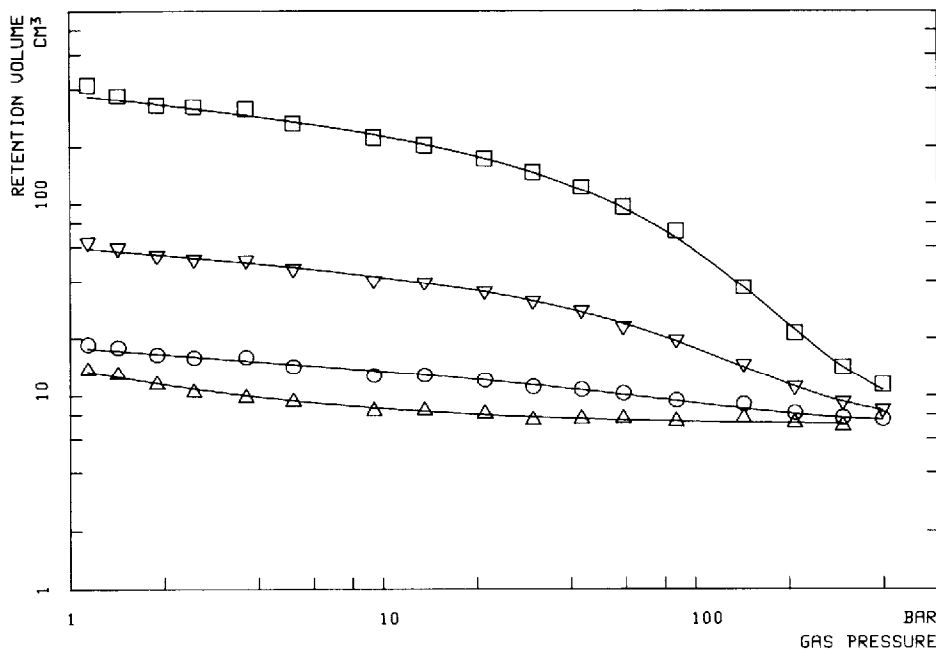


Fig. 3. Retention volumes on-column conditions,  $V_R$ , as a function of gas pressure,  $P$ , for normal hydrocarbons. Nitrogen mobile gas phase at 50°C and pressure range 1–400 atm. Silicone oil DC 200 stationary liquid phase on Chromosorb PDMCS deactivated support.  $\Delta$ , Propane;  $\circ$ , *n*-pentane;  $\nabla$ , *n*-heptane;  $\square$ , *n*-nonane.  $V_R$  and  $P$  are both in logarithmic scales.



nitrogen as mobile gas phase, under our conditions, the column efficiency is considerably reduced at high gas densities. At 400 atm it is reduced to 15 theoretical plates, resulting in relatively broad solute peaks. At the same time, at high gas densities, the retention volumes of the normal hydrocarbons in nitrogen seem to converge to a common limit value,  $V_M$  (Fig. 3). The combination of the two effects causes considerable loss of peak resolution: at 400 atm the precision for the retention volume was *ca.* 2%.

The possible effect of mobile phase flow-rate was investigated for several values of gas pressure in the range 1–400 atm. In all cases, a ten-fold reduction of the mobile phase flow-rate did not have any significant effect on the experimental retention volumes.

The practical realisation for the assumption of infinite dilution of solute was investigated at several values of gas pressure. In the GC experiment, typically at maximum sensitivity of the flame ionisation detector electrometer, sample size was adjusted to give a deflection of 50–90% on the recorder scale, corresponding to a signal peak of 0.5–0.9 mV. In any series of repeat experiments neither a ten-fold reduction nor a ten-fold increase of sample size produced any significant change of retention volume.

There is a qualitative agreement between our results and the results of other authors<sup>1,2,5,6,9,11,12</sup> with regard to the pressure effect of GC retention. However, the greatly increased accuracy that is made possible by the precision apparatus described in this paper has enabled us to find new, subtle effects of gas chromatographic behaviour not observed previously<sup>1–13</sup>.

In the low gas density range, *viz.* for gas pressures 2–12 atm, nitrogen at 25–50°C, Everett<sup>9</sup> and Cruickshank and co-workers<sup>5,6</sup> found a linear relationship for the retention volume  $V_N$  versus the gas pressure  $P$ , and a linear relationship for  $\log V_N$  versus  $P$ . However, the total pressure effect found by these authors<sup>5,6,9</sup> was only a few percent of  $V_N$ , whereas the deviations of actual gas pressure in their column may amount to a factor of two. Thus Everett<sup>9</sup> suggested that the experimental data available to him may not be sufficiently accurate for a quantitative test of his formal relationships. Obviously, for the same reasons, this difficulty would also apply to the experimental data and the formal relationships of Cruickshank and co-workers<sup>5,6</sup>.

On the other hand, in the same range of low gas densities, *i.e.* for gas pressures 1–12 atm, nitrogen at 50°C, our data (see Table I) suggest that the pressure effect could better be described as a linear relationship for  $\log V_N$  versus  $\log P$ , obtained for all four solutes where  $V_N = V_R - V_M$ . This new pressure effect could not have been predicted from current GC theories. In a next higher pressure range, *i.e.* in the range 10–100 atm, the data of Wičar and Novák<sup>10,11</sup> for several solutes in nitrogen gas at 50°C and 75°C, also suggest a linear relationship for  $\log V_N$  versus  $P$ . However, Wičar and Novák found that their pressure effect could not be explained as being due exclusively to the effect of the second cross-virial coefficient,  $B_{13}$ .

Our new data, covering a pressure range wider by a factor 40–60 in the range 1–400 atm (Table I and Fig. 4), show that for  $\log V_N$  versus  $P$ , an approximate linear relationship may indeed be obtained for any limited range of gas pressures, such as 2–12 atm or 10–100 atm. However, the linear relationship will not hold for any extended range of gas pressures. It should be of particular interest to note that in Fig. 4 the slope  $\kappa = (\partial \log V_N / \partial P)_T$  does not have a constant value for any pressure range,

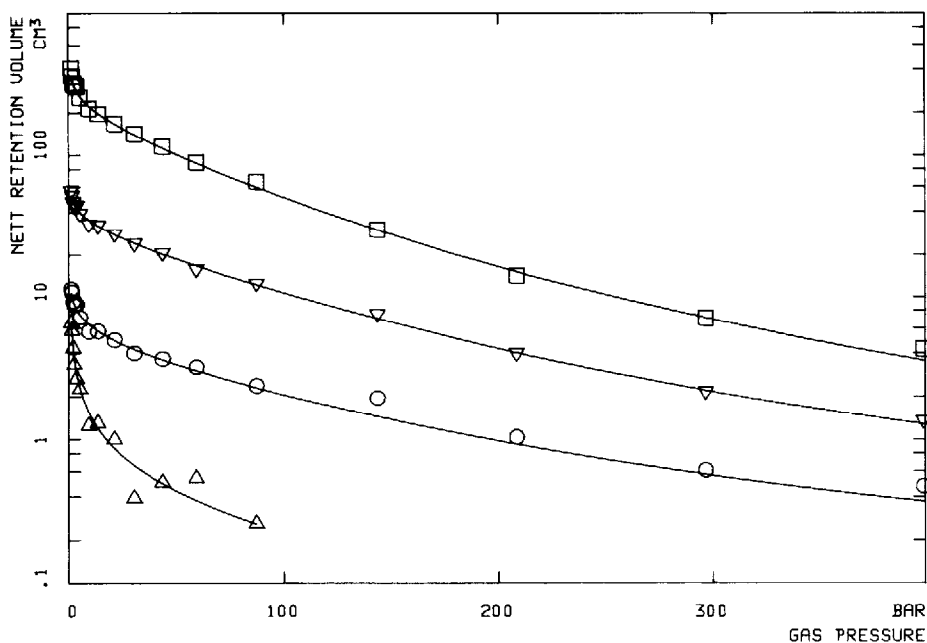


Fig. 4. Net retention volumes on-column conditions,  $V_N = V_R - V_M$ , as a function of gas pressure,  $P$ , for normal hydrocarbons. Nitrogen mobile gas phase at 50°C and pressure range 1-400 atm. Silicone oil DC 200 stationary liquid phase on Chromosorb PDMCS deactivated support.  $\Delta$ , Propane;  $\circ$ ,  $n$ -pentane;  $\nabla$ ,  $n$ -heptane;  $\square$ ,  $n$ -nonane.  $V_N$  in logarithmic scale and  $P$  in linear scale.

and that the slope is steepest at the lowest gas pressure. With the extended pressure range, the new experimental data suggest a singularity at low gas pressure. In the limit  $P = 0$  the slope may approach infinity,  $\kappa = -\infty$ , (*cf.*, Figs. 3 and 4). Anyway, whatever this limit value, it is practically impossible to decide which value of  $(\partial \log V_N / \partial P)_T$  is the correct one to choose from the experimental data, if we wish to use Everett's<sup>9</sup> formula for the estimate of the cross-virial coefficient  $B_{13}$ .

It is remarkable that in one system examined by Cruickshank *et al.*<sup>5</sup>, where they extended their pressure range to 25 atm, these authors found their plot of  $\log V_N$  versus  $p_0 J(\frac{2}{3})$  to be concave upwards instead of the straight line which they expected. However, they considered this effect might be due to anomalous behaviour or to some artefact, and they did not show this plot in any of their reports. By such trivial coincidence this indication of non-linearity might have escaped Everett's notice. We note that, by its description<sup>5</sup>, this unpublished plot for the extended pressure range might be in better agreement with the results of our investigation (*cf.* Fig. 4).

In a more recent paper by Schneider<sup>13</sup>, for the solutes naphthalene and fluorene in carbon dioxide at 40°C and gas density 0.1-0.7 g/cm<sup>3</sup> (*ca.* 40-110 atm), for both solutes the plots of  $\log k$  versus gas density are clearly concave upwards, having their steepest slope at lowest gas pressure. Schneider's plots also do not show a constant slope for any interval of the gas density. These qualities of Schneider's plots are in good agreement with our experimental results (*cf.* Fig. 4).

A new approach is necessary. Thus, in a later paper, the new pressure effect for GC retention will be accounted for. The retention volumes will be discussed in

terms of a single equation of state over the whole range of gas densities for 1–400 atm gas pressures.

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