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## THE GAS CHROMATOGRAPHIC DETERMINATION OF BINARY DIFFUSION COEFFICIENTS

### II. AN EXPERIMENTAL EVALUATION

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#### SUMMARY

The chromatographic determination of binary diffusion coefficients by means of the peak arrest method has been evaluated experimentally. Experimental deviations are generally in the range 0.5–1.0%.

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#### INTRODUCTION

This paper describes an experimental assessment of the potential of the peak arrest (PA) method for the chromatographic determination of binary gaseous diffusion coefficients. It is based on a theoretical analysis outlined in a previous paper<sup>1</sup>, to which the reader is referred for definitions of the symbols used. The primary concern is with the development of a reliable experimental method. This is a long-term project of which the present study is regarded as the first stage. It should therefore be seen as a design study of the relative importance of the basic elements of the method within the limits imposed by existing facilities. No attempt was made to extend the method to the limits of current technology. Most of the results are nevertheless within the 1% precision level, which compares favourably with the best determinations to date. The construction of a refined model for routine measurements at the 0.1% level appears to be possible.

#### INSTRUMENTATION

The theoretical analysis<sup>1</sup> has shown that it is irrational to aim at a precision much below 1% if peak measurements are carried out manually. Recognition of this limitation will consequently be the prime consideration in selecting the various components required for the analysis. The main items are the column, inlet, detector, recorder and the devices used for measuring the gas flow, peak width, time, temperature and pressure. These items are considered separately below.

### *Choice of material and dimensions of the column*

Two materials were considered, viz., stainless steel and glass, and there appears to be little to choose between them. Tolerances on the inner diameter appear to be of the same order. Surface characteristics were not investigated in detail; these are expected to become more relevant for larger molecules. The absence of  $k$  effects was monitored by comparing the retention times of a series of lower linear hydrocarbons. Order of magnitude calculations on the expansion effects indicated that, for the temperatures employed in this work, differences between the high and low temperature diameters are irrelevant.

The choice of the radius ( $a$ ) is influenced by the dependence of var  $a$  on  $a$  and the effect of  $a$  on pressure corrections and eddying. As will be shown below,  $u$  is of the order of 1 cm/sec, so that an inner diameter of about 5 mm is convenient. This value is in accord with the previous uses of open tubes<sup>2-9</sup>.

The column length should be adequate to contain the complete peak after diffusion and allow the flow system to regain its steady state before the front of the peak reaches the detector. For an upper limit of  $D \approx 1$  cm<sup>2</sup>/sec, a column length of about 5 m is a safe minimum. For columns much longer than this value, the retention time can become inconveniently long.

Coiling is not considered to be an important factor.

### *Measurement of radius and length of the column*

**Stainless-steel column.** The length of a short piece of column tubing,  $l$ , was measured accurately with a catharometer. The weights of  $l$  and of the connection tubing were determined on an analytical balance and the length,  $\Delta l$ , of the connective tubing was thus determined. The retention time of a sample peak and the column flow-rate were measured. By taking account of the internal volume of all the fittings calculated from the manufacturer's specifications, and using the lengths, the radius of the tube was calculated as 0.228 cm.

In the light of the uncertainties inherent in the measurement of the volume flow-rate by means of the soap-film method<sup>10,11</sup>, it was eventually decided to concentrate on developing a procedure of high reproducibility and to consolidate the various uncertainties into a single instrument factor by normalizing with respect to some reliable standard. The latter was chosen as the diffusion coefficient of the Ar-He system as given by Marrero and Mason<sup>12</sup>. The choice is motivated by the fact that (i) it is one of the few systems for which reliable experimental data are available and (ii) the concentration dependence of  $D$  is slight (within 1%) as the molecular masses are very unequal and the heavy component is the trace species<sup>12</sup>. The value of the radius obtained in this manner was  $a = 0.225$  cm, which differs by only 1.3% from the value determined via the retention time. The uncertainties have now been consolidated into a single diameter adjustment. It is felt that the phenomena are well enough understood to justify the normalisation.

The length of the column was determined by measuring the retention time of a sample passing through the column. Again, taking account of the internal volume of all the fittings, and using the retention time of the short column with an accurately measured length as well as the radius of the tube, the column length was determined as 276.5 cm.

**Glass column.** The dimensions of the glass column were obtained by staff-

standardizing on Marrero and Mason's recommended value of the He-Ar diffusion coefficient. Using the retention time method, the length was determined as 1084.5 cm. Measurement of the carrier gas flow-rate with the differential pressure flow meter yielded a radius of 0.222 cm.

### *Inlet*

Investigation of the ordinary gas-syringe inlet revealed satisfactory reproducibility. The syringe inlet is also known<sup>13</sup> to approximate the ideal gaussian form.

One of the important advantages of the chromatographic technique is that the sample size is essentially zero. No concentration dependence of  $D$  was found as the sample size varied from 10 to 250  $\mu$ l.

### *Detector*

The choice of the detector is critical as regards internal volume, applicability, sensitivity and linearity. Two types of detectors, *viz.*, thermal conductivity (TCD) and flame ionization (FID) were used.

The detector volume contributes a non-gaussian  $\sigma_e^2 = (V_{\text{eff}}/\dot{V})^2/12$  in time units, where  $V_{\text{eff}}$  is the effective detector volume and  $\dot{V}$  the volume flow-rate<sup>14</sup>.  $V_{\text{eff}}$  of both the TCDs used contributed well below 0.1% to the total  $\sigma_D^2$ , while  $V_{\text{eff}}$  for the FID was assumed to be even smaller.

No detector is of general applicability. The FID, for instance, fails to respond to some common inorganic substances, including the rare gases<sup>15</sup>, while the TCD has serious linearity problems for certain substances. Both detectors were evaluated, as between them they cover a fairly comprehensive range of gases.

The FID responded linearly over a wide range of inlet concentrations (5–250  $\mu$ l). This was unfortunately not true for the TCD, except for the rare gases. TCD determinations showing non-linearity were repeated with the FID.

### *Recorder*

Both types of recorders used conformed to the requirements of negligible var  $u_p/u_p^2$ .

### *Flow.*

Three aspects of flow require attention, *viz.*, the choice of the linear flow velocity, its control and its measurement.

*u value.* Consideration of the optimum flow criterion (eqn. 38 in ref. 1), the negligibility of the outlet effect (<0.1%  $D_p^2$ ) and the variation of var  $u$  with  $u$  indicated a  $u$  value of the order of 1 cm/sec, with a bias to lower values.

*Measurement.* Two types of flow measurement were used, the retention time method and the differential pressure flow meter (DPFM).

We regard the retention time method as the most reliable method for flow-rate measurements. The retention time,  $t_R$ , is defined as<sup>16</sup>

$$t_R = \int_0^l \frac{dz}{u(z)} = \frac{3}{2} \frac{(p^2 - 1) l}{(p^3 - 1) u} \quad (1)$$

where  $p = P_i/P_0$  (ratio of inlet pressure to pressure at outlet) and  $u_0 =$  velocity at

outlet. For the pressure gradients used in the study, compressibility corrections were of the order of 0.1 % and were neglected, *i.e.*  $u = u_0$ . Eqn. 1 then yields

$$\frac{\text{var } u}{u^2} = \frac{\text{var } l}{l^2} + \frac{\text{var } t_R}{t_R^2} \quad (2)$$

Eqn. 2 shows that the relative error in  $u$  can be diminished to an arbitrary level by increasing  $l$  and consequently  $t_R$  at constant  $u$ . Another major advantage is that the method measures the linear flow velocity directly, so that the column radius is not required. It is also applicable at arbitrary temperatures, the only constraint being on the thermostating of the total column volume. The disadvantages are that the method is time consuming and that it is not an on-line monitor. The precision was found to be well within the tolerance of less than 0.1 %.

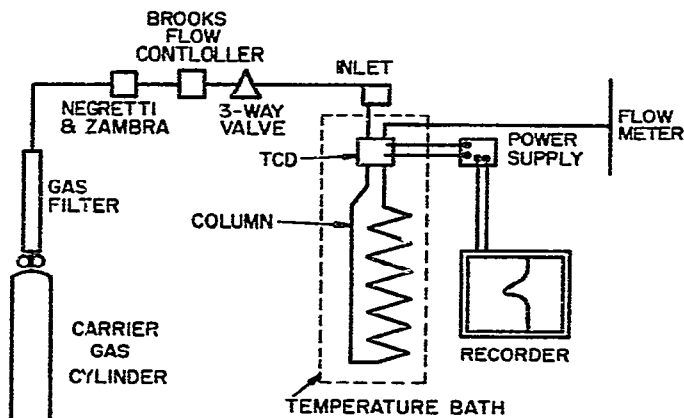


Fig. 1. Experimental apparatus. Stainless-steel column with TCD and soap-bubble flow meter.

The DPFM is a direct application of Poisseuille's law in which the pressure drop is measured across a known resistance. The specific arrangement used is depicted in Fig. 1. The attraction of this method lies in the fact that  $u$  can be measured during recording of the peak and errors due to flow fluctuations are thereby minimized. Calibration of the meter can be effected by either of the first two methods. Combination with the retention time method appears to be especially attractive, but in this study the more convenient traditional soap-film method was considered as more commensurate with the state of development of the DPFM. A thorough analysis and optimization of the DPFM will receive high priority in the next phase of the general project. The present bottleneck is, however, regarded as residing in the manual measurement of peak variances, so that undue attention to the flow measurement is not called for here.

**Control.** The flow of carrier gas from a high-pressure cylinder was controlled by a cascade of pressure regulators consisting of a multi-stage pressure regulator, a Negretti and Zambra precision pressure-regulating valve and a Brooks flow controller (Model 8287), coupled in series.

*Peak measurement*

The predictions of the theoretical analysis of peak width measurements (eqn. 32 in ref. 1) with the recommended parameter values of Ball *et al.*<sup>17</sup> were compared with actual measurements. The respective results are  $6.3 \cdot 10^{-5}$  and  $1.6 \cdot 10^{-5}$  for the relative variances in  $W_{\pm}$ . As the theoretical predictions constitute an upper limit for the actual measurements, the result increases our confidence in the basic soundness of the theoretical approach.

In accordance with the theoretical predictions, an effort was made to generate peaks with a shape factor  $s = h/W_{\pm} > 1$ . The fractional height, however, was taken as  $r = 0.5$ , which is larger than the optimum of  $r = 0.2$ . This is justified by the fact that non-gaussian effects become more pronounced as  $r$  decreases. Also, the optimum is fairly shallow so that the gain from 0.5 to 0.2 is not so pronounced as to vindicate the more serious risk of non-gaussian deviations.

It is possible, with a TCD, to record the peak before and after arrest, in an effort to eliminate non-reproducibility at the inlet. This two-point technique was investigated but no improvement in precision was found. This implies that the precision in the inlet width is at least as good as that of an actual peak width measurement. A typical value for the relative variance in the peak width is  $\text{var } W_{\pm}^2/W_{\pm}^4 \approx 4 \cdot 10^{-5}$ .

*Time measurement*

$t_2$  and  $t_R$  were measured with a stop-watch that had been checked against three other stop-watches. The accuracy was found to be within the precision limits of the response time of the operator, the standard deviation of which was well within 1 sec. As the times involved were of the order of at least 500 sec, no effort was made to improve upon this measurement.

*Temperature and pressure measurement and control*

Experiments were conducted at three temperatures of approximately 300, 370 and 500 °K. At these levels, control of the mean temperature within the enclosure was within 0.2%, but vertical differences showed a maximum of nearly 2 °K at the highest temperature where the temperature controls of a Beckman GC 4 was used. This is not entirely satisfactory and in future studies the design should be improved in order to obtain a more even distribution<sup>13,18-20</sup>. The high-temperature thermometers were found to be accurate to within 1 °K at 500 °K.

The atmospheric pressure was measured with a mercury barometer to within 0.05 mm Hg.

In summary, consider the relation of  $D$  to the various measurements in the symbolic form

$$(n, t_2, \sigma_p^2, u_p, u) \rightarrow (n, t_2, \sigma^2) \rightarrow b \rightarrow D$$

It is evident from the preceding discussion that for the present aim, *i.e.*, a 1% precision level in  $D$ , the source of random errors is practically confined to the  $\sigma_p^2$  measurements. The achievement of the required precision was not problematic, and the main concern was therefore the elimination of systematic errors.

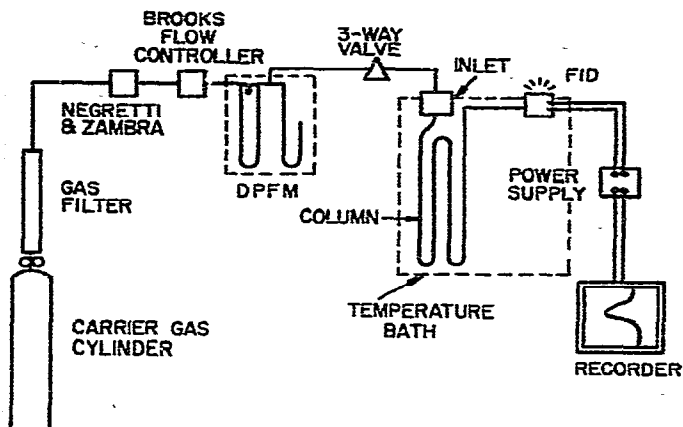


Fig. 2. Experimental apparatus. Glass column with FID and DPFM.

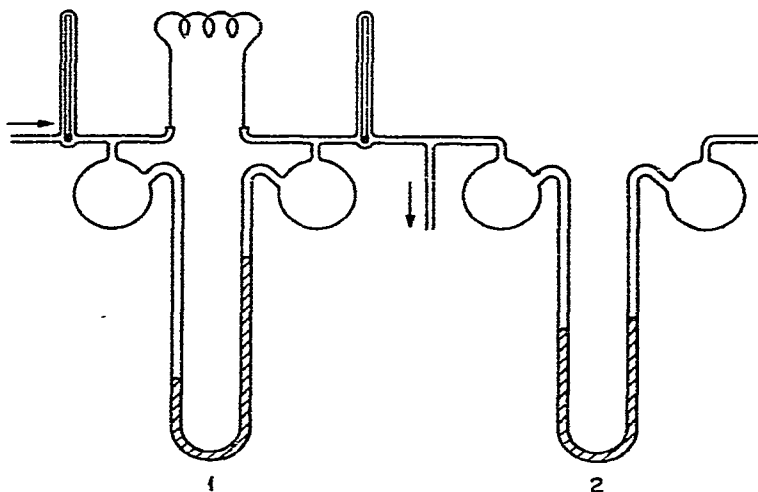


Fig. 3. Schematic diagram of the differential pressure flow meter (DPFM).

## EXPERIMENTAL

The experimental apparatus is shown in Figs. 2 and 3.

The experimental procedure was as follows. The system was purged with the carrier gas at a pre-selected flow-rate while waiting for the electronic components to stabilize and the temperature to come to a steady state. It was assumed that steady state had been reached when the recorder gave a stable base line. A 50–150- $\mu$ l sample was extracted with an S.G.E. 250- $\mu$ l gas syringe from the sample lecture bottle through a Hamilton lecture bottle septum. The sample was injected at the inlet and at the same time a stop-watch was set into motion. When the sample peak maximum was registered on the recorder, the stop-watch was stopped. The retention time,  $t_R$ , obtained was halved and noted. After injecting the next sample and waiting for a

time  $t_R/2$ , the gas flow was stopped by turning the three-way valve. After the required time (10 min), the three-way valve was turned back and the sample eluted. Throughout each run, measurements were made of the atmospheric pressure, differential pressures and temperature of the DPFM (when used) and column temperature. The averages of these measurements were taken as the conditions for that run. When the soap-film flow-meter was used, measurements of the flow-rate were made before and after each run and the average was taken.

The peaks obtained were measured at half-height. The temperature and pressures during the first run, and therefore the flow-rate, were taken as the reference conditions, and all other peaks were corrected to those conditions. A least-squares fit was carried out on the  $t_2$  versus  $(W_{\frac{1}{2}})_p^2$  measurements and the slope ( $b_p$ ) and standard deviation were calculated. The binary gaseous diffusion coefficient,  $D$ , was obtained from

$$D = (b_p/2) (u_c/u_p)^2/8 \ln r \quad (3)$$

The factor  $8 \ln r$  is the numerical relation between  $\sigma_p^2$  and  $(W_{\frac{1}{2}})_p^2$ .

The soap-bubble flow meter and DPFM give volume flow-rates, which must be divided by the column cross-sectional area to give linear flow-rates. In the retention time method, the column length,  $l$ , is divided by the retention time to give the linear flow-rate.

The experimental difficulties encountered were more or less routine.

## RESULTS

The experimental results are summarized in Tables I and II. Where available, the literature values are the recommended values of Marrero and Mason<sup>12</sup>; otherwise, available experimental data are included.

The values obtained by Jacobs *et al.*<sup>23</sup> show considerable scatter, even for diffusion coefficients where Marrero and Mason<sup>12</sup> prescribe accurate values, and are therefore not considered to be very reliable. Concentration corrections were made according to the formula recommended by Marrero and Mason<sup>12</sup>. The experimental and literature deviations should bracket the absolute error, especially in the case of values recommended by Marrero and Mason<sup>12</sup>.

It can be seen from Table I that non-linearity effects of the TCD gave values for the hydrocarbons that were several per cent too high. These determinations were repeated for the FID (Table II). Several previously undetermined diffusion coefficients are reported.

An example of a calculation is included in the Appendix.

## APPENDIX

### *Example of the calculation of D*

Retention time method for the binary gas pair N<sub>2</sub>-Ar, a TCD and a glass column.

TABLE I

## BINARY DIFFUSION COEFFICIENTS FOR OPEN STAINLESS-STEEL TUBE COLUMN

Detector: Gow-Mac 10-953 katharometer (TCD). Flow measurement: soap-bubble flow meter. Standard: Ar-He determined at 295.1 °K, 0.850 atm, with a standard deviation of 0.7%.

| Gas pair                      | n | Pressure (atm) | Temperature (°K) | D (trace), corrected to 1 atm (cm <sup>2</sup> /sec) | D (x <sub>1</sub> = 0.5), corrected to 1 atm (cm <sup>2</sup> /sec) | Exptl. deviation (%) | Literature value (cm <sup>2</sup> /sec) | Literature deviation (%) | Reference | Absolute error (%) |
|-------------------------------|---|----------------|------------------|--|---|----------------------|---|--------------------------|-----------|--------------------|
| Methane-Helium                | 7 | 0.849          | 294.7            | 0.662  | 0.680   | 0.4                  | 0.656                                   | 3.0                      | 12        | +3.6               |
| Ethane-Helium                 | 7 | 0.857          | 294.5            | 0.482  |   | 0.1                  | 0.501*                                  |                          | 21        |                    |
| Propane-Helium                | 6 | 0.857          | 294.4            | 0.392  |   | 0.2                  |   |                          |           |                    |
| Butane-Helium                 | 7 | 0.862          | 292.9            | 0.330  | 0.337   | 0.1                  | 0.354*                                  | 0.3                      | 22        | -4.8               |
| 2,2-Dimethylpropane-Helium    | 6 | 0.863          | 292.8            | 0.297  |   | 0.3                  |   |                          |           |                    |
| Sulphur hexafluoride-Helium   | 6 | 0.856          | 294.6            | 0.377  | 0.395   | 0.7                  | 0.403                                   | 3.0                      | 12        | -2.0               |
| Helium-Argon                  | 7 | 0.855          | 298.1            | 0.772  | 0.758   | 0.6                  | 0.747                                   | 1.0                      | 12        | +1.3               |
|                               | 8 | 0.858          | 298.1            | 0.750  | 0.737   | 0.4                  | 0.747                                   | 1.0                      | 12        | -1.4               |
|                               | 6 | 0.855          | 298.5            | 0.788  | 0.744   | 0.8                  | 0.749                                   | 1.0                      | 12        | -0.7               |
| Neon-Argon                    | 7 | 0.854          | 297.0            | 0.311  | 0.309   | 1.9                  | 0.319                                   | 1.0                      | 12        | -3.1               |
| Nitrogen-Argon                | 6 | 0.856          | 297.6            | 0.190  | 0.191   |                      | 0.195                                   | 2.0                      | 12        | -2.0               |
| Methane-Argon                 | 6 | 0.857          | 298.5            | 0.219  | 0.218   | 0.2                  | 0.205                                   | 3.0                      | 12        | +6.3               |
| Sulphur hexafluoride-Argon    | 6 | 0.855          | 298.7            | 0.078  | 0.079   | 0.6                  | 0.081                                   | 3.0                      | 12        | -3.1               |
| Helium-nitrogen               | 7 | 0.860          | 294.5            | 0.699  | 0.687   | 0.7                  | 0.703                                   | 2.0                      | 12        | -2.4               |
| Methane-nitrogen              | 7 | 0.859          | 294.4            | 0.226  | 0.226   | 0.6                  | 0.209                                   | 3.0                      | 12        | +7.8               |
| Propane-nitrogen              | 7 | 0.858          | 292.8            | 0.113  | 0.113   | 0.5                  | 0.151*                                  |                          | 23        | -25.2              |
| Butane-nitrogen               | 6 | 0.856          | 293.8            | 0.097  | 0.097   | 0.4                  | 0.094*                                  |                          | 24        | +3.2               |
|                               |   |                |                  |  |   |                      | 0.090*                                  |                          | 23        | +7.8               |
|                               |   |                |                  |  |   |                      | 0.110*                                  |                          | 21        | -11.8              |
| 2,2-Dimethylpropane-nitrogen  | 7 | 0.857          | 293.6            | 0.078  |   | 0.4                  |   |                          |           |                    |
| Sulphur hexafluoride-nitrogen | 7 | 0.861          | 294.2            | 0.092  | 0.093   | 0.4                  | 0.093                                   | 3.0                      | 12        | 0.0                |

\* Corrected to experimental temperature.



TABLE II

## BINARY DIFFUSION COEFFICIENTS FOR OPEN GLASS TUBE COLUMN

Detector: Beckman FID, Flow measurement: (1) retention time method; (2) DPFM, Standard: He-Ar determined at 295.8 °K, 0.857 atm, with a standard deviation of 0.4%.

| Gas pair                     | n  | Flow measurement* | Pressure (atm) | Temperature (°K) | D (trace), corrected to 1 atm (cm <sup>2</sup> /sec) | D (x <sub>1</sub> = 0.5), corrected to 1 atm (cm <sup>2</sup> /sec) | Exptl. deviation (%) | Literature value (cm <sup>2</sup> /sec) | Literature deviation (%) | Reference | Absolute error (%) |
|------------------------------|----|-------------------|----------------|------------------|--|---|----------------------|---|--------------------------|-----------|--------------------|
| Methane-Helium               | 8  | 2                 | 0.861          | 296.6            | 0.670  | 0.687   | 0.5                  | 0.663                                   | 3.0                      | 2         | +3.5               |
| Ethane-Helium                | 6  | 2                 | 0.856          | 372.0            | 0.999  | 1.027   | 0.6                  | 0.986                                   | 3.5                      | 2         | +4.1               |
| Propane-Helium               | 8  | 2                 | 0.859          | 298.1            | 0.516  |   | 0.9                  | 0.511**                                 |                          | 6         |                    |
| Butane-Helium                | 8  | 2                 | 0.859          | 296.6            | 0.411  |   | 0.4                  |   |                          |           |                    |
| 2,2-Dimethylpropane-Helium   | 8  | 1                 | 0.859          | 296.6            | 0.347  | 0.354   | 0.3                  | 0.361**                                 | 0.3                      | 8         | -1.9               |
| Nitrogen-Argon               | 6  | 1                 | 0.858          | 296.2            | 0.317  | 0.194   | 0.7                  | 0.193                                   | 2.0                      | 2         | +0.4               |
| Ethane-Argon                 | 6  | 1                 | 0.858          | 483.2            | 0.446  | 0.444   | 0.3                  | 0.456                                   | 3.0                      | 2         | -2.5               |
| Propane-Argon                | 6  | 1                 | 0.849          | 302.5            | 0.149  | 0.149   | 0.8                  | 0.114**                                 |                          | 4         | +29.8              |
| Butane-Argon                 | 6  | 1                 | 0.850          | 483.2            | 0.357  |   | 0.4                  |   |                          |           |                    |
|                              | 6  | 1                 | 0.849          | 301.8            | 0.106  |   | 0.9                  | 0.093**                                 |                          | 4         |                    |
|                              | 6  | 1                 | 0.851          | 483.2            | 0.247  |   | 1.2                  |   |                          |           |                    |
|                              | 12 | 1                 | 0.857          | 298.5            | 0.096  | 0.096   | 0.5                  | 0.104**                                 | 0.4                      | 8         | -7.4               |
|                              | 8  | 2                 | 0.862          | 297.1            | 0.096  | 0.096   | 0.9                  | 0.082**                                 |                          | 4         | +17.4              |
| 2,2-Dimethylpropane-Argon    | 20 | 2                 | 0.856          | 476.7            | 0.276  |   | 0.6                  |   |                          |           |                    |
| Ethane-nitrogen              | 8  | 2                 | 0.861          | 297.9            | 0.077  |   | 0.1                  |   |                          |           |                    |
|                              | 6  | 1                 | 0.849          | 301.0            | 0.167  | 0.167   | 0.3                  | 0.150**                                 |                          | 5         | +11.3              |
|                              | 6  | 1                 | 0.849          | 483.2            | 0.381  |   | 0.5                  | 0.162**                                 |                          | 6         | +3.1               |
| Propane-nitrogen             | 8  | 2                 | 0.860          | 297.5            | 0.122  | 0.123   | 0.8                  | 0.154**                                 |                          | 4         | -20.0              |
| Butane-nitrogen              | 6  | 2                 | 0.860          | 371.9            | 0.141  |   | 1.4                  |   |                          |           |                    |
|                              | 6  | 2                 | 0.861          | 479.1            | 0.238  |   | 0.9                  |   |                          |           |                    |
|                              | 20 | 2                 | 0.860          | 481.2            | 0.237  |   | 0.6                  |   |                          |           |                    |
| 2,2-Dimethylpropane-nitrogen | 8  | 2                 | 0.864          | 297.4            | 0.089  |   | 0.6                  |   |                          |           |                    |

\* 1 = Retention time method; 2 = DPFM.

\*\* Corrected to experimental temperature.

Experimental conditions for the first three peaks ( $t_2 = 0$ ):  $p_{\text{atm}} = 652.1 \pm 0.05$  mm Hg;  $T_{\text{column}} = 296.1$  °K. Average retention time = 567.8 sec, therefore  $u_c^2 = 3.648$  cm<sup>2</sup>·sec<sup>-2</sup> ( $l = 1084.5$  cm).  $u_p = 5$  in./min.

Measured  $(w_3)_p^2$  (in cm<sup>2</sup>):

| $t_2 = 0$ min | Retention time (sec) | $t_2 = 10$ min | Retention time (sec) |
|---------------|----------------------|----------------|----------------------|
| 21.16         | 567.7                | 39.81          | 567.7                |
| 21.16         | 567.9                | 39.56          | 567.6                |
| 21.16         | 567.8                | 39.69          | 567.8                |

Corrected  $(W_3)_p^2$ , adjusted to experimental condition of first peak:

| $t_2 = 0$ min | $t_2 = 10$ min |
|---------------|----------------|
| 21.16         | 39.80          |
| 21.16         | 39.53          |
| 21.16         | 39.60          |

$$b_p \cdot 8 \ln 2 = 0.0309 \text{ cm}^2/\text{sec.}$$

$$\text{Relative standard deviation} = 0.5\%$$

$$D(x_1) = b \frac{u_p^2}{u_c^2} \cdot \frac{1}{16 \ln 2}$$

$$= 0.227 \text{ cm}^2/\text{sec.}$$

Concentration correction:

$$\Delta_{12} = \rho (6c_{12}^* - 5)^2 \cdot \frac{ax_1}{1 + bx_1}$$

where

$$x_1 = \text{mole fraction of heavy component, (Ar).}$$

$$\rho = 1.0$$

$$\epsilon/\kappa = 107 \text{ °K } (\rightarrow T^* = 2.77)$$

$$a = 0.029$$

$$b = 0.010$$

$$\Delta_{12}(x_1 = \frac{1}{2}) = 0.00265$$

$$\Delta_{12}(x_1 = 1) = 0.00507$$

$$D(x_1 = \frac{1}{2}) = D(x_1) \left[ \frac{1 + \Delta_{12}(x_1 = \frac{1}{2})}{1 + \Delta_{12}(x_1)} \right]$$

$$= D(x_1) \cdot 0.998$$

$$D(x_1 = \frac{1}{2}) = 0.226 \text{ cm}^2/\text{sec.}$$

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