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## GAS CHROMATOGRAPHIC DETERMINATION OF DIFFUSION CONSTANTS BY MEANS OF MOMENT ANALYSIS

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### SUMMARY

Binary diffusion constants are reported for systems in which one or both of the components are low-molecular-weight alkenes. For ethene, propene and krypton the self-diffusion constant is determined by using radioactively labelled tracer gases. It is shown that the temperature dependence of the diffusion constant is  $T^{1.75}$  over the range 254–760 °K. The results are compared with correlations reported in the literature. The relationships of Fuller *et al.* and Hirschfelder *et al.* describe the data equally well. It is shown that the gas chromatographic determination of diffusion constants is reliable if moment analysis is used to describe the elution profiles.

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### INTRODUCTION

Gaseous diffusion plays an important role in gas chromatography and many other processes and systems. Although many reliable relationships have been reported, the amount of data published, especially for organic gases, is insufficient to decide which correlation is valid in the field of interest. After the introduction by Giddings and Seager<sup>1</sup> of the gas chromatographic method for the measuring of diffusion constants, many workers applied this method. Reviews on theoretical and practical aspects have been published<sup>2-5</sup>.

The reliability of this method has been greatly improved by the introduction of carefully designed gas chromatographic equipment and advanced data reduction procedures<sup>6-9</sup>. An advantage of gas chromatographic methods is that the experiments are simple and that measurements can be carried out easily over a large range of pressures and temperatures.

In this work, measurements were made of the diffusion constants of alkenes in helium and of alkenes in alkenes, which, as far as we know, have not previously been reported. Further, the self-diffusion constants of ethene, propene and krypton are reported. The calculations are based on statistical moment analysis. To check the

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temperature dependence of the diffusion constant, the self-diffusion constant of ethene was measured over a wide range of temperatures.

## THEORETICAL

### *Relationships for the diffusion constant*

Several relationships that can be used for estimation of the diffusion constant have been reported<sup>10,11</sup>. The rigid-sphere model of the kinetic gas theory leads to the following expression for the self-diffusion constant:

$$D_{11} = \frac{1}{3} \bar{v}_m \Lambda \quad (1)$$

where  $\bar{v}_m$  is the mean velocity of the molecules and  $\Lambda$  the mean free path. If it is assumed that the gas mixture behaves as an ideal gas, the following equation can easily be derived:

$$D_{11} = \text{constant} \cdot \frac{T^{1.5}}{p d_m^2 \sqrt{M}} \quad (2)$$

where  $d_m$  is the molecular diameter,  $T$  the absolute temperature and  $M$  the molecular weight.

Using the Chapman-Enskog kinetic gas theory and the theoretical approach of Stefan and Maxwell, the following equation can be derived:

$$D_{12} = \text{constant} \cdot \frac{T^{1.5}}{p d_{12}^2} \sqrt{\frac{M_1 + M_2}{M_1 M_2}} \quad (3)$$

where  $d_{12} = \frac{1}{2}(d_1 + d_2)$  = mean diameter, or distance between molecule 1 and molecule 2 at the moment of collision.

A number of relationships, such as those of Andrussov<sup>11</sup>, Arnold<sup>12</sup> and Gilliland<sup>13</sup>, were derived from this relationship. Gilliland's equation is based on the assumption that the distance between the molecules is proportional to the molar volumes of substances 1 and 2 in the liquid state at their normal boiling temperatures ( $V_{b1}$  and  $V_{b2}$ , respectively). Using the relationship given by Titani<sup>14</sup>:

$$d_{12} = (V_{b1}^{\frac{1}{3}} + V_{b2}^{\frac{1}{3}})^2 \quad (4)$$

Gilliland derived the following expression for the diffusion constant:

$$D_{12} = \frac{4.36 \cdot 10^{-8} T^{1.5}}{p (V_{b1}^{\frac{1}{3}} + V_{b2}^{\frac{1}{3}})^2} \sqrt{\frac{M_1 + M_2}{M_1 M_2}} \quad (5)$$

In this equation, the constant is not dimensionless and therefore its magnitude depends on the system of units used. In this paper, the SI system is followed and thus the diffusion constant is expressed in square metres per second and the pressure in megapascals.

At temperatures close to room temperature, Gilliland's equation gives fairly

good results; at elevated temperatures deviations between measured and calculated values become large. Experimentally it has been found that the dependence on the temperature varies between  $T^{1.7}$  and  $T^{1.8}$ . This empirical temperature dependence was used by Fuller *et al.*<sup>15</sup> in their equation for the diffusion constant:

$$D_{12} = \frac{1.01 \cdot 10^{-8} T^{1.75}}{P(V_m^{\frac{1}{2}} + V_m^{\frac{1}{2}})^2} \sqrt{\frac{M_1 + M_2}{M_1 M_2}} \quad (6)$$

where  $V_m = \sum_i V_i$  and  $V_i =$  volume increment of atom  $i$ . In this paper we shall refer to eqn. 6 as the FSG equation.

In modern kinetic gas theory, the attraction and repulsion forces are described by the model of Lennard-Jones<sup>16</sup>. The mean diameter,  $d_{12}$ , in eqn. 5 has to be replaced with the collision diameter,  $\sigma_{12}$ . Further, the rigid-sphere model is corrected by applying the collision integral,  $\Omega_{12}$ , which accounts for the potential energy field around the molecules. Eqn. 5 can then be rewritten as

$$D_{12} = \text{constant} \cdot \frac{T^{1.5}}{P\sigma_{12}^2\Omega_{12}} \sqrt{\frac{M_1 + M_2}{M_1 M_2}} \quad (7)$$

In the model of Hirschfelder *et al.*<sup>17</sup>, the constant is given by

$$\text{constant} = \left(2.17 - 0.498 \sqrt{\frac{M_1 + M_2}{M_1 M_2}}\right) \cdot 10^{-8} \quad (8)$$

The combination of eqns. 7 and 8 will be referred to as the HBS equation. The collision integral,  $\Omega_{12}$ , can be calculated from the table given by Hirschfelder *et al.*<sup>10</sup> or from the empirical relationship given by Chen<sup>18</sup>. As both are functions of  $kT/\epsilon_{12}$ , where  $\epsilon_{12}$  is the attraction energy, the temperature dependence of the HBS equation deviates from  $T^{1.5}$ .

#### Moment analysis

The statistical moments are defined as follows<sup>19</sup>:

$$n\text{th moment on the origin} = \mu_n = \int t^n c(L,t) dt \quad (9)$$

$$n\text{th moment on the mean} = \mu_n' = \int (t - \mu_1)^n c(L,t) dt \quad (10)$$

$$\text{where } \int c(L,t) dt \equiv 1 \quad (11)$$

For an empty tube with a circular cross-section, the following expressions can be derived<sup>20,21</sup>:

$$\mu_1 = \frac{L}{v} \quad (\text{"first moment"}) \quad (12)$$

$$\mu_2' = \frac{2\mathcal{D}L}{v^3} \quad (\text{"second moment"}) \quad (13)$$

where  $L$  is the length of the column,  $v$  the mean linear velocity and  $\mathcal{D}$  the dispersion coefficient.

In the literature, retention time and height equivalent to a theoretical plate are usually used instead of first and second moments. It should be noted, however, that this is correct only for gaussian curves. Moreover, for non-gaussian peaks the determination of the height equivalent to a theoretical plate is performed in a number of different ways, which makes comparison difficult<sup>22-26</sup>.

#### *The straight empty tube*

The mass transport equation for a straight empty tube with laminar flow was first solved by Taylor<sup>27</sup>. He assumed that the axial diffusion can be neglected. However, for gases, axial molecular diffusion is not negligible. Aris<sup>28</sup> and Levenspiel and Bischoff<sup>29</sup> showed that axial molecular diffusion gives an independent contribution to the effective dispersion coefficient, so that the resulting dispersion coefficient is the sum of the linear diffusion constant and the dispersion coefficient found by Taylor:

$$\mathcal{D} = D_{12} + \frac{d^2}{192} \frac{v^2}{D_{12}} \quad (14)$$

Solving eqn. 14 with respect to  $D_{12}$  results in

$$D_{12} = \frac{1}{2} [\mathcal{D} \pm \sqrt{(\mathcal{D}^2 - \frac{1}{48} d^2 v^2)}] \quad (15)$$

As we know the relationships for the first and second moments, the dispersion coefficient,  $\mathcal{D}$ , can be calculated from the experimental results and consequently the diffusion constant,  $D_{12}$ , can be found.

Now we have two methods for calculating the binary molecular diffusion constant:

(1) From eqn. 14: a plot of  $\mathcal{D}$  against  $v^2$  gives an intercept on the  $\mathcal{D}$ -axis which gives directly the binary diffusion constant. This solution will be called the graphical solution.

(2) From eqn. 15: at every experimental condition a  $D_{12}$  value can be calculated from the moments obtained. The arithmetic mean of the  $D_{12}$  values calculated in this way gives the final binary molecular diffusion constant with its standard deviation. This will be called the algebraic solution.

## EXPERIMENTAL

The apparatus reported earlier<sup>30</sup> was used, except that in the work with radioactively labelled tracers the tracer gas is recirculated via  $c-d$  (see Fig. 1) instead of being vented to the atmosphere. The experimental set-up is shown in Fig. 1.

Helium, nitrogen and ethene were obtained from HoekLoos (Amsterdam, The Netherlands; purity: chemical pure). Propene, butene-1, *cis*-butene-2 and 2-methylpropene were obtained from Matheson Gas Products (East Rutherford, N.J., U.S.A.) (purity: chemical pure). Argon and krypton were purchased from Baker (Deventer, The Netherlands; purity, research grade). [1,2-Di-<sup>14</sup>C]ethene and <sup>85</sup>Kr were obtained from The Radiochemical Centre (Amersham, Great Britain). [1,3-Di-<sup>14</sup>C]propene was synthesized from the corresponding propanol-2, obtained from The Radiochemical Centre. The propene was prepared by refluxing the propanol-2 over alumina at

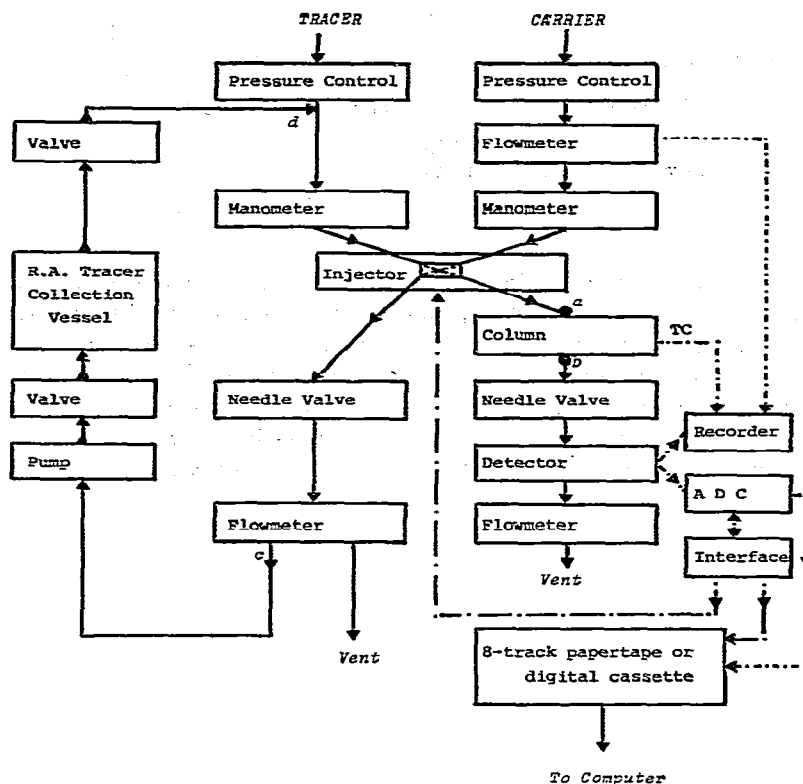


Fig. 1. Experimental set-up.

625 °K<sup>31</sup>. The resulting propene was analysed gas chromatographically and shown to be 99.5% pure.

Extra-column effects are not negligible. Therefore, "blank" experiments were performed for each set of tracer gas and carrier gas used. This was done by detaching the column and connecting the junctions *a* and *b* (see Fig. 1) to each other. In this way, for each combination of tracer and carrier gas a set of first and second moments was determined at various flow-rates. These moments will be referred to as  $\mu_1$  (blank) and  $\mu_2'$  (blank).

The experimental statistical moments  $\mu_1$  (measured) and  $\mu_2'$  (measured) can be corrected for extra-column effects by the following simple rules:

$$\mu_1 \text{ (corrected)} = \mu_1 \text{ (measured)} - \mu_1 \text{ (blank)} \quad (16)$$

$$\mu_2' \text{ (corrected)} = \mu_2' \text{ (measured)} - \mu_2' \text{ (blank)} \quad (17)$$

$\mu_1$  (blank) and  $\mu_2'$  (blank) apply to the same flow-rate as  $\mu_1$  (measured) and  $\mu_2'$  (measured). In the tables below,  $\mu_n$  (blank) will be referred to as  $\mu_{n,b}$  and  $\mu_n$  (measured) as  $\mu_{n,m}$ .

With respect to the gas pairs the following notation will be used: gas A (tracer gas) and gas B (carrier gas) will be written as A  $\rightarrow$  B (A injected into B). The physical properties of the columns used are given in Table I.

TABLE I  
DIMENSIONS OF THE COLUMNS

Column No.	Length (m)	Volume ( $10^{-6} \text{ m}^3$ )	Internal diameter ( $10^{-3} \text{ m}$ )
6	5.333	102.70	4.935
8	5.701	82.77	4.299

### Numerical methods

The method most commonly used in gas chromatography to describe the elution profile is to measure the retention time,  $t_r$ , and the variance,  $\sigma_b$ . In this study, it was preferred to calculate the first moment on the origin and the second central moment. The reason why both methods can differ considerably lies mainly in the occurrence of tailing. One of the major causes of tailing is the impossibility of injecting a perfect  $\delta$ -pulse. Blank experiments show particularly severe tailing, which is transformed to the response curve. This leads to a shift of the median to higher times and

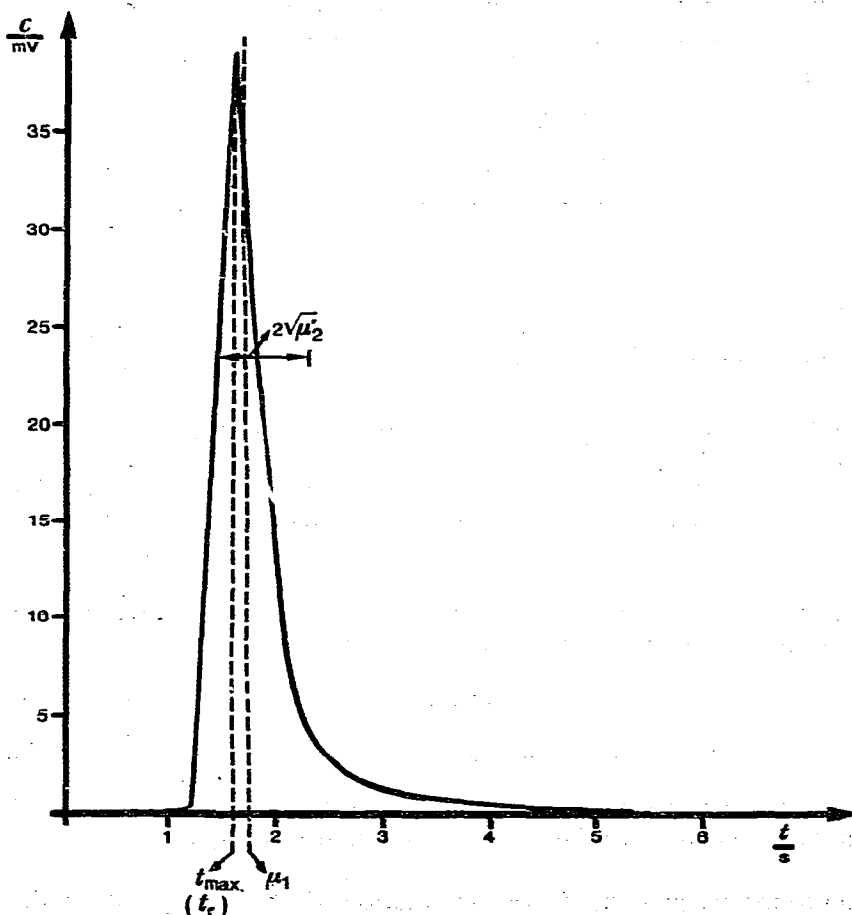


Fig. 2. Comparison of  $\mu_1$  with  $t_r$  and of  $\mu_2$  with  $\sigma_r$ . Run No. 402010; system, He  $\rightarrow$  Ar; Flow-rate, 290  $\text{cm}^3 \text{ min}^{-1}$ ; pressure, 0.80 MPa; column, 8.

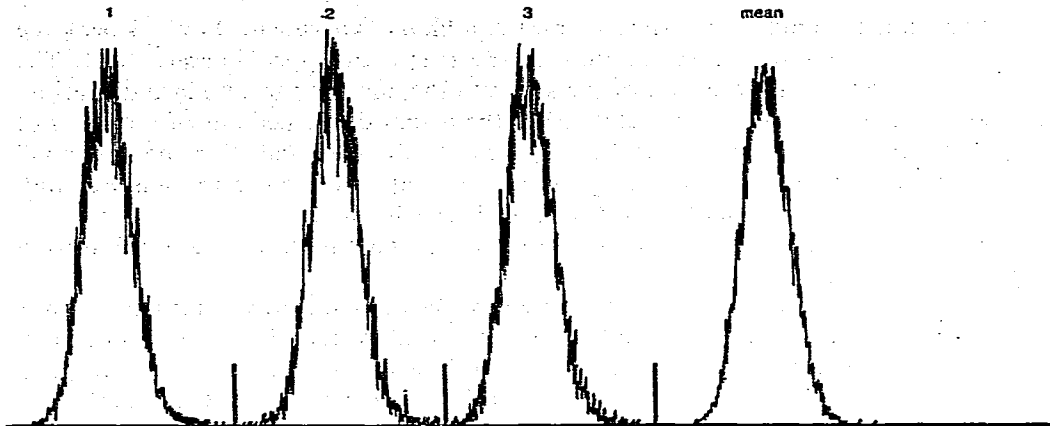


Fig. 3. Result of the smoothing by calculation of a mean peak.

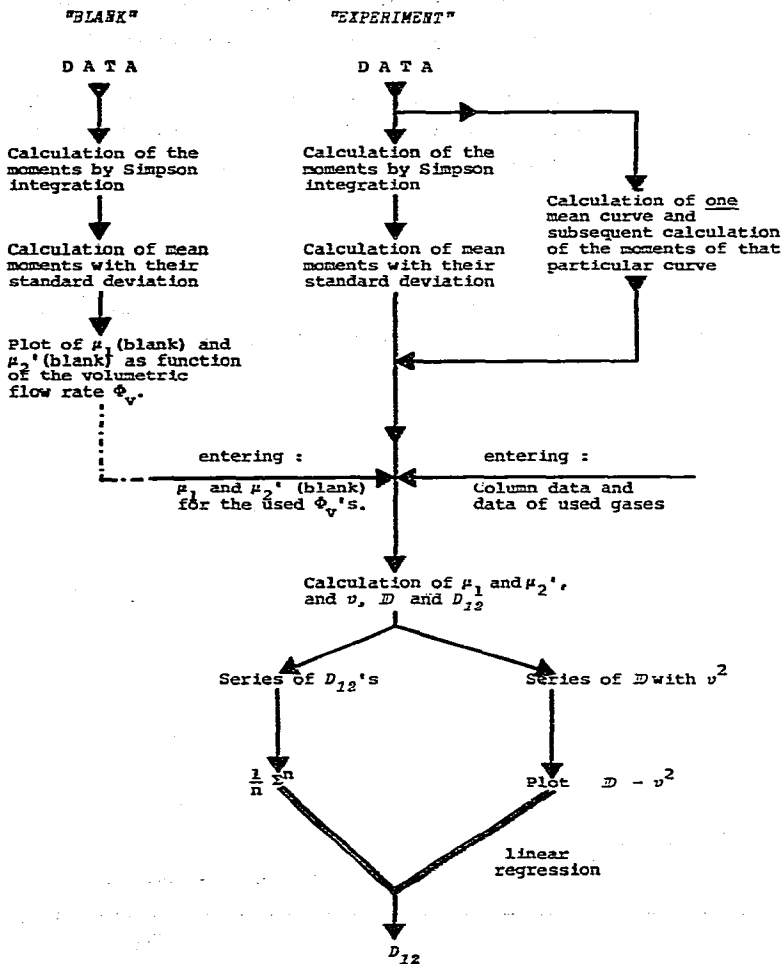


Fig. 4. Calculation procedure

an increase in the spread. Fig. 2 shows a plot of a blank experiment. For this peak the first moment exceeds the retention time to the extent of approximately 10%. The difference between the square root of the second moment and the standard deviation,  $\sigma$ , calculated from the peak width at 0.607 of the height of the peak, is of the order of 100%. Only for gaussian curves will  $2\sqrt{\mu_2'}$  and  $2\sigma$  be identical. For the "normal" experiments, in which a column was present, the peaks were close to gaussian and, therefore, for these experiments this difference is much smaller.

Calculation of the statistical moments was carried out with the aid of Simpson integration as reported earlier<sup>30</sup>.

As injection of tracer gas and treatment of the data are fully automated, it was possible to carry out each experiment several times under identical conditions. Such a set of experiments will be called a "run" in this work. In this way, a mean peak could be calculated from a set of experimental peaks. Especially in the experiments with radioactively labelled tracers this method was applied. An example of this technique is shown in Fig. 3. It can be seen that, even in the case of a set of three identical experiments, the mean peak is much more smooth than the original ones.

To obtain a measure of the precision for each run, the relative error ( $s$ ) was calculated.

The data flow through the computer is shown schematically in Fig. 4. In experiments at different temperatures, expansion of the column takes place. For this effect, which was not negligible, corrections were made in the calculations.

## RESULTS AND DISCUSSION

### *Experiments with helium, argon and nitrogen*

To check the method and the apparatus, a series of experiments was performed with helium, argon and nitrogen to correlate the results with literature data.

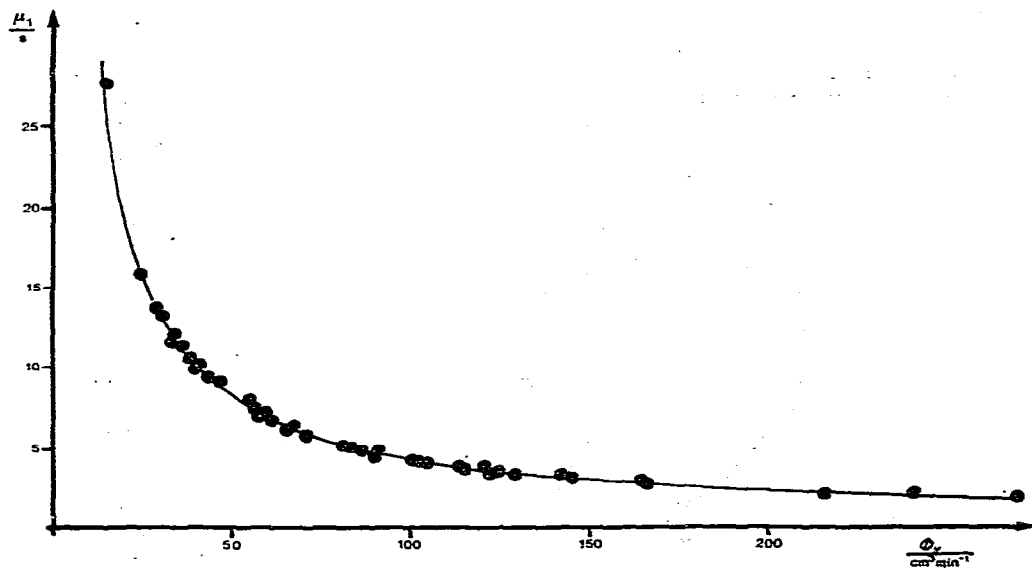


Fig. 5. First blank moment on the origin. Experimental results with He, Ar and  $\text{N}_2$ .



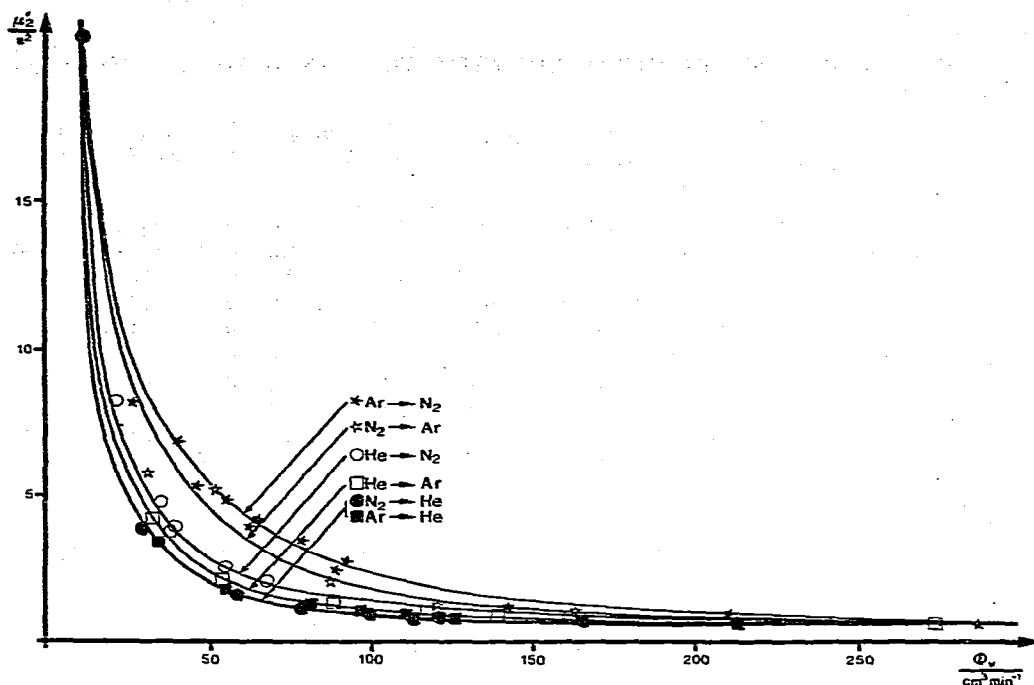


Fig. 6. Second central blank moment. Experimental results with He, Ar and N<sub>2</sub>.

Firstly, blank experiments were carried out. Fig. 5 gives the first moment on the origin with respect to the volumetric flow-rate,  $\Phi_v$ . As might have been expected, all points lie on one curve.

For the six possible pairs of gases, the results with respect to the second moment are given in Fig. 6.

TABLE II

CONDITIONS AND RESULTS OBTAINED WITH COLUMN 6 WITH NITROGEN AS CARRIER GAS

Tracer	Run No.	Temperature (°K)	Pressure (MPa)	Velocity (m sec <sup>-1</sup> )	$\mu_{1,b}$ (sec)	$\mu_{2,b}$ (sec <sup>2</sup> )	$\mu_{1,m}$ (sec)	<i>s</i> (%)	$\mu_{2,m}$ (sec <sup>2</sup> )	<i>s</i> (%)
Helium	402701	323.2	0.795	0.003753	12.3	5.90	1433.0	0.01	2111.0	2.8
	402801		0.795	0.006127	8.30	3.00	878.7	0.03	489.5	3.7
	402901		0.795	0.009362	6.10	1.60	575.7	0.06	152.3	1.8
	402903		0.794	0.01191	4.30	1.30	451.9	0.01	45.19	1.8
	403001		0.793	0.02784	2.00	0.200	193.5	0.13	10.96	1.9
Argon	402401	323.2	0.795	0.004111	11.9	7.60	1309.0	0.01	649.5	7.6
	402501		0.795	0.006228	8.30	4.80	864.5	0.01	221.7	0.43
	402601		0.795	0.009548	5.30	3.10	563.8	0.00	87.54	1.2
	402301		0.798	0.01219	4.20	2.00	441.6	0.02	58.07	1.2
	402303		0.797	0.01934	2.80	0.900	278.5	0.02	29.41	2.4
	403101*		0.793	0.007933	8.30	5.60	727.0	0.01	117.5	0.35

\* Column 8.

TABLE III  
CONDITIONS AND RESULTS OBTAINED WITH COLUMN 8 WITH ARGON AS CARRIER GAS

Tracer	Run No.	Temperature (°K)	Pressure (MPa)	Velocity (m sec <sup>-1</sup> )	$\mu_{1,b}$ (sec)	$\mu'_{2,b}$ (sec <sup>2</sup> )	$\mu_{1,m}$ (sec)	<i>s</i> (%)	$\mu'_{2,m}$ (sec <sup>2</sup> )	<i>s</i> (%)
Helium	403403	323.2	0.795	0.005560	10.8	4.40	1036.0	0.05	743.3	1.9
	403405		0.794	0.009754	6.70	1.70	591.2	0.05	150.0	0.04
	403407		0.794	0.01478	4.60	1.20	390.3	0.05	48.30	0.52
	403501		0.792	0.02527	2.90	0.600	228.5	0.04	13.22	0.89
	403503		0.792	0.03186	2.30	0.400	181.2	0.11	8.084	0.70
Nitrogen	403201	323.2	0.793	0.005196	11.9	7.60	1109.0	0.02	321.1	0.65
	403203		0.793	0.01029	6.10	3.90	560.2	0.03	67.21	0.45
	403205		0.792	0.01413	5.00	2.50	408.4	0.16	41.48	2.4
	403301		0.792	0.01911	3.70	1.25	302.1	0.19	25.44	2.7
	403401		0.791	0.03864	2.00	0.450	149.5	0.06	10.36	0.88

TABLE IV  
CONDITIONS AND RESULTS OBTAINED WITH COLUMN 8 WITH HELIUM AS CARRIER GAS

Tracer	Run No.	Temperature (°K)	Pressure (MPa)	Velocity (m sec <sup>-1</sup> )	$\mu_{1,b}$ (sec)	$\mu'_{2,b}$ (sec <sup>2</sup> )	$\mu_{1,m}$ (sec)	<i>s</i> (%)	$\mu'_{2,m}$ (sec <sup>2</sup> )	<i>s</i> (%)
Argon	403403	323.2	0.795	0.005560	10.8	4.40	1036.0	0.05	743.3	1.9
	403405		0.794	0.009754	6.70	1.70	591.2	0.05	150.0	0.03
	403407		0.794	0.01478	4.60	1.20	390.3	0.05	48.30	0.52
	403501		0.792	0.02527	2.90	0.600	228.5	0.04	13.22	0.89
	403503		0.792	0.03186	2.30	0.400	181.2	0.11	8.084	0.70
Nitrogen	403601	323.2	0.796	0.005901	10.5	3.40	976.6	0.06	569.6	2.2
	403603		0.796	0.009879	6.70	1.00	583.8	0.04	133.0	1.6
	403605		0.795	0.01331	5.20	0.800	433.6	0.03	58.21	0.88
	403607		0.795	0.01671	4.20	0.700	345.3	0.06	32.37	1.4
	403609		0.797	0.03671	2.00	0.600	157.3	0.04	5.690	0.69
Ethene	403803	324.2	0.800	0.008080	10.4	3.80	715.9	0.54	189.2	3.3
	403804		0.799	0.01409	6.00	1.60	410.7	0.11	43.10	0.63
	403805		0.798	0.01734	5.00	1.40	333.7	0.17	26.02	0.22
	403801		0.799	0.02068	4.40	1.10	280.1	0.35	17.71	1.9
	403802		0.797	0.04691	1.60	0.400	123.1	0.03	4.309	0.70
Propene	404201	324.2	0.798	0.006043	13.6	6.30	957.0	0.02	359.7	0.47
	404202		0.797	0.01033	8.40	2.40	560.3	0.03	86.44	1.0
	404203		0.796	0.01435	6.00	1.50	403.4	0.02	38.55	0.32
	404204		0.795	0.01875	4.80	1.30	308.9	0.05	21.53	0.14
	404205		0.796	0.03872	2.00	0.700	149.3	0.06	6.436	0.41
<i>cis</i> -Butene-2	404005	324.2	0.791	0.008678	10.0	4.60	666.9	0.29	118.4	6.5
	404004		0.791	0.01494	6.40	2.20	387.9	0.05	32.20	2.2
	404003		0.790	0.01751	5.00	1.70	330.5	0.09	23.81	4.5
	404002		0.790	0.02202	4.40	1.00	263.3	0.06	15.31	2.9
	404001		0.788	0.05140	1.20	0.500	112.1	0.16	4.575	5.5
2-Methylpropene	404101	324.2	0.802	0.005519	15.0	8.80	1048.0	0.15	397.2	3.7
	404102		0.801	0.009790	10.4	4.40	592.7	0.01	87.52	1.1
	404103		0.800	0.01511	5.60	1.90	382.8	0.04	32.43	0.56
	404104		0.800	0.01928	4.50	1.40	300.2	0.04	20.18	0.38
	404105		0.799	0.04323	1.60	0.070	133.5	0.03	6.117	1.5

TABLE V  
CONDITIONS AND RESULTS OBTAINED WITH COLUMN 8 WITH ETHENE AS CARRIER GAS

Tracer	Run No.	Temperature (°K)	Pressure (MPa)	Velocity (m sec <sup>-1</sup> )	$\mu_{1,b}$ (sec)	$\mu'_{2,b}$ (sec <sup>2</sup> )	$\mu_{1,m}$ (sec)	<i>s</i> (%)	$\mu'_{2,m}$ (sec <sup>2</sup> )	<i>s</i> (%)
Helium	403905	324.2	0.799	0.004343	19.2	14.0	1332.0	0.09	1109.0	2.0
	403904		0.799	0.007862	10.4	6.00	735.6	0.03	229.5	7.4
	403903		0.799	0.01592	5.00	2.60	363.1	0.14	34.92	2.1
	403901		0.798	0.01905	4.40	1.60	303.7	0.02	21.98	4.7
	403902		0.798	0.02581	3.40	0.600	224.3	0.05	11.51	6.5
Propene	405101	324.2	0.794	0.001958	39.0	70.0	2950.0	0.22	3088.0	20.0
	405201		0.795	0.004583	18.0	12.0	1262.0	0.08	347.8	10.0
	405203		0.795	0.01156	10.8	4.40	504.0	0.14	81.32	7.5
	405301		0.794	0.01401	6.00	1.60	413.0	0.15	70.54	3.7
	405303		0.796	0.02021	4.00	1.30	286.2	0.47	29.49	7.4
<i>cis</i> -Butene-2	405910	324.2	0.797	0.004569	14.0	39.0	1262.0	0.66	197.4	1.1
	405801		0.796	0.008640	10.0	20.0	669.9	0.34	140.9	13.0
	406001		0.796	0.01134	7.30	10.0	509.9	0.16	125.6	38.0
	405803		0.795	0.01282	6.50	10.0	451.2	0.30	82.92	18.0
	405701		0.795	0.01945	4.40	3.20	297.5	0.19	36.11	6.1
2-Methylpropene	405401	324.2	0.798	0.004776	18.8	30.0	1213.0	0.22	386.4	2.6
	405501		0.797	0.008624	9.60	15.5	670.7	0.25	191.6	16.0
	405601		0.797	0.01149	7.20	10.0	503.5	0.42	90.83	30.0
	405503		0.796	0.01422	6.00	8.00	406.8	0.15	62.07	20.0
	405603		0.796	0.01929	4.40	2.50	299.9	0.62	45.67	4.9
[ <sup>14</sup> C]Ethene	410603	254.2	0.802	0.008974	5.60	4.10	641.8	—	114.9	—
	410602		0.802	0.01103	5.50	3.10	522.5	—	121.4	—
	410601		0.801	0.01533	4.10	2.60	376.0	—	82.20	—
	410604	314.2	0.798	0.02391	3.00	1.60	241.5	—	51.77	—
	410304		0.802	0.006373	12.4	12.0	907.0	—	229.5	—
	410303		0.801	0.01369	5.60	3.20	421.9	—	79.70	—
	410302		0.800	0.01861	4.50	2.80	310.8	—	71.50	—
	410301		0.800	0.02283	3.60	2.40	253.3	—	49.34	—
	410404	573.2	0.804	0.01171	12.2	11.2	499.1	—	672.5	—
	410403		0.803	0.02244	6.20	3.80	260.2	—	19.60	—
	410402		0.802	0.02769	4.90	2.90	210.8	—	14.72	—
	410401	760.2	0.801	0.03611	4.20	2.60	162.1	—	11.99	—
	410504		0.803	0.01506	14.8	16.0	393.4	—	98.40	—
	410503		0.802	0.02161	6.20	3.80	181.0	—	12.57	—
	410502		0.801	0.04140	4.90	2.80	142.6	—	8.148	—
410501	0.801		0.05161	4.10	2.60	113.4	—	6.382	—	

It is obvious that there are differences between the pairs used. This is due to differences in the diffusion constants, the viscosities of the carrier gases and the sensitivity of the thermal conductivity cell for the pairs involved.

Experimental results are given in Tables II–VII.

To check the results with theoretical predictions,  $D_{12}$  values were calculated according to the HBS and FSG equations. The results of the calculations and theoretical values are given in Table VIII, and Fig. 7 gives a plot of the  $\mathcal{D}$  values obtained as function of  $v^2$ .

TABLE VI

CONDITIONS AND RESULTS OBTAINED WITH COLUMN 8 WITH PROPENE AS CARRIER GAS

Tracer	Run No.	Temperature (°K)	Pressure (MPa)	Velocity (m sec <sup>-1</sup> )	$\mu_{1,b}$ (sec)	$\mu'_{1,b}$ (sec <sup>2</sup> )	$\mu_{1,m}$ (sec)	<i>s</i> (%)	$\mu'_{2,m}$ (sec <sup>2</sup> )	<i>s</i> (%)
Helium	404410	324.2	0.791	0.004994	15.2	10.4	1157.0	0.15	685.8	6.4
	404710		0.792	0.01063	7.60	3.40	543.8	0.04	101.2	5.8
	404801		0.792	0.01359	5.80	2.40	425.2	0.13	57.11	13.0
	405010		0.788	0.01837	4.40	2.40	314.8	0.13	36.12	32.0
Ethene	405101	324.2	0.794	0.001958	39.0	70.0	2950.0	0.22	3088.0	19.0
	405201		0.795	0.004583	18.0	12.0	1262.0	0.08	347.8	10.0
	405203		0.795	0.01156	10.8	4.40	504.0	0.14	81.32	7.5
	405301		0.794	0.01401	6.00	1.60	413.0	0.15	70.54	3.7
	405303		0.796	0.02021	4.10	1.30	286.2	0.47	29.49	7.4
[1,3-di- <sup>14</sup> C] Propene	401705	327.2	0.801	0.008810	15.6	19.7	663.0	—	647.4	—
	401701		0.791	0.01121	11.1	11.1	519.5	—	508.4	—
	401704		0.810	0.01766	6.52	4.73	329.3	—	322.8	—
	401702		0.805	0.02380	5.04	2.89	244.5	—	239.4	—

From Table VIII, it can be seen that the binary diffusion constants are only slightly dependent on concentration; the difference between the two opposite combinations of each pair of gases is within the accuracy of the experiments (5%).

It is always difficult to compare measured diffusion constants with those reported in the literature because the experimental conditions are seldom identical. Extrapolation to different conditions is possible only when it can be assumed that a certain relationship holds. We applied the HBS and FSG equations to make these comparisons possible. From Table VIII, it can be concluded that our results agree closely with those predicted by both equations. In order to compare our results with literature data, diffusion constants reported in the literature<sup>1,22,32,33</sup> for N<sub>2</sub> → He, He → N<sub>2</sub> and Ar → He were also compared with predictions from these equations under the reported experimental conditions. The average deviation was 4% with respect to the HBS equation and 3% for the FSG equation, while our own results showed deviations of 2 and 3%, respectively. The deviations between A → B and

TABLE VII

CONDITIONS AND RESULTS OBTAINED WITH COLUMN 8 USING KRYPTON AS CARRIER GAS AND KRYPTON-85 AS TRACER

Run No.	Temperature (°K)	Pressure (MPa)	Velocity (m sec <sup>-1</sup> )	$\mu_{1,b}$ (sec)	$\mu'_{1,b}$ (sec <sup>2</sup> )	$\mu_{1,m}$ (sec)	<i>s</i> (%)	$\mu'_{2,m}$ (sec <sup>2</sup> )	<i>s</i> (%)
313203	336.0	0.709	0.00922	11.9	12.0	629.9	0.81	314.9	8.9
313204		0.709	0.00944	11.9	12.0	616.0	0.15	270.6	14.0
313206	336.0	0.709	0.00974	11.7	10.9	597.3	0.23	223.2	3.4
313205		0.710	0.00988	11.7	10.9	588.9	0.21	235.5	11.0
313202		0.703	0.0135	7.8	7.1	430.6	0.49	183.1	4.4
313201	336.0	0.700	0.0161	6.8	4.5	362.0	0.39	137.5	9.9

TABLE VIII

BINARY DIFFUSION CONSTANTS ( $10^{-6} \text{ m}^2 \text{ sec}^{-1}$ ) FOR THE POSSIBLE COMBINATIONS OF He, Ar AND  $\text{N}_2$

Pressure, 0.80 MPa; temperature, 344 °K; columns, 6 and 8. Theoretical values calculated from eqn. 6 (FSG) and eqns. 7 and 8 (HBS).

System	Algebraic method		Graphical method		HBS: $D_{12}$	FSG: $D_{12}$
	$D_{12}$	$\frac{1}{2}(D_{12} + D_{21})$	$D_{12}$	$\frac{1}{2}(D_{12} + D_{21})$		
$\text{N}_2 \rightarrow \text{He}$	10.2	10.2	10.2	10.2	10.5	10.3
$\text{He} \rightarrow \text{N}_2$	10.3		10.1	10.2		
$\text{N}_2 \rightarrow \text{Ar}$	2.96	3.02	3.10	3.15	3.08	2.94
$\text{Ar} \rightarrow \text{N}_2$	3.08		3.21	3.15		
$\text{He} \rightarrow \text{Ar}$	11.2	11.0	11.0	10.8	10.8	10.6
$\text{Ar} \rightarrow \text{He}$	10.7		11.6	10.8		

$\text{B} \rightarrow \text{A}$  for a particular pair of gases, as can be seen in Fig. 7, can easily be explained by the fact that two different columns were used. As the columns have different diameters, the slopes of the curves will be different, as can be seen from eqn. 14.

The relative independence of the diffusion constant of the concentration reported here is in good agreement with the results of a study made by Carson and Dunlop<sup>34</sup>. They found in experiments with helium as the tracer gas and a mixture of argon and helium as the carrier gas that the diffusion constant varied by only a few percent, whereas the molar fraction of argon varied from 0.08 to 0.95. Also, Giddings and Seager<sup>26</sup> found for the systems helium–nitrogen and helium–carbon dioxide that differences in concentration influence the binary diffusion coefficient, but not by more than a few percent.

From these results, the conclusion can be drawn that the determination of diffusion constants by means of gas chromatographic techniques, combined with the

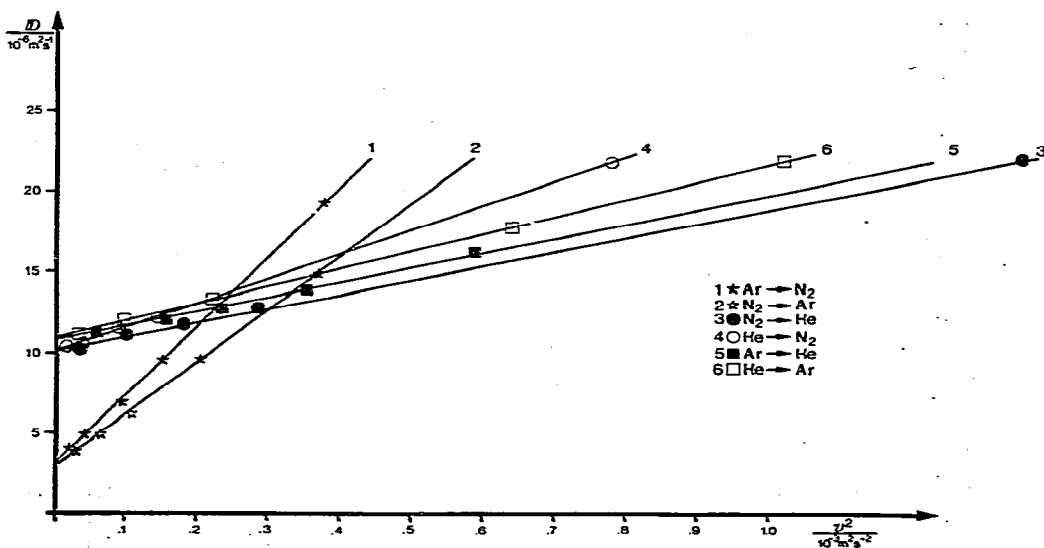


Fig. 7. Results of the experiments with He, Ar and  $\text{N}_2$ . Intercept =  $D_{12}$ .

method of moment analysis, results in reliable diffusion constants if the approach presented here is followed.

### Experiments with alkenes

The results of the measurements are given in Tables IV–VI, from which it is clear that the values for the blank first moments are higher than the experimental values with helium, argon and nitrogen. These differences are due to the application of a different set of column junctions in these experiments. This also influences the results for the second central moment with respect to the blank experiments. Moreover, the accuracy of the detector is lower for the alkene  $\rightarrow$  alkene systems, as the differences in thermal conductivities are small; if an alkene is used as the carrier gas, the stability of the detector is also lowered. This particularly influences the accuracy of the second central moment. In agreement with this is the fact that the spread for the blank second moments is lower in instances when helium is used as the carrier gas than when an alkene is used.

The resulting diffusion constants and the theoretical values are summarized in Table IX, and Fig. 8 is a plot of the dispersion coefficient as a function of  $v^2$ .

In this instance also the results for the pairs A  $\rightarrow$  B and B  $\rightarrow$  A do not coincide exactly. Here it cannot be explained by the use of different columns with different diameters. Probably the convective term in the model of Taylor and Aris<sup>27,28</sup> is not completely correct for these systems, because the intercept that represents the situation for  $v = 0$ , where diffusion is the only process that takes place, is nearly the same for both cases.

It can be concluded that the relationship of Fuller *et al.*<sup>15</sup> matches the results slightly better than the relationship of Hirschfelder *et al.*<sup>17</sup>. Further, the relationships of Gilliland<sup>13</sup> and Arnold<sup>12</sup> were tested but proved to be inadequate, giving large deviations from the experimental results, as could be expected. The results from the graphical method are more consistent than those from the algebraic method. Also in

TABLE IX  
BINARY DIFFUSION CONSTANTS ( $10^{-6} \text{ m}^2 \text{ sec}^{-1}$ ) FOR THE EXPERIMENTS WITH ALKENES

Pressure, 0.80 MPa; temperature, 344 °K; column, 8. Theoretical values calculated from eqn. 6 (FSG) and eqns. 7 and 8 (HBS). Et = ethene; Pr = propene; He = helium; cB = *cis*-butene-2; iB = *iso*-butene. Accuracy: algebraic method, 15%; graphical method, 5% with He and 7.5% with other gases.

System	Algebraic method		Graphical method		$D_{12}$ (HBS)	$D_{12}$ (FSG)
	$D_{12}$	$\frac{1}{2}(D_{12} + D_{21})$	$D_{12}$	$\frac{1}{2}(D_{12} + D_{21})$		
Et $\rightarrow$ He	7.48	7.87	7.60	7.84	8.39	7.32
He $\rightarrow$ Et	8.26		8.07			
Pr $\rightarrow$ He	6.43	8.57	6.40	6.33	7.03	5.94
He $\rightarrow$ Pr	10.7		6.27			
Et $\rightarrow$ Pr	—	1.48	1.49	1.42	1.43	1.49
Pr $\rightarrow$ Et	1.48		1.34			
cB $\rightarrow$ He	5.54		5.31		6.31	5.10
iB $\rightarrow$ He	5.20		5.17		6.23	5.10
cB $\rightarrow$ Et	1.33		1.33		1.24	1.27
iB $\rightarrow$ Et	1.45		1.44		1.24	1.27

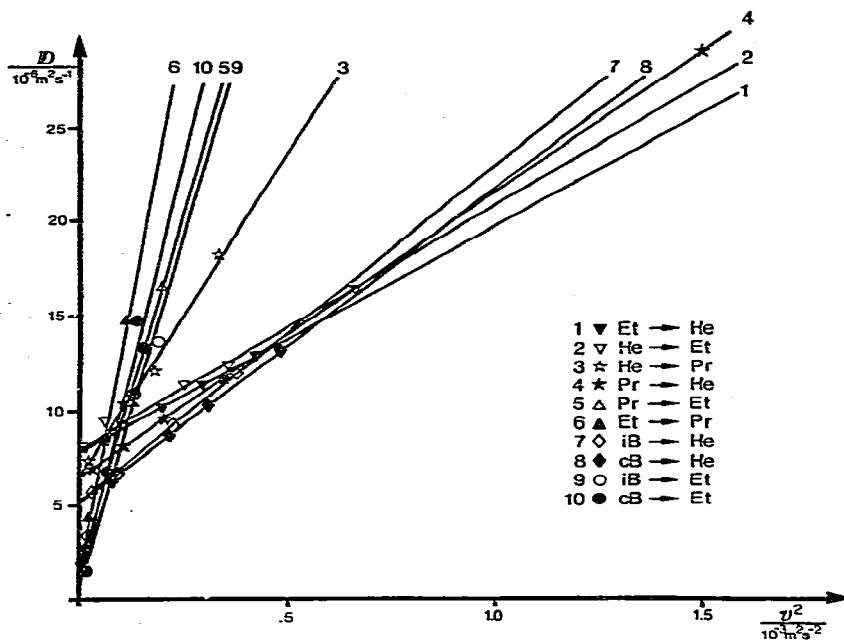


Fig. 8. Results of experiments with alkenes. Intercept =  $D_{12}$ . He = helium; Pr = propene; Et = ethene; cB = *cis*-butene-2; iB = isobutene = 2-methylpropene.

these experiments, with the low mean gas velocities used here, it can be seen that the Aris and Taylor relationship<sup>27,28</sup> gives good agreement with the experimental data.

#### Self-diffusion constant and temperature dependence

The self-diffusion constants for ethene, propene and krypton were measured using radioactively labelled gases. The radioactive species was always used as the tracer gas and the unlabelled compound as the carrier gas. With the pair [<sup>14</sup>C]-ethene → ethene we also checked the temperature dependence of the diffusion constant. In our opinion this is the best method of correlating the temperature function as the system is better defined than for a carrier gas with a different tracer gas which obviously have different physical properties (viscosity, density, etc.). Further, there is a possibility that those differences may be functions of the temperature. Therefore,

TABLE X

SELF-DIFFUSION CONSTANTS ( $10^{-6} \text{ m}^2 \text{ sec}^{-1}$ ) FOR THE EXPERIMENTS WITH RADIOACTIVELY LABELLED TRACERS

Pressure, 0.80 MPa; column, 8. The experimental values were determined by the graphical method.

System	$T$ (°K)	$D_{12}$ (exp.)	$D_{12}$ (HBS)	$D_{12}$ (FSG)
*Et → Et	254	$1.20 \pm 0.06$	1.15	1.19
*Et → Et	314	$1.77 \pm 0.09$	1.73	1.73
*Et → Et	573	$4.9 \pm 0.3$	5.21	4.94
*Et → Et	760	$8.5 \pm 0.8$	8.55	8.10
*Pr → Pr	327	$11.5 \pm 0.5$	—	11.67
*Kr → Kr	336	$1.7 \pm 0.15$	1.70	1.69

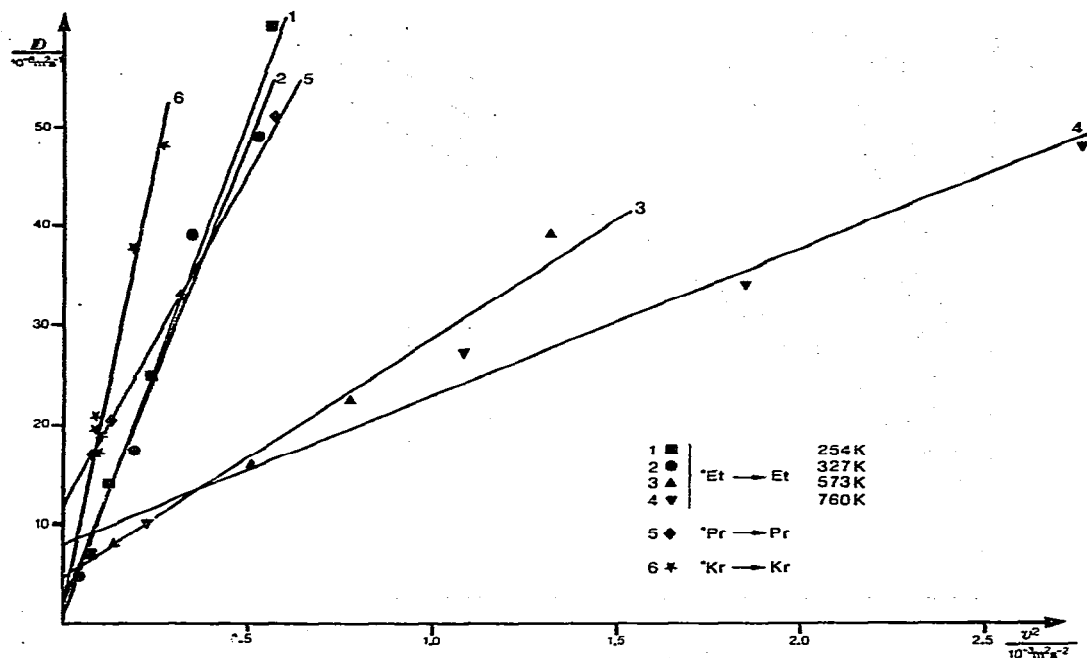


Fig. 9. Results of experiments with labelled tracers. Intercept =  $D_{11}$ . The labelled species are marked with asterisks.

we checked the temperature dependence of the diffusion constant with ethene as carrier gas and  $^{14}\text{C}$ ethene as tracer gas. Except for a change of detector<sup>21</sup>, the experiments were carried out in the same way as the previous experiments. The results are given in Table X and Fig. 9.

From the results, it can be concluded that the performance of the detector system for the radioactively labelled tracers is as good as the thermal conductivity cell for the normal gases investigated. The Aris and Taylor model<sup>27,28</sup> also gives good results. Only at the highest temperatures is an increase in spread observed. This can be attributed to the thermal instability of the fluid-bed oven used in the experiments at higher temperatures. Only the graphical solution was used.

In addition to the calculations reported in Table X, we also linearized the function  $D_{12} = aT^b$  in order to find the temperature dependence:

$$\ln D_{12} = \ln a + b \ln T \quad (18)$$

The results obtained using eqn. 18 are given in Fig. 10, from which it can be concluded that although the accuracy of the binary diffusion constants is about 7.5%, the correlation of the data is reasonable.

The results of linear regression analysis based on the least-squares method are given in Table XI, together with the theoretical values based on the relationship of Fuller *et al.*<sup>15</sup>.

These results are in good agreement with those reported by Huang *et al.*<sup>35</sup>, who found a value for  $b$  varying from 1.71 to 1.75, with an accuracy of 0.02. Thus, the temperature function reported by Huang *et al.* can be represented by  $T^{1.73 \pm 0.05}$ ,



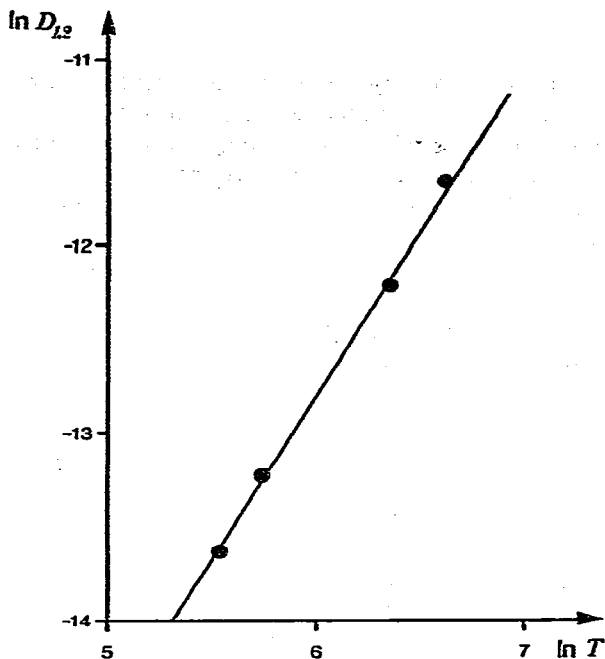


Fig. 10. Temperature dependence of the self-diffusion constant of ethene.

whereas we obtained  $T^{1.76 \pm 0.01}$ . The greater accuracy of our results is mainly due to the fact that we studied a wider range of temperatures (254–760 °K) than Huang *et al.* (298–423 °K). Obviously the relationship of Fuller *et al.* gives the best description of the results. However, deviations found with respect to the relationship of Hirschfelder *et al.* are not large enough to reject their theory.

#### *Influence of coiling*

One of the possible errors in experiments for the measurement of diffusion constants is the effect of the coiling of the applied columns. The coil diameter of both columns was 85 mm. From Figs. 7, 8 and 9 it can be seen that the plots of the dispersion coefficient as a function of the square of the velocity are straight lines. This means that the Taylor and Aris relationship<sup>27,28</sup> holds in the range of our measurements. This conclusion is also supported by the study on the influence of coiling<sup>30</sup>. As a result of the measurements in that investigation, we stated that the influence of coiling can be neglected for  $De < 10$ . For columns 6 and 8 used in this study, this means  $Re < 40$ , which is fulfilled in our experiments.

TABLE XI

COMPARISON OF THE RESULTS OF THE LINEAR REGRESSION ANALYSIS WITH THE THEORETICAL VALUE ACCORDING TO EQN. 6 (FULLER *et al.*)

Derivation	$a$	$b$	Correlation coefficient
From Fig. 10	-23.40	1.76	0.9995
Theoretical value from FSG equation	-23.33	1.75	1.0

## CONCLUSIONS

(1) The determination of diffusion constants by gas chromatography, combined with the method of moment analysis, is a simple and reliable method.

(2) The diffusion constants of pairs of gases with helium, argon and nitrogen as components agree with literature values, within the experimental error.

(3) The temperature dependence of the diffusion constant can be written as  $D_{12} = D_{12}^0 T^{1.75}$ , where  $D_{12}^0$  is a constant.

(4) The means of calculating diffusion constants from the second moment is by extrapolation to zero velocity.

(5) Both the semi-empirical relationship of Fuller *et al.*<sup>15</sup> and the theoretical relationship of Hirschfelder *et al.*<sup>17</sup> predict reliable diffusion constants.

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