

## MEASUREMENT OF DIFFUSION COEFFICIENTS VIA DIFFUSION IN FLOWING GAS\*

### I. METHOD

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Diffusion of gases was investigated by a method in which one gas ("admixture gas") in a tube diffuses against a constant flow of another gas ("main gas") in such a way that a stationary concentration distribution builds up. The (exponential) upstream decrease in concentration of the admixture gas was measured. This decrease, together with the flow velocity, gives the diffusion coefficient. This so-called back-diffusion method is suitable for use with gases up to high temperatures. The apparatus consisted basically of a straight tube for the main gas flow, with four narrow extraction holes to permit mass spectrometric analysis of the local gas mixture, and a side tube at one end to admit the admixture gas. The tubes, made of fused silica, were in a furnace.

A description is given of the apparatus and the measuring procedure, and it is shown how the diffusion coefficient can be calculated from the measured quantities. At the end of this paper the results of the measurements of helium (<1%) in krypton (>99%) at temperatures from 300 to 1300 K are given in detail. A subsequent paper will deal with other gas combinations.

### 1. Introduction; objectives

Several methods which are very suitable for the measurement of diffusion coefficients at room temperature present technical difficulties at much lower or much higher temperatures, e.g. at 1000°C. This is particularly true with regard to methods where the two gases are at first in separate vessels linked by a valve. It is very difficult to ensure the proper functioning of such a valve at extreme temperatures. No problem of this kind does arise with the cataphoresis method proposed by Freudenthal [3] and used by Hogervorst [2]. With this method at the start of the measurement a partial separation is brought about in a gas mixture by means of an electric current (a discharge). Determination of the mixture composition as a function of time after the discharge has been switched off gives the diffusion constant. This method proved very useful for noble gases at moderate and at high temperatures. Other gases, however, were sometimes absorbed by the electrodes and/or the tube wall, which hindered the

measurements. Therefore we preferred a measuring method that did not involve a discharge and yet was practicable at extreme temperatures. We came to a method in which one gas diffuses into a steady stream of another gas. Measurements of the stationary gas composition at upstream points give the quotient of diffusion constant and stream velocity.

As appears from literature this back-diffusion method has been used by Harteck and Schmidt [4] for the determination of diffusion coefficients of hydrogen isotopes at low temperatures. Hertz [5], Eindhoven, had proposed the method originally as a gas separation method. Later on the principle was applied by van der Held and Spier [6, 7]. In their treatise on diffusion Mason and Marrero [8] mention the method as being a good one for measurements at extreme temperatures and they say that it deserves a wider application.

The aim of our investigation was to see whether the back-diffusion method is in fact useful for the measurement of diffusion coefficients at high temperature. For this purpose we chose to study the diffusion of noble gases at temperatures between 300 and 1300 K.

\* Adapted version of part of the thesis of K. W. Reus [1].

In this way we were able to compare our results with those of other methods, especially with the results that Hogervorst [2, 9] obtained with the cataphoresis method.

## 2. Principle of the apparatus and of the theory

Fig. 1a shows the scheme of the essential part of the back-diffusion apparatus. Through the tube  $XY$  there is a laminar flow of "main" gas with velocity  $\bar{v}$  to the right. At point  $x = 0$  "admixture" gas comes in through tube  $Z$ . At this mixing place an admixture concentration  $n(0)$  builds up. In our measurements  $n(0)$  was relatively low, about 1% of the main gas. The admixture gas flows away along with the main gas through tube  $Y$ . Due to the diffusion, with diffusion coefficient  $D$ , in tube  $X$  there will be an admixture concentration  $n(x)$  in every cross section, from  $n(0)$  decreasing to the left, cf. fig. 1b.

Let us consider the situation in tube  $X$  in more detail. The downstream throughput (volume  $\times$  pressure / time) of admixture gas  $\phi_v$  through a cross section  $Q$  of  $X$ , due solely to the laminar flow of the mixture, is found by integration over that cross section:

$$\phi_v = \iint_Q v n \, dq,$$

where  $dq$  is an area element of the cross section. The upstream transport  $\phi_d$  of admixture gas relative to the mixture, due to the diffusion, is found by

$$\phi_d = \iint_Q D \cdot \left( -\frac{dn}{dx} \right) dq.$$

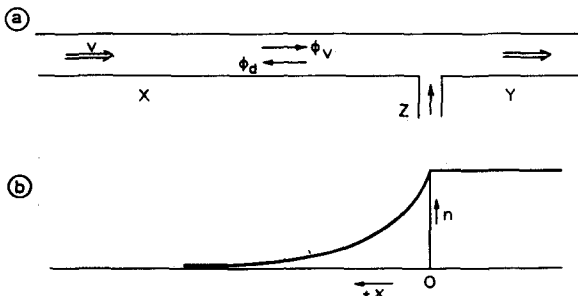


Fig. 1. a) Admixture gas transport (single arrow) and main gas flow (double arrow) in a back-diffusion set-up. b) Admixture gas concentration  $n$  in the  $X$ - and  $Y$ -tubes as a function of the distance  $x$  from the point of admixture gas inlet.

Both types of transport occur simultaneously in the stationary state. The net transport through  $Q$  must be zero, so  $\phi_v = \phi_d$  and it follows that

$$\iint_Q \left( v n + D \frac{dn}{dx} \right) dq = 0. \quad (1)$$

Because in our measurements the values for the longitudinal coordinate  $x$  are always considerably greater than the tube diameter, it can be said that  $n$ , as well as  $dn/dx$ , are constant over a cross section, in good approximation. In addition, because of the low admixture gas concentration and the practically constant gas pressure and constant temperature,  $D$  is constant along the whole tube length. So formula (1) can be simplified to

$$n \iint_Q v \, dq + QD \frac{dn}{dx} = 0 \quad \text{or} \quad n \bar{v} + D \frac{dn}{dx} = 0, \quad (2)$$

where  $Q$  is the area of a tube cross section and  $\bar{v}$  the flow velocity averaged over the cross section. As  $v$  and  $D$  are independent of  $x$ , the solution of form. (2) is:

$$n(x) = n(0) \exp(-x\bar{v}/D). \quad (3)$$

The flow velocity,  $\bar{v}$ , can be determined by measuring the amount of gas,  $G$  (pressure  $\times$  volume at tube temperature), which passes per second through a cross section of tube  $X$ . Then the expression  $\bar{v} = G/Qp$  holds, in which  $p$  is the gas pressure. So form. (3) can be written as

$$n(x) = n(0) \exp(-xG/QpD). \quad (4)$$

Measurement of  $G$ ,  $Q$  and the admixture gas concentration ratio  $n(x)/n(0)$  (or  $n(x)/n(x')$ ) thus gives  $pD$ .

Naturally there are radial concentration differences due to the sideways influx of admixture gas and to the fact that the velocity  $v$  is smaller at the tube wall than on the axis. However, the condition of constant admixture gas concentration over a tube cross section can be fulfilled satisfactorily through an appropriate choice of the velocity  $\bar{v}$  in relation to  $D$  and to the dimensions of the flow tube  $X$ . If the characteristic diffusion length  $D/\bar{v}$  is much greater than the tube radius, one

can expect that radial concentration differences will be small enough to be neglected. This hypothesis was confirmed by numerical estimates about the radial transport and also by a more complete theory about the longitudinal and radial concentration distribution [1].

### 3. Apparatus

#### 3.1. The flow tubes and the inlet and outlet system

Fig. 2 shows the flow tube in which the diffusion process takes place, its inlet and outlet tubes and the extraction holes. In fact the furnace contains two flow tubes. They are cylindrical tubes made of fused silica and have a length of 88 cm and internal diameters of 5.11 and 3.11 mm, respectively. Tubes and furnace will withstand temperatures of up to more than 1300°C. The tubes are connected to each other at one end by a third silica tube through which the gas is pumped away. The other ends of the two tubes are outside the furnace where they are connected to a system of cocks with which it is possible to select the broad tube for the main gas and the narrow one for the admixture gas or vice versa. This switching possibility permits checks to be made.

In both tubes there are four extraction holes. These are very narrow channels through the tube walls which permit a small sample of the gas to be extracted in order to measure the local composition of the gas in the flow tube. The distance from the connection between the two tubes to the first extraction is 45 mm in the case of the wide tube, and 90 mm in the case of the narrow one. The distances between the successive extraction holes are 97.5 mm and 149.1 mm and

149.8 mm respectively in the wide tube and 99.5 mm, 149.5 mm and 150.5 mm respectively in the narrow tube. To each hole a three way cock is connected, by means of which the extracted gas is fed to a mass spectrometer for analysis or to an oil diffusion pump that pumps the gas away.

#### 3.2. The construction of the extraction holes

The holes had to satisfy three requirements: they had to (a) be able to withstand high temperatures, (b) have a very small diameter, (c) be constructed in such a way that the inside wall of the flow tube remained undistorted. After several methods of obtaining suitable holes had been investigated a method was chosen in which a laser "shoots" the holes in the tube wall. The glass-technology department of Philips Natuurkundig Laboratorium in Waalre was able to make the desired holes in a 5 mm thick silica wall. For this purpose first a little silica cylinder was fused to the tube at a place where a hole had to be formed. This cylinder was drilled in such a way that 5 mm silica was left between the bore and the inside of the tube wall; see fig. 3. Thereafter this silica layer was perforated with the laser. It was possible then to fuse a connection tube to the cylinder without damaging the extraction hole or the flow tube. The result was a set of holes in the form of channels with a diameter of less than 40  $\mu\text{m}$  at the inside wall of the flow tube and a conductance of about  $2 \times 10^{-3} \text{ cm}^3/\text{s}$ . Nevertheless it was found necessary to make some corrections owing to the fact that some of the holes were not narrow enough (see section 7). It must be stated that shorter channels with smaller diameters and somewhat lower conductance would have been better for our purpose.

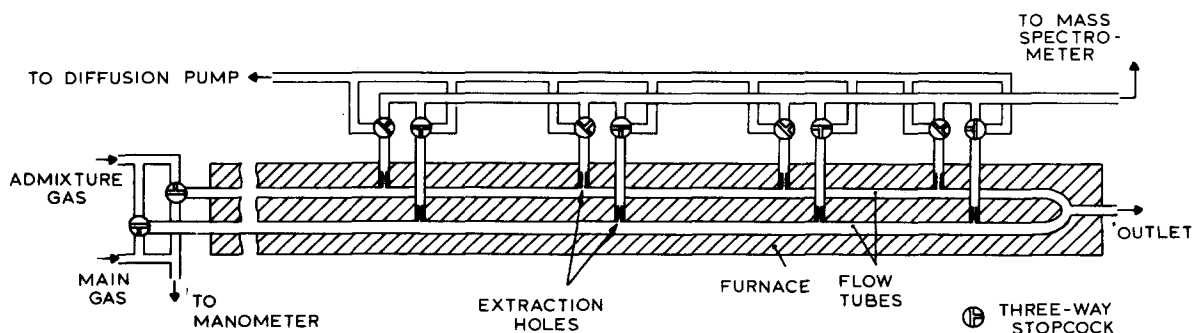


Fig. 2. The two flow tubes in the furnace, with their extraction holes and connections. Dimensions: see sect. 3.1.

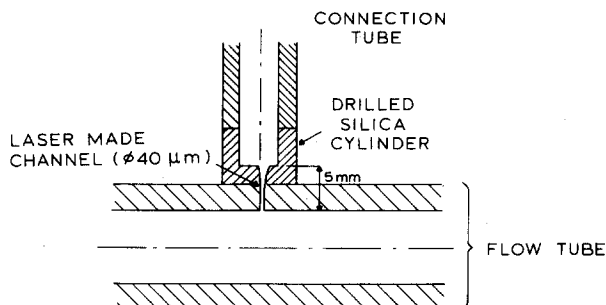


Fig. 3. Scheme of the extraction hole construction.

### 3.3. The control of gas pressure and gas flow

Fig. 4 shows a rough scheme of the control system for the main gas and the admixture gas.

At the inlet to the flow tube the desired pressure  $p$  of the main gas (in our measurements usually 1 to 20 Torr) was established and held constant with an automatic pressure controller driven by a capacitance manometer. The capacitance manometer was connected to the flow tube at one side, and to high vacuum at the other side of its membrane. As the pressure drop along the flow tube is very small, the pressure at the outlet of the flow tube is practically equal to  $p$  and is thus kept constant by the automatic pressure controller too.

At the outlet of the flow tube a needle valve forms the connection with a diffusion pump which extracts the gas. The desired main gas velocity  $\bar{v}$  (in our measurements 2 to 20 cm/s) is established via the gas throughput  $G$  (usually between 1 and 60 Torr cm<sup>3</sup>/s)

which is held constant with the needle valve. This functions because the pressure in front of the valve is constant ( $p$ ) and behind the valve negligibly small (about  $10^{-4}$  Torr).

The supply of admixture gas is kept constant with a second needle valve which is connected to a gas supply vessel. The amount of admixture gas in this vessel is so large (0.5 to 1 Torr m<sup>3</sup>) that the very small admixture gas flow does not cause a measurable pressure change during a series of diffusion measurements.

### 3.4. The measurement of the gas flows and gas composition

The gas supply vessel for the main gas is connected via a stopcock to a vessel with a precisely known volume (2495 cm<sup>3</sup>). From this second vessel the gas passes via the servo needle valve of the automatic pressure controller to the flow tube. A capacitance manometer (MKS Baratron) measures the pressure difference between the two vessels; see fig. 4. After the stopcock has been closed, the output signal of the manometer is recorded as a function of time. If the flow velocity is constant and there is a constant temperature in both vessels, then a straight line is registered. The gas throughput  $G_T$  from the vessel of known volume with temperature  $T_T$  is found by multiplying the measured pressure drop per unit of time by the known volume. The throughput  $G$  passing the flow tube with temperature  $T$  then follows via the relationship  $G/G_T = T/T_T$ .

In order to correct for possible deviations from molecular flow that result from the widths of the ex-

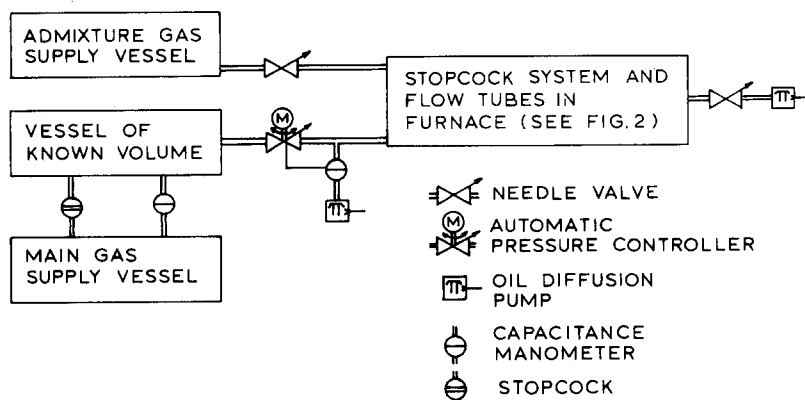


Fig. 4. Scheme of gas flow control and gas flow measurement.

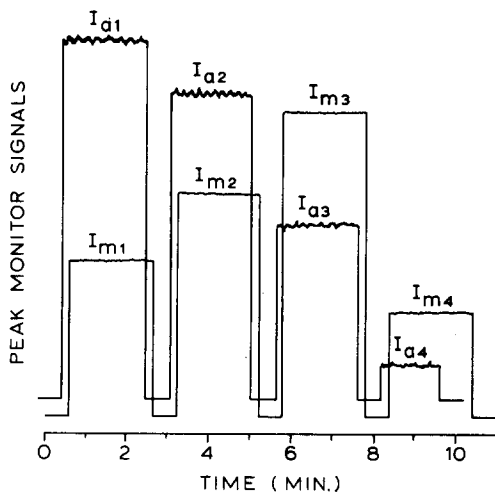


Fig. 5. Peak monitor signals recorded with a two-pen recorder. m = main gas; a = admixture gas; 1 . . . 4 = extraction hole number.

traction holes (section 7) it is necessary to know the throughput of the extraction holes. The total throughput of all the extraction holes together is found by closing the needle valve in the gas outlet tube, cutting off the admixture-gas supply, and measuring the gas throughput by the method described above. At the same time the mass-spectrometer signal is registered for each extraction hole in turn. As this signal is proportional to the gas throughput passing the extraction hole this throughput can easily be calculated.

The local gas composition in the flow tube is measured via the extraction holes, with the help of a quadrupole mass spectrometer (Riber QMM 17) equipped with two peak monitors. Each peak monitor gives a signal that is proportional to the height of the main- or admixture-gas peak in the mass spectrum. The peak-monitor signals are fed into a low pass filter and then registered on a two pen-recorder; see fig. 5. In this way it is also possible to check whether the stationary state has been achieved.

### 3.5. The control and measurements of the temperature

The flow tubes are in an electrically heated furnace, the temperature of which can be varied from room temperature up to 1300 K and beyond.

The temperature is measured with chromel-alumel thermo-couples. By replacing the thermo-couples we verified that they showed no ageing effects.

With the use of a temperature control unit the temperature variations were limited to less than 1 degree during long periods. By placing extra heating coils at the extremities of the furnace we were able to restrict temperature differences over the tube length to 1 degree.

Given the wall thickness and the flow velocities the length of the tube in the furnace preceding the measuring trajectory is amply sufficient to eliminate temperature differences of more than 1 degree between oven and gas.

## 4. Choice of values for the parameters

**Gas pressure.** We aimed at obtaining a viscous flow in the flow tube and a molecular flow through the extraction holes. To achieve this the gas pressure in the flow tube has to be chosen in such a way that for both components in the gas mixture the mean free path of the atoms is small with respect to the diameter of the flow tube (5 or 3 mm, see section 3.1) and is big with respect to the diameters of the extraction holes ( $<0.04$  mm, see section 3.2). A complicating factor here is that the two mean free paths can differ considerably (e.g. He in Xe 0.08 mm but Xe in Xe 0.03 mm, both at 1 Torr and 300 K). To fulfil the above requirements as well as possible over the whole temperature range of 300 to 1300 K we had to increase the pressure with increasing temperature in such a way that the mean free paths were kept approximately constant; cf. table I.

**Flow velocity.** One finds the diffusion coefficient  $D$  by determining the relative concentration gradient of the admixture gas through measuring the ratio  $n_j/n_i$  of the admixture gas percentages at two extraction holes in relation to the distance  $x_j - x_i$  between the holes (see sect. 2). For an accurate determination of the diffusion coefficient  $D$  the difference between the admixture gas percentage at the first and at the last extraction hole had to be sufficiently large, but not too large. The most suitable value of the quotient  $n_1/n_4$  turned out to be between 4 and 10. According to form. (3)  $\ln(n_1/n_4)$  is proportional to  $\bar{v}/D$ , so it is possible to give  $n_1/n_4$  the desired value by an appropriate choice of the velocity  $\bar{v}$ . In our experiment we increased  $\bar{v}$  with temperature and thus we kept  $\bar{v}/D$  about constant for the measurements from 300 to 1300 K; cf. table I.

**Percentage of admixture gas.** The supply of admixture gas was generally chosen such that the concentration of the admixture gas at the first extraction hole was about 1%. Due to the limitations of the mass spectrometer a much lower level would result in an inaccurate determination of the gas ratio at the fourth extraction hole. On the other hand, at a much higher level the diffusion coefficient at the first extraction hole would differ perceptibly from that at the last hole. The reason for this is that the diffusion coefficient depends (slightly) on the composition of the gas mixture. This difference of diffusion coefficient would complicate the interpretation of the measurements.

**Temperature.** Measurements were performed at room temperature and above. Cooling of the gas was not considered because we were interested in the  $D$  values at high temperatures rather than in those at low temperature [10]. As an upper temperature limit we took 1300 K so that we could use the furnace and the tube over a long period without risk of damage.

**Dimensions of the apparatus.** Given the apparatus available, the length of the flow tubes and of the furnace was not a free parameter. But one might wonder whether for example it would be possible to reduce the apparatus by a factor of 2, so to reduce the length to about 0.5 m. In order to avoid a radial concentration gradient (cf. sect. 2) the diameter of the flow tube would have to be reduced as well, for example to 2 mm. To fulfil the requirements with respect to the mean free path (cf. sect. 4) the gas pressure would have to be a factor of 2 higher. This would halve  $D$ . As the distance between the extraction holes would be halved too, the desired admixture concentration ratio ( $n_1/n_4 \approx 4$  to 10) would be achieved at an unchanged velocity  $\bar{v}$ . All this seems possible. Advantages: lower energy demand due to shorter length of the furnace and lower gas consumption (despite the higher pressure) due to the smaller tube cross section. Drawback: need for extraction holes with smaller diameters, which are difficult to make.

## 5. Diffusion measurement procedure

We started each measurement by setting the furnace at the desired temperature. The temperature was regulated by a control unit. About half an hour was needed to achieve a constant temperature. The main gas pressure was controlled with the automatic pressure con-

troller (cf. sect. 3.3). The pressure had to be such that the mean free paths of the gas atoms had a suitable value (between tube diameter and extraction hole diameter, cf. sect. 4). Then by means of the needle valve at the outlet of the flow tube the flow velocity was set to an appropriate value (cf. sect. 3.3). The velocity was chosen such that a favourable concentration gradient built up (cf. sect. 4). The admixture gas supply rate was adjusted with the relevant needle valve (cf. sect. 3.3). We aimed at an admixture gas concentration of about 1% at the first extraction hole (cf. sect. 4). After that we had to wait until a stationary state was reached. The criterion for the stationary state was the fact that over a 10 min period (the time needed for one measurement; cf. fig. 5) the admixture gas concentration did not change noticeably (less than 1%).

The measurement proper consisted of recording the peak heights of the main and admixture gas through each of the four extraction holes: see fig. 5 ( $I_{mj}$  and  $I_{aj}$ ). During the period that one hole was connected with the mass spectrometer, the other ones were connected with the diffusion pump (cf. fig. 2), so the experimental conditions in the flow tube remained constant. During the peak height recording, the pressure drop in the vessel of known volume was recorded versus time (cf. sect. 3.4:  $G_T$ ). The temperature of that vessel was noted (for the computation of  $G$  from  $G_T$ ).

At least three measurements were done at each chosen furnace temperature. In this way the short-term reproducibility was checked. A complete set of measurements with one gas combination consisted of such measurements at about 20 different temperatures. This took place in two series: one series starting at room temperature and another one starting at circa 50 degrees above that temperature. Within each series the temperature was increased in steps of circa 100°C. This procedure served as a check on the long term reproducibility. We did not use a measuring method with decreasing temperature, because the furnace was not equipped with forced cooling and it took a long time to cool down on its own (cf. sect. 4).

## 6. Computation of the diffusion coefficients from the measurements

If it is assumed that there is molecular flow through the extraction holes then the registered peak height  $I_j$  at hole  $j$  is proportional to the gas concentration  $n(x_j)$

(abbreviated to  $n_j$ ) in the flow tube at hole  $j$ . This applies to both admixture gas and main gas, so:

$$I_{aj} = \alpha_{aj} n_{aj} \quad \text{and} \quad I_{mj} = \alpha_{mj} n_{mj}, \quad (5)$$

where  $\alpha$  is a constant of proportionality, dependent on the type of gas, the dimensions of the extraction hole and the mass spectrometer. So at the first hole it holds that

$$I_{a1} = \alpha_{a1} n_{a1} \quad \text{and} \quad I_{m1} = \alpha_{m1} n_{m1}. \quad (5')$$

In the case of molecular flow  $\alpha_{aj}/\alpha_{mj}$  is independent of the dimensions of hole  $j$ , so  $\alpha_{aj}/\alpha_{mj} = \alpha_{a1}/\alpha_{m1}$ . Further it holds that the pressure in the flow tube is practically equal at all the holes so we can put  $n_{mj} = n_{m1}$ . The quotient of the four relations (5) and (5') can therefore be simplified to

$$\frac{n_{aj}}{n_{a1}} = \frac{I_{aj}/I_{mj}}{I_{a1}/I_{m1}}. \quad (6)$$

The  $I$  values are registered on a recorder (fig. 5). The quotient  $n_{aj}/n_{a1}$  is found from these values via form. (6). With this result  $G/QpD$  can be calculated via form. (4). After substitution of the measured  $G$  and  $Q$  values  $pD$  is obtained. This is the  $pD$  value that relates to the circumstances ( $p$ ,  $T$ ) in the tube. We note in passing that we use  $I_a/I_m$  instead of  $I_a$  alone because for molecular flow  $I_a/I_m$  does not depend on the extraction hole diameter, whereas  $I_a$  does. The four extraction hole diameters were not equal.

The procedure according to form. (6) can be employed for  $j = 2, 3$  and  $4$  (in which especially the last value is important). The results should be independent of  $j$ . In practice we plotted  $I_{aj}/I_{mj}$  logarithmically against  $x_j$ . The four points ( $j = 1 \dots 4$ ) should be on a straight line, the slope of which will give  $G/QpD$ .

The procedure outlined above is valid assuming that the functioning of the apparatus is "ideal". Unfortunately not all extraction holes were sufficiently narrow. Therefore some corrections were necessary for the computation of  $pD$  from the measurements via the method given above; see next section.

## 7. Systematic errors and their correction

### *Non-molecular flow through the extraction holes.*

If there is molecular (not viscous) flow through the extraction holes the ratio of the main and admixture gas signals (cf. fig. 5) will be equal for all holes whenever there is a homogeneous mixture in the flow tube. However, checks showed deviations from this equality. With rising gas pressure, the first deviations were seen at the holes with the greatest flow conductance. These deviations could be explained by assuming that for the gas component with the smallest mean free path the gas flow was not molecular. We determined, per extraction hole, correction factors for each gas combination as a function of the mean free path to correct for the nonmolecular flow.

The correction which had to be applied was at most 12% (at the biggest extraction hole with the gas combination He–Xe), but was in general less than 10% [1]. Fortunately the first and the last extraction hole of the broadest flow tube which we used most were narrow and of practically equal conductance; here the corrections were at most 1%. The results from these holes ( $j = 1$  and  $j = 4$ ) gave the most important contribution to our determination of  $D$ .

*Gas loss through the extraction holes.* In some cases the amount of gas which flowed through the extraction holes was not negligibly small with respect to the throughput in the flow tube. This gave rise to two effects for which a correction had to be made. Firstly, the throughput  $G$  in the flow tube decreases after each extraction hole  $j$  (in downstream direction) with the amount of gas throughput  $\Delta_j$  through this hole. Secondly, an amount of admixture gas  $\phi_j$  passes through each hole, so there is a net admixture gas transport through the flow tube by way of a stronger diffusion against the viscous flow direction. This situation is depicted in fig. 6. The corrections required in our measurements, due to the transports  $\Delta_j$  and  $\phi_j$  were always less than 4% [1].

*Main gas pressure gradient along the flow tube.* As the flow tube was not narrow and the flow velocities were not great the pressure gradient along the flow tube was always very small. The pressure difference between the first and last extraction hole was at most a few promille. This applies to the total gas pressure. Because the admixture gas percentage at the first extraction hole ( $j = 1$ ) was about 1% and at the last hole

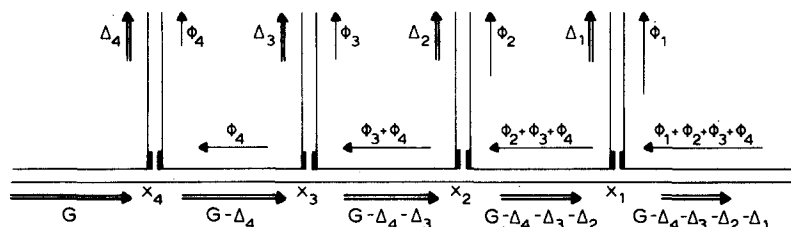


Fig. 6. Throughputs of main gas ( $G$  and  $\Delta_j$ ) and admixture gas ( $\phi_j$ ) in flow tube and extraction holes.

( $j = 4$ ) mostly about 0.2%, the partial pressure of the main gas at the first hole was a little smaller than at the last hole. This can be taken into account in the interpretation of the recording  $I_m$  (fig. 5 and sect. 6).

**Additional information.** The tube diameters and the distances between the extraction holes (sect. 3.1) were measured at room temperature; however, the thermal expansion of the silica per 1000°C is so small that these measured values can be used over the whole temperature range. Leakage of gas, especially of helium, due to the porosity of the silica was negligible in our case. Also no correction was necessary for admixture gas which was present as a contaminant in the main

gas. But with a few main gases a small correction had to be made to the gas velocity measurement because (probably) the valve between the high pressure bottle and the connected low pressure supply vessel was not completely tight.

### 8. Example: $D(T)$ for helium in krypton

As an example we show in table I the results of a series of measurements for the diffusion of helium ( $\leq 1\%$ ) in krypton ( $\geq 99\%$ ). The meaning of the columns is as follows:

Table I  
Helium in krypton

$T$ (K)	$p$ (Torr)	$G$ (Torr $\times$ $\text{cm}^3/\text{s}$ )	$\bar{v}$ (cm/s)	$D$ ( $\text{cm}^2/\text{s}$ )	$\Delta D$ (%)	$D_s$ ( $\text{cm}^2/\text{s}$ )	$D_{s, 50}$ ( $\text{cm}^2/\text{s}$ )	$D_{m, 50}$ ( $\text{cm}^2/\text{s}$ )	$D_{f, 50}$ ( $\text{cm}^2/\text{s}$ )
307.0	1.93	3.05	7.85	282	0.8	0.716	0.68	0.68	0.70
351.5	2.43	4.74	9.68	290	1.2	0.928	0.88	0.87	0.88
398.5	2.86	6.22	10.79	306	0.1	1.15	1.09	1.09	1.09
448.0	3.40	8.62	12.58	311	0.4	1.39	1.33	1.33	1.32
496.0	3.82	10.50	13.64	324	1.2	1.63	1.56	1.58	1.56
547.5	4.36	10.67	12.14	331	0.6	1.93	1.85	1.86	1.85
595.0	4.83	16.41	16.86	352	0.5	2.24	2.14	2.13	2.12
645.0	5.35	13.66	12.67	361	0.9	2.54	2.43	2.43	2.43
692.0	5.83	22.31	18.99	370	0.0	2.84	2.73	2.73	2.73
738.5	6.39	19.33	15.01	382	0.2	3.21	3.09	3.04	3.04
785.5	6.89	27.62	19.90	385	0.4	3.49	3.36	3.37	3.37
836.0	7.45	21.60	14.39	387	0.5	3.79	3.66	3.74	3.74
879.5	7.91	31.08	19.50	405	0.3	4.22	4.07	4.07	4.07
927.5	8.45	27.99	16.44	420	0.7	4.67	4.51	4.45	4.46
974.0	8.95	34.56	19.16	422	0.4	4.97	4.80	4.83	4.83
1024.5	9.49	33.72	17.63	436	0.7	5.44	5.26	5.26	5.26
1072.0	9.96	39.86	19.86	446	0.3	5.85	5.66	5.68	5.67
1119.0	10.56	36.02	16.93	456	0.2	6.33	6.11	6.12	6.10
1170.0	10.99	52.02	23.49	465	0.5	6.73	6.50	6.60	6.57
1218.5	11.58	40.78	17.47	490	0.6	7.46	7.20	7.08	7.03
1274.0	12.14	60.43	24.71	500	0.4	7.98	7.71	7.64	7.57



- $T$  = temperature of the flow tube in which the diffusion took place;
- $p$  = chosen (measured) gas pressure in the flow tube;
- $G$  = chosen (measured) gas throughput;
- $\bar{v}$  = averaged flow velocity, computed from  $G$ ,  $p$  and the tube cross section;
- $D$  = diffusion coefficient at pressure  $p$  and temperature  $T$ , according to sect. 6 + 7;
- $\Delta D$  = % standard deviation of  $D$ , computed from at least three measurements;
- $D_s$  = diffusion coefficient at 1 atm. and temperature  $T$ , computed from  $D$ ;
- $D_{s,50}$  = idem, converted to relative composition 50% helium/50% krypton;
- $D_{m,50}$  = approximation for  $D_{s,50}$ , computed with 4 fitted parameters;
- $D_{f,50}$  = idem, computed according to  $cT^\gamma$ , so with only 2 fitted parameters;

*Explanation and remarks.* These measurements were done with the broad flow tube, which had a cross section of  $0.206 \text{ cm}^2$ . The distance  $x_4 - x_1$  was  $39.6 \text{ cm}$ , see sect. 3.1. The table is composed from two series of alternating temperatures, see sect. 5. At least three measurements were taken at each temperature, see sect. 5. The standard deviation  $\Delta D$  contains a contribution computed from the differences between the three values of  $D$  (see above) and a contribution computed from the uncertainties in each of these three values (derived from the spread of the results of the various extraction hole combinations). The value of  $D$ , and therefore the value of  $D_s$ , should be independent of  $G$  and the value of  $D_s$  should be independent of  $p$ .  $D_s$  has been computed from  $D$  according to  $D_s = Dp/760$ .  $D_{s,50}$  has been computed from  $D_s$  after Mason and Marrero [8].  $D_{m,50}$  has been calculated with a formula also derived from Mason and Marrero [8] with fitted coefficients [1]:

$$\ln D_{m,50} = -5.875 + 1.760 \ln T$$

$$- \ln (\ln 1.42 \times 10^8 / T)^2$$

$$+ 340/T - 53 \times 10^3 / T^2.$$

$D_{f,50}$  has been calculated thus:  $D_{f,50} = 4.87 \times 10^{-5} T^{1.672}$ , so

$$\ln D_{f,50} = -9.930 + 1.672 \ln T.$$

The figures in table I show that up to  $1200 \text{ K}$   $D_{f,50}$  is a good approximation, about as good as  $D_{m,50}$ . Apparently it is not necessary to use more than two fitted parameters in our temperature range (above  $0^\circ \text{C}$ ). The deviating  $D_{s,50}$  values at the extreme temperatures in table I are probably only accidental because with the other gas combinations these deviations do not occur. In the other gas combinations the trend of  $D_{s,50}$  against  $T$  sometimes shows some irregularities too, but at other temperatures. In the graphs of  $\ln D_{s,50}$  versus  $\ln T$  for the various gas combinations the measurements do not show a clear systematic deviation from the fitted straight lines.

In our example (He + Kr) fig. 7 shows an analogous graph, viz.  $\ln (D_{s,50}/T^{1.5})$  versus  $\ln T$ . If gas molecules would behave like smooth hard spheres  $D_{s,50} \sim T^{1.5}$  would hold. The slope of the straight line in fig. 7 shows to what extent the exponent  $\gamma$  differs from 1.5, and therefore to what extent the molecular collisions differ from hard sphere collisions. The value  $\gamma = 1.672$  used in table I is based on the experimental results between  $350 \text{ K}$  and  $1200 \text{ K}$ . If the results at  $300 \text{ K}$  and beyond  $1200 \text{ K}$  are taken into account too,  $\gamma \approx 1.68$ . Attention is drawn to the fact that the parameter values in  $\ln D_{f,50}$  differ considerably from the values of the first two parameters in  $\ln D_{m,50}$ ; so it is not possible to read the  $\gamma$  value simply from the formula for  $D_{m,50}$ .

In the next publication (= part II) the results for all ten noble gas combinations will be presented and compared with the results obtained by other authors.

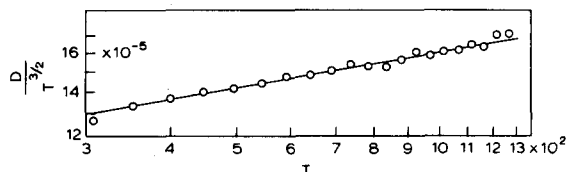


Fig. 7. Temperature dependence of the diffusion constant of helium in krypton. The circles refer to  $D_{s,50}$ , the straight line refers to  $D_{f,50}$  (cf. table I). The horizontal and vertical scales are both logarithmic.

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