

ELECTRON DRIFT AND DIFFUSION IN PARAHYDROGEN AT 77°K

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Summary

This paper reports a series of experiments to measure electron diffusion and drift in pure parahydrogen at 77°K. Tables of data are given for the electron drift velocity W in the range $1.2 \times 10^{-19} \leq E/N \leq 9.5 \times 10^{-17}$ V cm² and for the ratio of diffusion coefficient to mobility D/μ for $2 \times 10^{-20} \leq E/N \leq 6 \times 10^{-17}$ V cm². As expected, these data are indistinguishable from the data for normal hydrogen in the thermal region and at the higher values of E/N where vibrational excitation is the dominant process controlling the electron energy distribution. However, at intermediate values of E/N , the values of W and D/μ differ by more than 10 and 20% respectively from the corresponding values in normal hydrogen, demonstrating the influence of the difference in the statistical weights of the rotational levels in the two gases.

I. INTRODUCTION

Measurements of the transport coefficients of a swarm of electrons drifting and diffusing through a gas under the influence of a uniform electric field can be used to determine the energy dependence of the cross sections for the elastic and inelastic collisions between the electrons and the gas molecules (Frost and Phelps 1962; Engelhardt and Phelps 1963; Crompton, Elford, and Jory 1967). In a previous paper (Crompton, Elford, and McIntosh 1968) it was pointed out that, although the momentum transfer cross section can be deduced with adequate precision in the inert gases at energies below the first excitation threshold (see, e.g. Crompton, Elford, and Jory 1967), the results obtained in the molecular gases have been less satisfactory. Although this situation is partly due to the spread in some of the experimental data, it is largely the result of the difficulties in obtaining a unique set of elastic and inelastic cross sections.

The first of the limitations described above has been largely removed for hydrogen and deuterium by recent determinations of the drift velocity W and the ratio D/μ of diffusion coefficient to mobility (Lowke 1963; Crompton, Elford, and McIntosh 1968) but the second limitation remains. Thus, although it is now possible to determine unambiguously whether a particular set of cross sections is consistent with the experimental data, the more fundamental difficulty associated with the necessity to determine the cross sections for three or more processes from measured values of only two transport coefficients has not been overcome. For this reason we have measured electron transport coefficients in parahydrogen at 77°K. At this temperature, provided the mean energy of electrons in the swarm is not much greater

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than the mean molecular energy, energy transfer between electrons and gas molecules can occur only through elastic collisions or by the excitation of the $J = 0 \rightarrow 2$ rotational transition. Thus, in analysing the transport data, cross sections for only these two processes need be considered and it should be possible to make a unique determination of their energy dependence in this special case.

A preliminary account of the work described in this paper has been given elsewhere (Crompton and McIntosh 1967).

II. APPARATUS AND EXPERIMENTAL TECHNIQUES

The measurements of the electron drift velocity W were made using the Bradbury-Nielsen time-of-flight technique, while the measurements of D/μ , the ratio of diffusion coefficient to mobility, were made using the Townsend-Huxley lateral diffusion method. The experimental techniques and the apparatuses used have been described previously (Crompton and Jory 1962; Lowke 1963; Crompton, Elford, and Gascoigne 1965; Crompton, Elford, and McIntosh 1968) and the present description is therefore restricted to those features peculiar to the parahydrogen experiments.

Although parahydrogen is commonly prepared in liquid form, it is difficult to prepare gas that contains almost 100% of the para-modification and that has the degree of purity required for the D/μ measurements at 77°K, where the oxygen concentration must be less than one part in 10^9 (Crompton, Elford, and McIntosh 1968). The techniques used to prepare the gas samples and to test their parahydrogen content are described in detail in the Appendix. The gas samples used were of a purity comparable with that of the normal hydrogen and deuterium used by Crompton, Elford, and McIntosh and were shown to contain not less than 98% of the para-form. The possible 2% of unconverted gas would not significantly alter the values of either W or D/μ .

In previous measurements of the electron transport coefficients, thermionic emission from platinum filaments was used as the source of electrons. However, initial tests of the stability of the parahydrogen samples when in contact with a heated filament showed that reconversion to normal hydrogen (25% para, 75% ortho at 77°K) occurred very rapidly. On the other hand, when the filament was replaced by a silver-coated foil of americium 241 to provide electrons by volume ionization of the gas, the parahydrogen samples remained stable over a period of several days.

The use of the radioactive source introduced a difficulty into the D/μ measurements that was not present in the work described previously. It was now possible for some electrons to be present within the diffusion chamber that had not entered through the source hole. These electrons, which would falsify the distribution of current at the anode, could be produced either by α -particles entering the chamber through the source hole or by the accompanying weak γ -radiation. The first possibility was eliminated by the suitable design of the source itself. The foil was formed into a cylinder that fitted within a supporting copper cylinder mounted in place of the filament normally used and a series of annular baffle plates was then fitted within the cylinder to prevent the incidence of α -particles on the hole.

Since the entry of the γ -rays into the diffusion chamber could not be prevented, compensation had to be made for the small background currents which they caused. Since these currents were a function of the gas pressure and the electric field, the compensation had to be adjusted for each determination of a current ratio. At the highest gas pressures the background current to the annular electrode was a few per cent of the current to be measured, while that to the disk, which had only a small fraction of the area, was almost negligible. Compensation was effected by means of a high resistor (10^{13} ohms) and variable potential connected to each of the electrometers. After applying a field in the reverse direction in the region above the source hole, the compensating devices were adjusted to ensure negligible drift of the electrometers during the 50 sec integrating cycle. The smallness of the currents and their stability were such that no difficulty was experienced in annulling them. Since the current-measuring technique is based on an integrating null method, the shunting effect of the high resistors was negligible, the time constants of the electrometers being still of the order of 300 sec.

In both the W and D/μ experiments, the values of E/N , the ratios of electric field strength to gas number density, were found from the known values of the electric field strength and accurate measurements of the gas temperature T and pressure p . All the experimental parameters were measured in the manner described by Crompton, Elford, and McIntosh (1968).

III. RESULTS

(a) Drift Velocity

As in previous work, values of the drift velocity were determined at a series of E/N values, using several gas pressures for each value. In each determination, the characteristic frequency f_0 was found by measuring the frequencies corresponding to the first two maxima in the graph of transmitted current as a function of frequency (see, e.g. Elford 1966). The pairs of values of f_0 found in this way were in agreement to within 0.2% for all the measurements used to calculate the measured drift velocities W' shown in Table 1. Errors from contact potential differences were kept below 0.25% by including only those data for which the electric field strength was 5.0 V cm^{-1} or greater.

Two experimental runs in parahydrogen were made, one covering the pressure range $10 \leq p \leq 250$ torr and the other the range $10 \leq p \leq 350$ torr. At the pressures common to the two runs the agreement between the sets of data was always better than 0.3%. This suggests that the single set of data taken at pressures of 300 and 350 torr can also be considered reliable.

The mean temperature (77.0°K) at which the results were recorded for pressures greater than 100 torr has been taken as the gas temperature to which all the measurements refer. For $p \geq 100$ torr, fluctuations about this temperature were less than 0.2 degK . At pressures less than 100 torr somewhat larger temperature variations (but still less than 0.5 degK) were observed. However, the lower pressures were required only for the measurements at higher values of E/N where the energy distribution, and hence the value of W , is substantially independent of the temperature; consequently, provided the correct temperature is used to calculate the

value of the number density from the pressure, no significant error is made in assuming all the results to apply to 77.0°K .

TABLE 1

EXPERIMENTAL VALUES OF DRIFT VELOCITY FOR ELECTRONS IN PARAHYDROGEN AT 77.0°K
The number in square brackets following a value is the power of 10 by which this and subsequent values are to be multiplied: $1.195[-19]$ means 1.195×10^{-19}

E/N (V cm ²)	W' (cm sec ⁻¹)							Best Estimate, W (cm sec ⁻¹)
	$p = 350$	300	250	200	100	50	20 torr	
1.195 [-19]	3.78 [4]							
1.435	4.40	4.41 [4]						
1.594	4.80	4.80	4.80 [4]					
1.992	5.73	5.73	5.73	5.72 [4]				
2.391	6.58	6.58	6.58	6.57				
3.188	8.14	8.14	8.14	8.13				
3.985	9.57	9.58	9.59	9.58	9.57 [4]			
4.782	1.094 [5]	1.094 [5]	1.096 [5]	1.095 [5]	1.095 [5]			
5.579	1.226	1.227	1.230	1.229	1.230			
6.376	1.356	1.357	1.359	1.360	1.362			
7.173	1.483	1.485	1.487	1.487	1.491			
7.970	1.606	1.608	1.611	1.612	1.615	1.614 [5]		
9.564	1.846	1.848	1.850	1.852	1.857	1.858		
1.195 [-18]	2.18(3)	2.18(8)	2.19(0)	2.19(2)	2.19(7)	2.20(1)		
1.435	2.49(8)	2.50(2)	2.50(6)	2.50(8)	2.51(5)	2.52(1)		
1.594	2.69(6)	2.70(1)	2.70(5)	2.70(7)	2.71(4)	2.71(8)		
1.992	3.15	3.16	3.16	3.16	3.17	3.18	3.17 [5]	
2.391	3.56	3.57	3.57	3.57	3.58	3.59	3.58	
3.188		4.26	4.27	4.27	4.28	4.29	4.28	
	$p = 300$	250	200	100	50	20	10 torr	
3.985 [-18]		4.84 [5]	4.85 [5]	4.85 [5]	4.86 [5]	4.86 [5]		4.84 [5]
4.782			5.33	5.33	5.33	5.33		5.33
5.579				5.73	5.73	5.73		5.73
6.376				6.07	6.08	6.07		6.07
7.173				6.37	6.38	6.37		6.37
7.970				6.64	6.65	6.64		6.64
9.564				7.09	7.10	7.09		7.09
1.195 [-17]					7.64	7.64		7.64
1.435					8.09	8.09		8.09
1.594					8.36	8.36		8.36
1.992					8.96	8.97		8.96
2.391						9.53	9.54 [5]	9.52
3.188						1.064 [6]	1.066 [6]	1.063 [6]
3.985						1.174	1.178	1.173
4.782						1.282	1.286	1.281
5.579							1.339	1.387
6.376							1.487	1.485
7.173							1.582	1.580
7.970							1.675	1.673
9.564							1.850	1.848

Values of W' are shown in Table 1 for the range $1.2 \times 10^{-19} \leq E/N \leq 9.5 \times 10^{-17}$ V cm². The "best estimate" values of the drift velocity W have been found by correcting the values of W' for the influence of diffusion using the procedure described previously (Lowke 1963; Crompton, Elford, and Jory 1967; Crompton, Elford, and McIntosh 1968). The corrections made to the values of W' were very

small, the greatest difference between the values of W' and W being 0.15% at $E/N = 5.579 \times 10^{-17}$ V cm². An error limit of $\pm 2\%$ is placed on the best estimate values of W in Table 1.

Below $E/N = 3.985 \times 10^{-18}$ V cm² no best estimate values of W are given because, as in nitrogen (Lowke 1963) and deuterium (Crompton, Elford, and McIntosh 1968), the values of W' increase more rapidly as p is lowered than can be accounted for by the effects of diffusion. The differences not accountable for by diffusion are about 0.5% for values of E/N of the order of 10^{-18} V cm² where it was possible to take the results over the widest range of pressures. If account is taken of the departure of hydrogen from a perfect gas, this difference can be decreased by, at most, 0.1%. The discrepancies are very small but are considered significant when compared with the experimental scatter which was no more than $\pm 0.15\%$.

TABLE 2
EXPERIMENTAL VALUES OF D/μ FOR ELECTRONS IN PARAHYDROGEN AT 77.3°K

E/N (V cm ²)	D/μ (V)						
		1.0×10^{-19}	0.00795	1.0×10^{-18}	0.0181(4)	1.0×10^{-17}	0.0786
		1.2	0.00830	1.2	0.0194(1)	1.2	0.0935
		1.4	0.00866	1.4	0.0206	1.4	0.107(7)
		1.6	0.00904	1.6	0.0219	1.6	0.124(0)
		1.8	0.00944	1.8	0.0231	1.8	0.139(0)
2.0×10^{-20}	0.00683	2.0	0.00983	2.0	0.0243	2.0	0.153(9)
2.5	0.00689	2.5	0.0106(8)	2.5	0.0273	2.5	0.189(1)
3.0	0.00695	3.0	0.0114(8)	3.0	0.0303	3.0	0.220
3.5	0.00699	3.5	0.0122(3)	3.5	0.0333	3.5	0.250
4.0	0.00705	4.0	0.0129(0)	4.0	0.0364	4.0	0.276
4.5	0.00710	4.5	0.0135(4)	4.5	0.0395	4.5	0.300
5.0	0.00716	5.0	0.0141(0)	5.0	0.0428	5.0	0.323
6.0	0.00730	6.0	0.0150(7)	6.0	0.0496	6.0	0.365
7.0	0.00745	7.0	0.0159(3)	7.0	0.0565		
8.0	0.00761	8.0	0.0167(3)	8.0	0.0638		
9.0	0.00778	9.0	0.0174(6)	9.0	0.0710		

(b) *Ratio of Diffusion Coefficient to Mobility*

Each experimental observation resulted in a value of E/N and a corresponding value of D/μ . All of the results for parahydrogen were plotted on a graph with scales sufficiently large to allow the values of D/μ to be read off at the required intervals of E/N with an error of no more than 0.3%.

Crompton, Elford, and McIntosh (1968) reported a number of sources of error which caused them to reject some of the data they obtained for H₂ and D₂ at 77°K when the field strength was less than 5.0 V cm⁻¹. In the present experiments the greater difficulties in preparing samples of pure parahydrogen made it impracticable to take results with many samples of gas, and therefore all the measured values of D/μ , including all those taken with field strengths of less than 5.0 V cm⁻¹, were used in the final graphs of the data.

Three experimental runs were made in parahydrogen. Above $E/N = 4 \times 10^{-18}$ V cm² all the data were obtained with field strengths of 5.0 V cm⁻¹ or greater. Excellent agreement was obtained in this range, all of the 60 data points from the three runs lying within $\pm 1\%$ of the line of best fit. For many of the values of E/N below this limit, field strengths of 5.0 V cm⁻¹ or greater could still be used, at least at the higher pressures, but the lower values called for the use of progressively smaller field strengths until, at the lowest values, field strengths of only 1.0 or 2.0 V cm⁻¹ could be used. Although, as is to be expected, the results show more scatter in this region ($E/N < 4 \times 10^{-18}$ V cm²), the data from two of the experimental runs were in satisfactory agreement. The third set of data showed evidence of a systematic error that resulted in the majority of points lying above this line. Subsequently, evidence was found that the voltage divider chain feeding the guard electrodes could possibly have been slightly defective during the low E/N portion of the third experimental run. The final curve from which the tabulated data were derived was therefore biased towards the results of the first two runs, but, nevertheless, all the data lay within 2% of the final curve. About 130 data points were measured and plotted in this range.

The values of D/μ in parahydrogen at 77.3°K were read from the graphs described above and are listed in Table 2. The error limit placed on the data is $\pm 2\%$ for $4 \times 10^{-18} \leq E/N \leq 6 \times 10^{-17}$ V cm² and $\pm 3\%$ for $E/N < 4 \times 10^{-18}$ V cm².

IV. DISCUSSION

There have been no previous measurements of electron transport coefficients in parahydrogen. Comparisons of the present values of W and D/μ with similar data taken in normal hydrogen are shown in Figures 1 and 2. The values of D/μ and W in normal hydrogen are taken from the data of Crompton, Elford, and McIntosh (1968) and Lowke (1963) respectively.

The accuracy of the data is sufficient to show the small differences in the transport coefficients that result from the differences in the statistical weights of the rotational levels in the two gases. At low values of E/N the electrons are almost in thermal equilibrium with the gas molecules and, since the momentum transfer cross section is identical in normal and parahydrogen, the values of W and D/μ are the same in both gases. As the value of E/N is increased the electrons obtain sufficient energy to cause rotational excitation of the molecules and, as is shown in the figures, there is also a significant divergence between the data for the two gases. In parahydrogen at 77°K, 99.5% of the molecules occupy the $J = 0$ rotational state. Since the cross section for the transition $J = 0 \rightarrow 4$ is negligibly small compared with that for $J = 0 \rightarrow 2$, and since the electron currents are too small to raise significantly the population of molecules with $J = 2$, excitation of the $J = 0 \rightarrow 2$ transition is the only rotational excitation process that contributes significantly to the energy loss of the swarm. On the other hand, in normal hydrogen at this temperature 75% of the molecules occupy the $J = 1$ level and only 25% occupy the $J = 0$ level, the populations of higher levels being negligibly small (Farkas 1935). Since the cross sections for the $J = 0 \rightarrow 2$ and $J = 1 \rightarrow 3$ transitions are different (e.g. thresholds of 0.045 and 0.075 eV respectively) it follows that rotational energy losses

in normal hydrogen differ from those in parahydrogen, causing the observed divergences in the transport data in this region. When the mean electron energy approaches 0.5 eV the majority of the electrons in the swarm have sufficient energy to cause vibrational excitation (for which the threshold is 0.516 eV; Herzberg 1950). Because the cross section for vibrational excitation is so much larger than those for rotational excitation (Engelhardt and Phelps 1963) and is the same for both gases, the differences in the rotational levels become unimportant and the two curves merge again.

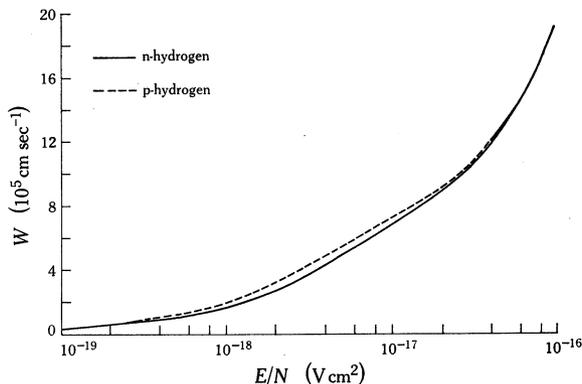


Fig. 1.—Electron drift velocities in parahydrogen at 77°K with the results in normal hydrogen shown for comparison.

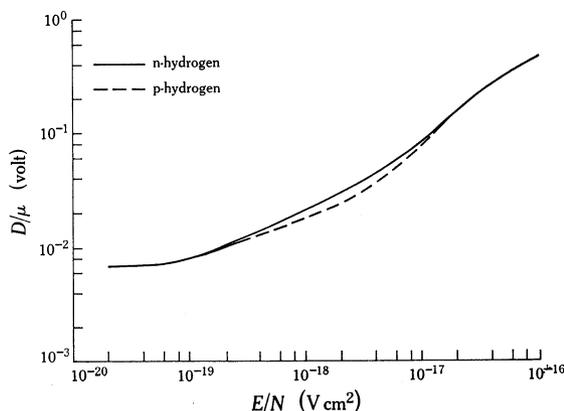


Fig. 2.—Experimental values of D/μ in parahydrogen at 77°K with the results in normal hydrogen shown for comparison.

Various theoretical forms of the cross section for rotational excitation (Gerjuoy and Stein 1955; Dalgarno and Moffett 1963; Sampson and Mjolsness 1965; Takayanagi and Geltman 1965; Lane and Geltman 1967) have been proposed. An analysis is in progress to determine which of them is most consistent with the present experimental data.

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APPENDIX

The Preparation and Analysis of Pure Parahydrogen Gas

When a sample of normal hydrogen (consisting of 75% orthohydrogen and 25% parahydrogen) is cooled, the ortho-para ratio remains unchanged unless the cooling is done in the presence of a paramagnetic catalyst (Farkas 1935). The catalyst used in the present work was iron oxide that had been activated by baking at 140°C for 24 hr at a pressure of 10–20 μ Hg (Barrick, Weitzel, and Connolly 1954).

Although liquid parahydrogen is commonly prepared, it is more difficult to prepare gaseous parahydrogen having a low concentration of the ortho-modification and free of other impurities, especially oxygen (see Crompton, Elford, and McIntosh 1968). In order to meet the second requirement it is necessary for the conversion apparatus and storage tank to form a closed system with a low outgassing rate, and therefore special precautions are required to ensure that the content of the para-modification in the converted gas samples is very nearly 100%.

A block diagram of the experimental arrangement is shown in Figure 3. Details of the construction of the conversion chamber are shown in Figure 4. The gas reservoir was a stainless steel tank of 15 litres capacity fitted with a Granville-Phillips high pressure UHV valve. The heat exchanger consisted of 24 ft of $\frac{1}{8}$ in. internal diameter copper tubing closely wound into a 1 in. diameter coil. The conversion chamber, containing the heat exchanger and catalyst, and the reservoir were leak tested and thoroughly outgassed before the commencement of the experiment. The reservoir was then filled with high purity normal hydrogen to a pressure of about two atmospheres, using the silver-palladium alloy osmosis tubes described by Crompton and Elford (1962).

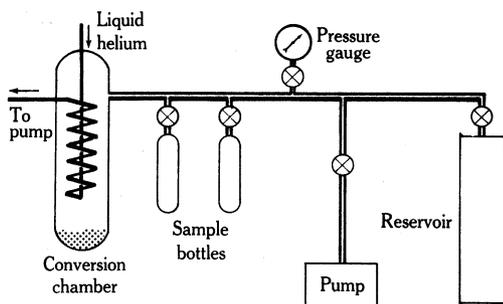


Fig. 3 (above).—Schematic diagram of the apparatus used for the preparation of pure parahydrogen gas.

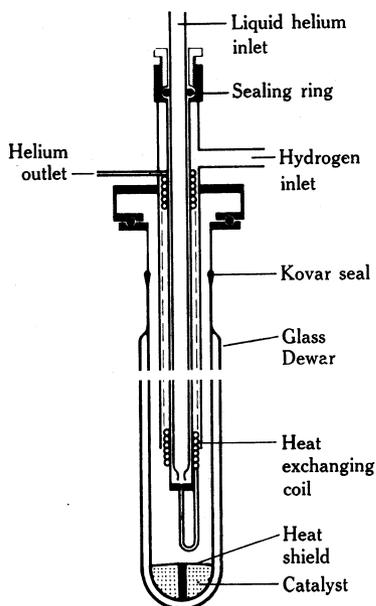


Fig. 4 (right).—Schematic section of the parahydrogen conversion chamber.

To commence the conversion cycle, hydrogen was admitted to the conversion chamber to a pressure of several hundred torr while at the same time liquid helium was drawn through the heat-exchanging coil. The temperature of the system decreased until hydrogen condensed on the copper coil and dripped to the bottom of the chamber where it came into intimate contact with the catalyst. The supply of hydrogen to the conversion chamber was maintained from the reservoir and the cooling continued until the pressure throughout the system (conversion chamber + reservoir) corresponded to the triple point ($\sim 14^\circ\text{K}$, 50 torr). Further cooling resulted in the formation of solid hydrogen and reduced the pressure still further, thereby reducing the amount of unconverted normal hydrogen remaining in the reservoir. At this point the chamber was isolated and the reservoir evacuated. The conversion chamber was also pumped for a short period to remove as much as

possible of the unconverted gaseous hydrogen without undue wastage of parahydrogen by evaporation from the solid state. With the pump isolated and the reservoir connected to the conversion chamber, evaporation was allowed to continue for some time before the system was cooled again to convert most of the hydrogen back to the solid state. The cycle was repeated several times to ensure that all the hydrogen in the chamber had been in contact at some time with the cold catalyst and the system was finally allowed to warm slightly. The solid and liquid parahydrogen then partially evaporated until the reservoir was filled to atmospheric pressure.

Since the parahydrogen must be made in a closed system, the catalyst remains in the conversion chamber during the warm-up cycle and it is therefore necessary to ensure that the temperature of the catalyst does not rise to a point at which a significant fraction of the gas could be converted back to the ortho-modification. A number of precautions were taken to keep the catalyst cold during the evaporation of the parahydrogen. Firstly, the amounts of catalyst and gas were carefully regulated to ensure that when the reservoir reached atmospheric pressure there was still a substantial amount of liquid hydrogen left in contact with the catalyst. Secondly, a radiation shield was placed over the surface of the catalyst; the shield was attached to a heavy copper rod which ran through the catalyst and into the residual liquid hydrogen. This arrangement improved the thermal contact between the catalyst and the residual liquid hydrogen and also minimized the radiant heating of the upper surface of the catalyst. Finally, a small flow of liquid helium was maintained through the heat-exchanging coil; the effect of this flow was to maintain the coil at a low temperature, thereby minimizing the transfer of heat by radiation to the submerged layers of the catalyst.

Figure 3 shows two small glass sample bottles connected to the line between the conversion chamber and the reservoir. During the preparation of the parahydrogen gas, one bottle was filled at the beginning of the evaporation cycle and the other at the end. In this way samples of gas were obtained that were representative of the gas made under the most favourable and least favourable conditions for preparing 100% parahydrogen.

Analysis of the ortho-para ratios for the samples relies on the difference in thermal conductivity of the two forms (Farkas 1935). For our work a simple analyser based on the design of Grilly (1953) was used. A pair of Sylvania Pirani tubes matched in resistance to within 0.01Ω formed two arms of a Wheatstone bridge network, the remaining arms being a pair of resistance boxes variable to 0.001Ω . The tubes were immersed in a liquid nitrogen bath to obtain greater sensitivity. Hydrogen at a pressure of 40 torr was admitted to both the Pirani tubes and balance of the bridge obtained by adjusting the resistance boxes. One of the Pirani tubes was then isolated while the other was evacuated and then filled to a pressure of 40 torr with the gas to be analysed; the out-of-balance current in the bridge circuit was then a measure of the parahydrogen content of the gas sample. The current to the bridge was supplied by a stabilized d.c. supply and was adjusted so that 100% parahydrogen produced full-scale deflection on the meter which measured the out-of-balance current.

The device was calibrated with a sample of parahydrogen collected under the most favourable conditions for its preparation. It was assumed, therefore, that this sample contained 100% of the para-modification.* The sensitivity was found by preparing a 90% parahydrogen sample from a mixture of this gas and normal hydrogen. The resolution was such that a 0.5% change in the parahydrogen concentration could be detected.

The gas sample obtained at the end of the evaporation cycle was indistinguishable from the 100% sample. Similarly, gas samples taken from the stainless steel reservoirs and from the drift velocity apparatus at the end of an experimental run were also indistinguishable from the 100% sample. The parahydrogen content of all the samples used is claimed to be greater than 98%.

* The para-ortho ratio was checked at the Division of Physics, CSIRO, Sydney, using a Gow-Mac Instrument Co. Ortho-parahydrogen Analyzer. Within the limits of detection of the instrument, which were of the order of 1%, no orthohydrogen could be detected in the sample.

