THE DRIFT VELOCITY OF ELECTRONS IN HYDROGEN AND NITROGEN

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Summary

Experimental results are given for the drift velocity of electrons in hydrogen and nitrogen at 293°K and 77·6°K over the range $0·001 \leqslant E/p \leqslant 20$ V cm⁻¹ mmHg⁻¹. The results were obtained using the method of Bradbury and Nielsen and have in general an accuracy of 1% at 293°K and 2% at 77·6°K. The measurements were made over as wide a range of gas pressures as possible for each value of E/p and all results are presented in tabular form. In the final results that are presented corrections have been made for errors due to diffusion. Experiments are also discussed which were designed to investigate the extent of the existence of errors due to factors such as distortion of the d.c. field from voltages on the shutter wires and the presence of gaseous impurities. It has been shown that measurements of the drift velocity are particularly sensitive to traces of water vapour as impurity.

I. INTRODUCTION

In studies of the motions of electrons in gases, knowledge of the electron drift velocity is essential for the determination of quantities such as the effective collision cross section of the gas molecules and the average fractional energy loss of the electrons in collisions with the gas molecules. Whenever macroscopic quantities such as the drift velocity are used to deduce values of microscopic parameters it is desirable that the raw data be obtained to as high an accuracy as possible.

There are many investigations of the drift velocity reported in the literature and a great variety of methods have been used. Nevertheless, when comparisons are made of the results of different investigations, it is found that differences of well over 5% occur. Not only is it desirable to obtain data of greater precision than this, but the fact that the results of earlier investigations usually differ by more than the claimed experimental error makes it possible that factors are influencing the experimental results of which no account has been taken. Furthermore, it is frequently not possible to compare accurately the results of different investigations because of the different temperatures at which the results have been taken and also because the graphical presentation of the results either obscures the degree of accuracy of the initial data or makes its recovery impossible.

The method of Bradbury and Nielsen was chosen as a method which seemed capable of high accuracy and a systematic investigation made of all likely sources of error. In the first place, the influence of diffusion, often neglected in time-of-flight methods, has been taken into account in assessing the results. Secondly, since gas purity is often cited as a possible explanation of the discrepancies between the results

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of various workers, the magnitude of the errors introduced by known amounts of likely impurities has been determined. In addition an examination has been made of the possible influence of non-uniformity of the d.c. electric field, field interpenetration due to the a.c. voltages on the shutters, temperature gradients, space charge repulsion, and phase differences in the voltages applied to the shutters. A demonstration of the accuracy of the shutter method has been made by measuring the velocity of positive ions in vacuum in a field-free space and comparing the results with the velocity predicted theoretically from the voltage used to accelerate the ions initially.
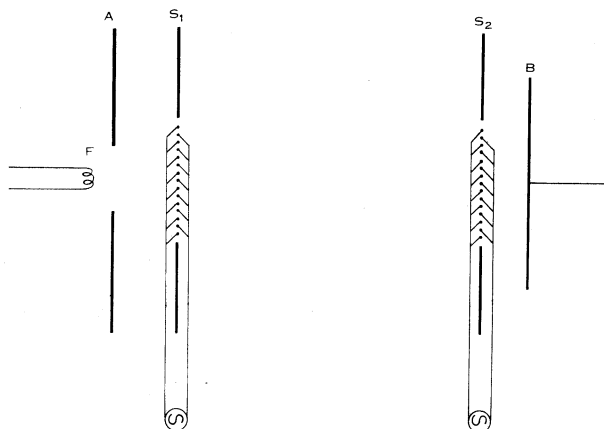

Fig. 1.—Schematic diagram of shutter apparatus.

The values of the drift velocity that have been obtained at 293°K and 77·6°K are presented in tabular form. The overall accuracy can be assessed from the tables by examining the consistency of the results taken at various gas pressures for any given value of E/p. (E/p is the ratio of electric field strength to gas pressure, where the units of E/p are always V cm^{-1} mmHg^{-1}). The accuracy, in general, is considered to be 1% at 293°K and 2% at 77·6°K. Errors arising in the measurement of gas pressure and from diffusion are greatest when low pressures are used. Consequently errors in the results at 293°K for $E/p > 7$ may be slightly greater than 1%. The results in nitrogen at 77·6°K for $E/p < 0·02$ are slightly dependent on the gas density; the origin of this dependence, which cannot be explained in terms of the influence of diffusion, is at present unknown.

II. Experimental Procedure and Description of Apparatus

The method of measurement is identical with that of Nielsen (1936). Electrons are emitted from a filament F (Fig. 1) and drift through the gas to the collecting electrode B under the influence of a uniform electric field which is maintained between electrodes A and B. Two shutters S_1 and S_2 each consisting of a plane grid of parallel wires, of which alternate wires are connected together, are placed in the path of the electrons, the distance h between the shutters being known accurately. An a.c. voltage, whose frequency can be varied while maintaining a constant amplitude, is applied to the two halves of S_1. The voltages applied to each half of the shutter are

exactly $180°$ out of phase. Similar voltages exactly in phase with those applied to S_1 are applied to S_2. All a.c. voltages have superimposed on them the appropriate d.c. voltage required to maintain the uniform d.c. field between A and B. The frequency of the a.c. voltage is then varied and the current collected at B is measured. When a graph is drawn of current against frequency a series of maxima will be obtained as shown in Figures 3 and 4.

The action of S_1 is to divide the stream of electrons into a series of pulses, as electrons will be admitted through the shutter only when the a.c. voltage on the shutter wires approaches zero. If f is the frequency of the a.c. signal, $2f$ will be the frequency at which the shutters open. S_2 will have a similar influence on the electron current and the first maximum of the current-frequency curve will correspond to the frequency f_1 for which pulses of electrons produced by S_1 arrive at S_2 when the shutters are again open. Other current maxima will occur at integral multiples of f_1. The drift velocity W is then determined from $W = 2hf_1$ or $W = 2hf_n/n$, where f_n is the frequency corresponding to the nth current maximum of the current-frequency curve.

The distance between the two shutters in the present apparatus was $5 \cdot 985 \pm 0 \cdot 005$ cm. The shutters were constructed by threading nichrome wire of diameter $0 \cdot 003$ in. through holes pierced in mica such that the distance between adjacent grid wires was $0 \cdot 5$ mm. Guard rings, positioned by accurately ground glass spacers, were placed every $0 \cdot 5$ cm to maintain a uniform electric field. The electrode system is shown in Figure 2. All metal surfaces of the apparatus, including the shutter wires, were coated with gold to reduce errors due to contact potential differences.

The a.c. voltage applied to the shutters was supplied from an oscillator whose frequency was calibrated with a precision counter to an accuracy of better than $\frac{1}{2}\%$. An amplifier was constructed so that grid voltages of up to 70 V r.m.s. on each half of the grids could be maintained over the frequency range 1 kc/s to 1 Mc/s; the voltage remaining constant to $\frac{1}{2}$ dB with change of frequency over each range of the oscillator. Precautions were taken to ensure the equality of the magnitude of each of the a.c. voltages and also that the phases of the voltages applied to each shutter were equal to within $0 \cdot 5°$. The effect of slight departures from the correct phase and voltage of these a.c. voltages is discussed in Section IV. The voltages applied to the electrodes to maintain the uniform d.c. field were derived from a Fluke type 301E power supply which enabled the voltages to be set with an error of less than $0 \cdot 1\%$.

The apparatus was evacuated first with a backing pump and then with a getter-ion pump, so that the pressure as recorded by the pump was less than 10^{-6} mmHg. When the experimental tube was isolated from the pumping system, the outgassing rate, as determined by a Pirani gauge and without the liquid air traps normally used, was found to be $0 \cdot 1$ μ in 3 hr.

Hydrogen was admitted to the apparatus through a palladium osmosis tube, observing the precautions described by Crompton and Elford (1962). Nitrogen was prepared by heating sodium azide in a glass tube which had previously been strongly flamed. While the tube containing the azide was being evacuated, it was heated to a temperature just below the temperature for the breakdown of the azide. The possibility of introducing impurities through the outgassing of the tube or azide

during the preparation of the nitrogen, was thus reduced to a minimum.   Before gases were admitted to the apparatus they were passed over several liquid air traps. Subsequent investigations discussed in Section V show that the standard vacuum techniques employed were adequate for the experiments in the diatomic gases nitrogen and hydrogen.
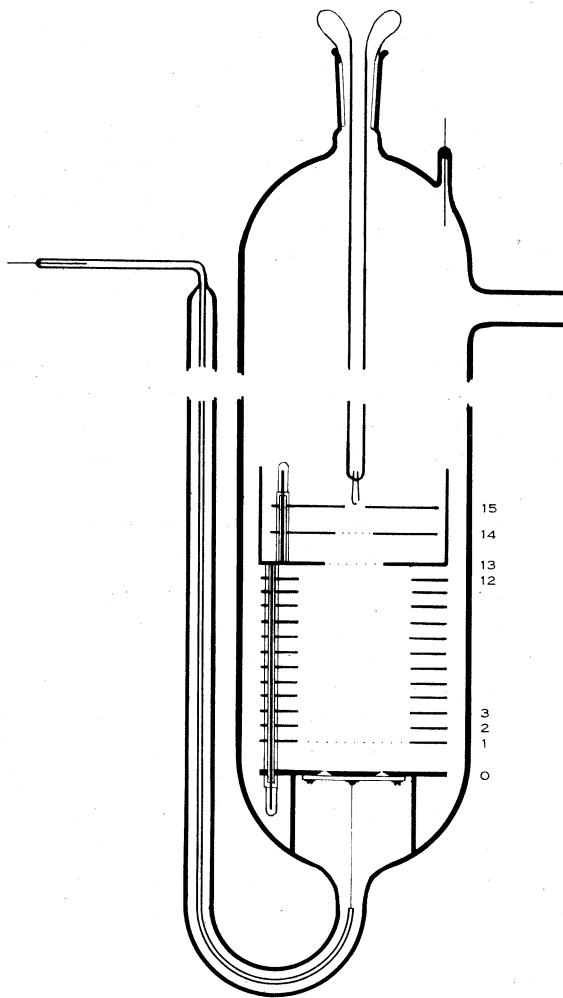
Fig. 2.—Diagram of the experimental tube.

Gas pressures were recorded on two precision-type capsule gauges (Crompton and Elford 1957), which together covered the pressure range of 2–500 mmHg.   The low-pressure gauge, recording pressures up to 20 mmHg, was calibrated with a dead-weight pressure standard and the high-pressure gauge with a standard mercury manometer as described in Crompton and Elford's paper.   The overall error in the measurement of pressure was of the order of 0.5% at the lowest scale readings and less for higher scale readings.

The electron currents in the drift chamber were less than 10^{-12} A and were measured by means of a Vibron electrometer in conjunction with a 10^{10} Ω resistance.

Temperatures were measured by means of two copper-constantan thermocouples. One thermocouple was connected to the guard ring just below the first shutter and enabled an assessment to be made of temperature variations caused by the heating action of the filament. The temperature rise as recorded by this thermocouple could be greatly reduced by immersing the apparatus in a water bath, which acted as a heat sink. The second thermocouple was placed in this bath. Temperature stability was facilitated by conducting the experiments in an air-conditioned room where the temperature was maintained at 293°K.
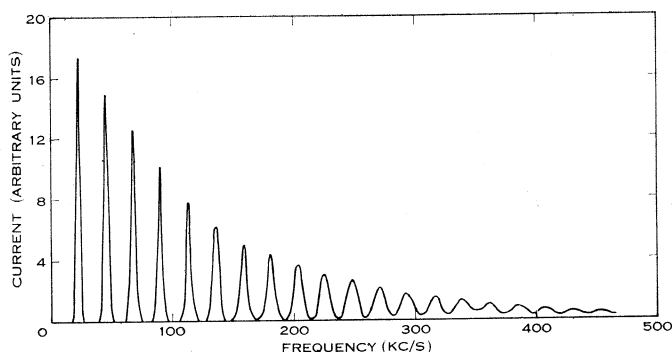
Fig. 3.—Variation of electrometer current with change of frequency
(H_2, $E/p = 0 \cdot 08$, $p = 500$, $T = 293$°K).

When measurements were made at $77 \cdot 6$°K, the bath surrounding the apparatus consisted of liquid nitrogen having a purity close to 100%. At these temperatures, the thermocouple that was attached to the electrode system could not be used because errors were introduced due to the presence of temperature gradients over the tungsten seals by which the thermocouple leads are brought out from the experimental tube. However, experiments conducted prior to assembly of the apparatus showed that the temperatures inside the experimental tube below the level of the liquid nitrogen bath was the same as the temperature of the bath to within $0 \cdot 5$°K.

The thermocouples were calibrated by means of a number of fixed points covering the temperature range 77–373°K, following the procedure outlined by Scott (1941).

III. EXPERIMENTAL RESULTS

The drift velocity was measured by determining the frequency of the maximum of the first or second current peak of the current-frequency curve. Figures 3 and 4 give two extreme examples of current-frequency curves and it is seen that the resolving power possible from any peak varies considerably under different conditions (Lowke 1962).

In all instances where current-frequency curves were prepared, as for example in Figure 3 which exhibits 20 maxima, the values of f_n/n corresponding to each

maximum were found to agree to within 1%. This agreement is strong evidence confirming that no errors are present due to:

(1) displacement of the current maximum due to a variation in the value of the a.c. voltage on the shutters with change of frequency,

(2) incorrect frequency calibration, and

(3) phase differences between a.c. voltages applied to the first and second shutter (discussed in Section IV).

Corresponding to each determination of f_n the temperature and pressure of the gas was recorded to enable small corrections to W to be made to allow for small deviations from the standard values of E/p employed. At each value of the gas
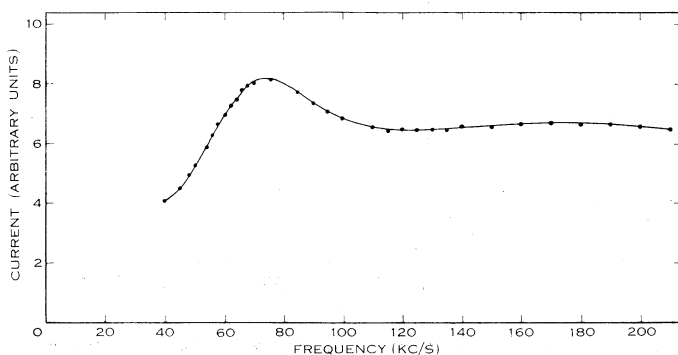
Fig. 4.—Variation of electrometer current with change of frequency
(N_2, $E/p = 1$, $p = 2$, $T = 293°K$).

pressure, two sets of measurements were made using different gas samples. Agreement between the results was always to within 1% at high values of E. At low values of E experimental errors become larger because of the greater influence of spurious contact potential differences and also because the greater degree of diffusion of the electrons results in a loss of resolving power. Where differences of more than 1% existed between the two series of results, the measurements were repeated with a third gas sample and the average value of the three results was obtained.

The results at 293°K are presented in Tables 1 and 2 as a function of the ratio E/p, where p is the pressure of the gas at 293°K. It is not, however, the physical pressure p that is significant, but the concentration N of the gas molecules per cm³, of which p is a measure, provided that the temperature remains constant. Since $N = 3 \cdot 30 \times 10^{16} p$ cm^{-3} at 293°K, the parameter E/p is the same as $3 \cdot 30 \times 10^{16} E/N$.

The results at 77·6°K, which are presented in Tables 3 and 4, are also presented as a function of $3 \cdot 30 \times 10^{16} E/N$, so that results for any value of E/N can easily be compared at the two temperatures. At 77·6°K, the values of $3 \cdot 30 \times 10^{16} E/N$ can be regarded as being equal to E/p, where p in this case has the particular meaning of being the pressure of the gas at 293°K that has the same molecular concentration N as the gas at 77·6°K. In Tables 3 and 4 p is used in this way.

TABLE 1
HYDROGEN 293°K: VALUES OF $W \times 10^{-5}$ CM/S
$E/p = 3 \cdot 30 \times 10^{16} E/N, \ N = 3 \cdot 30 \times 10^{16} p$

E/p \ p	2	5	10	20	50	100	200	400	500	Best Estimate
18	63·2									62·8
15	51·7									51·3
12	42·3									41·9
10	37·2									36·8
9	34·5									34·2
8	32·1									31·9
7	29·7	29·6								29·5
6	27·1	26·9								26·7
5	24·3	24·1								24·0
4	21·5	21·2	21·1							21·0
3	18·3	18·0	18·0							17·9
2·5	16·6	16·3	16·2							16·1
2	14·7	14·4	14·4	14·3						14·3
1·8	13·9	13·6	13·6	13·5						13·5
1·5	12·7	12·4	12·4	12·3						12·3
1·2	11·4	11·1	11·0	11·0						11·0
1·0	10·4	10·2	10·1	10·1						10·1
0·9		9·72	9·63	9·59						9·56
0·8		9·23	9·15	9·11	9·08					9·08
0·7		8·73	8·64	8·62	8·58					8·57
0·6		8·19	8·12	8·09	8·05					8·04
0·5		7·59	7·53	7·50	7·46					7·45
0·4		6·91	6·86	6·83	6·80	6·81				6·81
0·3			6·02	5·98	5·97	5·97				5·97
0·25			5·50	5·46	5·45	5·45				5·45
0·2			4·89	4·85	4·84	4·84	4·85			4·85
0·18				4·57	4·56	4·56	4·56			4·56
0·15				4·09	4·08	4·08	4·09			4·09
0·12				3·57	3·55	3·55	3·56			3·56
0·1				3·16	3·14	3·15	3·15	3·15		3·15
0·09					2·92	2·94	2·94	2·94		2·94
0·08					2·68	2·70	2·70	2·70	2·70	2·70
0·07					2·44	2·45	2·45	2·45	2·45	2·45
0·06					2·18	2·18	2·19	2·18	2·18	2·18
0·05					1·89	1·90	1·90	1·90	1·89	1·89
0·04					1·58	1·58	1·59	1·58	1·59	1·59
0·03						1·25	1·26	1·25	1·26	1·26
0·025						1·06	1·07	1·07	1·07	1·07
0·02						0·876	0·878	0·879	0·879	0·878
0·018							0·799	0·800	0·798	0·797
0·015							0·675	0·675	0·677	0·676
0·012							0·547	0·549	0·550	0·549
0·01							0·461	0·462	0·464	0·463
0·009								0·419	0·420	0·419
0·008								0·374	0·375	0·374
0·007								0·330	0·330	0·329
0·006								0·284	0·284	0·283
0·005								0·236	0·236	0·235
0·004									0·189	0·188

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TABLE 2
NITROGEN 293°K: VALUES OF $W \times 10^{-5}$ CM/S

$$E/p = 3 \cdot 30 \times 10^{16} E/N, \quad N = 3 \cdot 30 \times 10^{16} p$$

E/p \ p	2	3	4	5	10	20	50	100	200	400	500	Best Estimate
20	71·2											70·9
18	65·4											65·1
15	57·2	57·1										56·8
12	48·4	48·3	48·3									48·2
10	42·4	42·2	42·1	42·1								42·0
9	39·2		39·0	39·1								39·0
8	36·1		35·8	35·9								35·7
7	32·5			32·4								32·3
6	29·0			28·9								28·8
5	25·6			25·3								25·0
4	21·9			21·5	21·2							21·1
3	18·0			17·4	17·2							17·1
2·5	15·9			15·3	15·0							14·9
2	13·7			12·9	12·8	12·8						12·7
1·8	12·9			12·1	11·8	11·8						11·7
1·5	11·4			10·6	10·4	10·3						10·2
1·2	10·2			9·04	8·87	8·79						8·73
1·0	9·26			8·04	7·84	7·77						7·72
0·9				7·52	7·33	7·25						7·19
0·8				6·97	6·82	6·72	6·68					6·66
0·7				6·49	6·31	6·22	6·20					6·18
0·6				5·97	5·80	5·72	5·70					5·68
0·5				5·49	5·31	5·23	5·21					5·19
0·4				5·03	4·85	4·78	4·77	4·77				4·76
0·3					4·39	4·32	4·28	4·29				4·28
0·25					4·13	4·05	4·03	4·03				4·02
0·2					3·84	3·77	3·76	3·75	3·76			3·76
0·18						3·66	3·63	3·63	3·63			3·63
0·15						3·46	3·43	3·43	3·43			3·43
0·12						3·26	3·23	3·23	3·22			3·22
0·1						3·12	3·09	3·10	3·09	3·09		3·09
0·09							3·03	3·04	3·04	3·03		3·03
0·08							2·97	2·97	2·97	2·96	2·96	2·96
0·07							2·91	2·91	2·90	2·89	2·90	2·90
0·06							2·83	2·83	2·83	2·82	2·81	2·81
0·05							2·72	2·72	2·72	2·71	2·71	2·71
0·04							2·56	2·56	2·55	2·55	2·55	2·55
0·03								2·29	2·29	2·28	2·28	2·28
0·025								2·07	2·08	2·08	2·08	2·08
0·02								1·82	1·82	1·82	1·82	1·82
0·018									1·71	1·70	1·71	1·71
0·015									1·49	1·49	1·49	1·49
0·012									1·25	1·26	1·25	1·25
0·01									1·07	1·07	1·07	1·07
0·009										0·977	0·975	0·974
0·008										0·879	0·878	0·877
0·007										0·778	0·776	0·774
0·006										0·674	0·673	0·672
0·005										0·567	0·565	0·564
0·004											0·456	0·455

TABLE 3

HYDROGEN 77·6°K: VALUES OF $W \times 10^{-5}$ CM/S

$E/p = 3 \cdot 30 \times 10^{16} E/N, \; N = 3 \cdot 30 \times 10^{16} p$

p / E/p	10	20	50	80	200	500	1000	2000	Best Estimate
3	18·3								18·1
2·5	16·5								16·3
2	14·7	14·5							14·4
1·8	13·9	13·7							13·6
1·5	12·7	12·6							12·5
1·2	11·4	11·2							11·1
1·0	10·5	10·4							10·3
0·9	9·99	9·90							9·85
0·8	9·55	9·46	9·42						9·40
0·7	9·06	8·98	8·95						8·93
0·6	8·55	8·49	8·44						8·42
0·5	8·03	7·94	7·89	7·89					7·87
0·4	7·39	7·31	7·29	7·30					7·29
0·3	6·59	6·55	6·51	6·49					6·48
0·25	6·10	6·03	6·01	6·02					6·01
0·2	5·51	5·45	5·41	5·41	5·37				5·36
0·18		5·17	5·13	5·13	5·12				5·11
0·15		4·68	4·64	4·63	4·63				4·63
0·12		4·12	4·09	4·10	4·08				4·08
0·1		3·71	3·68	3·68	3·66				3·66
0·09			3·44	3·44	3·41				3·41
0·08			3·20	3·19	3·16	3·15			3·15
0·07			2·94	2·93	2·91	2·90			2·90
0·06			2·65	2·65	2·63	2·62			2·62
0·05			2·34	2·34	2·33	2·32			2·32
0·04			2·02	2·01	2·00	1·99	1·97		1·97
0·03				1·63	1·62	1·63	1·62		1·62
0·025				1·44	1·43	1·43	1·43		1·43
0·02					1·23	1·24	1·24	1·23	1·23
0·018					1·14	1·14	1·14	1·14	1·14
0·015					1·01	1·01	1·01	1·01	1·01
0·012					0·868	0·868	0·871	0·869	0·869
0·01					0·764	0·764	0·768	0·767	0·767
0·009						0·709	0·712	0·715	0·715
0·008						0·651	0·656	0·655	0·655
0·007						0·590	0·598	0·594	0·594
0·006						0·525	0·533	0·530	0·530
0·005						0·457	0·459	0·458	0·458
0·004						0·382	0·381	0·383	0·383
0·003							0·300	0·297	0·297
0·0025							0·255	0·254	0·254
0·002							0·208	0·207	0·207
0·0018								0·188	0·188
0·0015								0·158	0·158
0·0012								0·129	0·129
0·001								0·108	0·108

TABLE 4

NITROGEN $77 \cdot 6°$K: VALUES OF $W \times 10^{-5}$ CM/S

$$E/p = 3 \cdot 30 \times 10^{16} E/N, \quad N = 3 \cdot 30 \times 10^{16} p$$

E/p \\ p	20	40	50	80	200	500	1000	2000	Best Estimate
2	12·9								12·8
1·8	11·9								11·8
1·5	10·4								10·3
1·2	8·93								8·81
1	7·89	7·82							7·77
0·9	7·38	7·31							7·26
0·8	6·82	6·80	6·77						6·73
0·7	6·33		6·27						6·24
0·6	5·80		5·76						5·73
0·5	5·35		5·29	5·28					5·24
0·4	4·89		4·84	4·82					4·80
0·3	4·42		4·38	4·36					4·33
0·25	4·20		4·14	4·11					4·09
0·2	3·91		3·88	3·87	3·85				3·85
0·18	3·80		3·76	3·75	3·74				3·74
0·15	3·63		3·59	3·58	3·58				3·58
0·12	3·49		3·44	3·44	3·43				3·43
0·1	3·43		3·40	3·40	3·39				3·39
0·09			3·40	3·40	3·39				3·39
0·08			3·41	3·42	3·41	3·42			3·42
0·07			3·45	3·46	3·46	3·47			3·46
0·06			3·52	3·53	3·53	3·53			3·53
0·05			3·60	3·61	3·60	3·60			3·60
0·04		3·66	3·66	3·66	3·66	3·67	3·67		3·67
0·03			3·67	3·68	3·67	3·67	3·68		3·68
0·025			3·63	3·62	3·63	3·63	3·63		3·63
0·02					3·49	3·49	3·49	3·48	3·48
0·018					3·41	3·41	3·41	3·38	
0·015					3·22	3·23	3·21	3·19	
0·012					2·94	2·94	2·93	2·89	
0·01					2·69	2·68	2·67	2·64	
0·009						2·53	2·52	2·48	
0·008						2·35	2·34	2·29	
0·007						2·16	2·14	2·10	
0·006						1·93	1·92	1·88	
0·005						1·68	1·66	1·62	
0·004						1·41	1·38	1·36	
0·003							1·08	1·05	
0·0025							0·918	0·894	
0·002							0·744	0·724	
0·0018								0·656	
0·0015								0·548	
0·0012								0·443	
0·001								0·372	

When the values of E/N are deduced from gas pressures measured at $77 \cdot 6°$K, account must be taken of the deviation of the behaviour of nitrogen from that of a perfect gas. The second virial coefficient B has been measured in this temperature region by Keesom and Van Lammeren (1932) and also by Van Itterbeck, Lambert, and Forrez (1956) using the indirect method involving the measurement of the velocity of sound. Both investigations give $B = -11 \cdot 3 \times 10^{-3}$ at $77 \cdot 6°$K, where B is defined such that $pV = RT(1+B/V)$, where p is the pressure of the gas in atmospheres, T is the temperature in degrees K, and R is a constant such that $p = V = 1$ at $273°$K. At the highest gas pressures used, the correction to E/N amounts to $2 \cdot 5\%$. For hydrogen at $77 \cdot 6°$K the corresponding correction is much less than 1%.

From an inspection of the tables, it can be seen that the results for a given value of E/N are in general not entirely independent of N. It has been shown in a previous paper (Lowke 1962) that the influence of electron diffusion leads to an increase in the measured value of the drift velocity from the true velocity, the measured value W_M being given approximately by

$$W_M = W[1+3/h(W/D)], \tag{1}$$

where W is the true velocity, h is the drift distance, and D is the coefficient of diffusion of the electrons. Equation (1) is not an exact relation because the increase in the measured value of the drift velocity from the true velocity is dependent on the fraction of the time that the shutters are effectively "open", and the results are thus to some extent dependent on the amplitude of the a.c. voltage. Nevertheless, the variation of the measured values of W with N is closely represented by equation (1) (Lowke 1962).

In the present investigation, the dependence of the values of W on N gives evidence of the validity of equation (1) in addition to that given in the earlier paper. With few exceptions, close agreement with equation (1) is obtained at all values of E/p for both hydrogen and nitrogen at $293°$K and $77 \cdot 6°$K. The expression for W_M can be evaluated using the independent measurements of W/D that have been made by Crompton and Sutton (1952), Crompton and Jory (1962), and the unpublished results for $77°$K of Warren and Parker (1962). The variation with N that is observed for $E/p > 8$ is not as great as is predicted by equation (1), the explanation being attributed to the fact that very high a.c. voltages were not used for these measurements because of the possibility of electrical breakdown within the shutters. Such high a.c. voltages are necessary to obtain boundary conditions of the electron density at the shutters comparable with the boundary conditions that exist at low E/p, when the electron energies are much lower.

The variations of W with N at values of E/p less than $0 \cdot 02$ in nitrogen at $77 \cdot 6°$K cannot be explained by the influence of diffusion. For example at $E/p = 0 \cdot 005$ the measured value of the drift velocity at $p = 2000$ is $3 \cdot 1\%$ lower than the result at $p = 500$. Equation (1) predicts a variation of W of less than $0 \cdot 2\%$ over this range of p. As no variations with p at low values of E/p have been observed for the corresponding results in hydrogen, it is unlikely that the variation of the results in nitrogen is caused by an experimental error. The observed dependence of the results on N is illustrated in greater detail in Figure 5, in which additional experimental points

to those of Table 4 are given. It is seen that the dependence of the results on N is such that the variations of W are closely proportional to N. No explanation has been found for this variation.

It is of interest to note that, if no correction had been made taking account of the high value of the second virial coefficient, the variation of the results at $E/p = 0 \cdot 005$ would have been $4 \cdot 8 \%$ instead of $3 \cdot 1 \%$.

For all other measurements of the drift velocity the correct value, free of any falsification due to the influence of diffusion, is the asymptotic value that would be measured when very high gas pressures are used. The figures given in the tables under the column "Best Estimate" are an estimate of these asymptotic values of the drift velocity, this estimate being based on the trend of the measured values
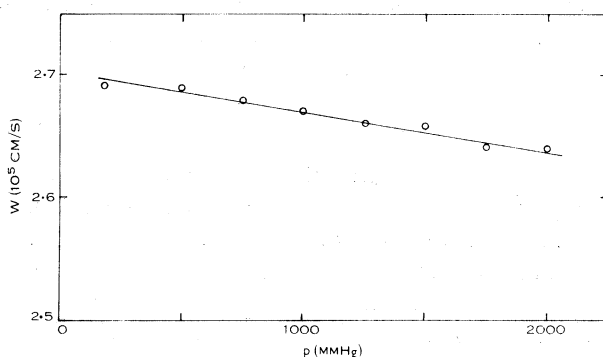
Fig. 5.—Variation of the measured value of the drift velocity with N
(N_2, $E/p = 0 \cdot 01$, $T = 77 \cdot 6°$K).

given in the tables. Supplementary measurements were made in nitrogen for $p = 3$ and 4 at $293°$K and $p = 40$ at $77 \cdot 6°$K to enable the asymptotic value to be assessed more accurately. Because of the observed real dependence of W on N for $E/p < 0 \cdot 02$ in nitrogen at $77 \cdot 6°$K it is impossible to give a Best Estimate of W at these values of E/p.

IV. DISCUSSION OF ERRORS

(a) Errors due to Diffusion

For any value of E/p the errors due to diffusion are least for the results that are taken at the highest value of N. As these results differ from the Best Estimate values at most by $1 \cdot 3 \%$, it is seen that the magnitude of the correction is small and as a consequence it is considered that the values of the Best Estimate are correct to 1%. The results most likely to be in error are for $E/p > 7$, where results could not be taken over a large range of N to enable an accurate assessment of the asymptotic limit to be made.

If equation (1) is regarded as giving the upper limit of the error due to diffusion, the results taken at the highest gas pressure for any value of E/p are in error due to diffusion by less than $0 \cdot 5 \%$ for $0 \cdot 006 \leqslant E/p \leqslant 0 \cdot 8$ in hydrogen at $293°$K,

$0 \cdot 006 \leqslant E/p \leqslant 0 \cdot 4$ in nitrogen at 293°K, $E/p \leqslant 0 \cdot 8$ in hydrogen at 77·6°K, and $E/p \leqslant 0 \cdot 2$ in nitrogen at 77·6°K.

(b) Errors due to Contact Potential Differences and Surface Charges

No results have been taken using values of E less than 2 V cm^{-1} because of the possibility of such effects as stray contact potential differences introducing errors. Experiments performed in this laboratory using the Kelvin method of determining contact potential differences have shown that contact potential differences of 200 mV can exist between gold surfaces if the gold is deposited by different methods. Although all metal surfaces were gilded, it was considered possible that contact potential differences could introduce appreciable errors at values of $E < 2$ V cm^{-1}.

Furthermore, on one occasion when measurements were being made with the present apparatus when $E = 2$ V cm^{-1} the measured value of the drift velocity slowly increased by 6% when very high currents were used. The effect was removed after both shutters were freshly gilded. It seems most likely that the surface of the shutter wires had formerly become charged, thus altering the effective d.c. voltage across the drift space.

The practice of always basing the "Best Estimate" of the drift velocity for a given value of E/p on the measurement made at the highest possible gas pressure means that the value of E for these measurements is always greater than 5 V cm^{-1} for all values of E/p except $E/p \leqslant 0 \cdot 01$. Thus if any effects due to contact potential differences or surface charges are in existence, the results most likely to be in error are the values for $E/p < 0 \cdot 01$. However, no evidence of such errors was found in the final results that were taken.

(c) Distortion of the Electric Field

To test the effect on the results of any non-uniformity of the electric field, the electric field was deliberately grossly distorted by changing the potentials of guard rings 4, 5, and 6 from their correct values to the potential of guard ring 3. At $E/p = 0 \cdot 2$ for $p = 150$ using hydrogen, the measured value of the drift velocity decreased by 2% from the value obtained when the guard electrodes were connected normally.

The remarkably small influence of pronounced field distortion was verified by finding the field distribution within the drift tube by means of an electrolytic tank and performing a rough calculation to find the time of flight of an electron pulse drifting through the region of non-uniform field between the shutters. Such a calculation shows that, provided the correct potential difference is applied between the two shutters, the effect of field distortion produces only a second-order error in the measured value of the drift velocity. Since the field distortion required to reduce the values of the drift velocity by 1% is so much greater than the distortion likely to be present experimentally, errors due to d.c. field distortion were considered to be negligible.

Errors are possible due to field distortion from the a.c. voltages that are applied to the shutter wires. One of the advantages of the method of Bradbury and Nielsen

results from the use of alternating potentials on the shutter. As a result, the effect of field distortion on any electron pulse is compensated by the effect on the next pulse and consequently there are only second-order effects on the measured value of the drift velocity. Experimental confirmation of the lack of influence of the a.c. voltages on the drift velocity values was obtained at $E/p = 0.005$ by varying the r.m.s. voltage from 0.2 to 4 V. Over this range of r.m.s. voltage the drift velocity remained constant to within 1%, even though the d.c. field E was only 2.5 V cm^{-1}.

It should be noted that, when the experimental conditions are such that W/D is small, the drift velocity has been observed to be a function of the a.c. voltage. This variation can, however, be shown to arise from the diffusion of the electron pulses (Lowke 1962).

(d) Temperature

The drift velocity is a function of both E/N and temperature. Consequently, if the temperature of the gas deviates slightly from say 293°K, deviations of the measured value of the drift velocity from the value at 293°K are introduced owing both to the change in the gas density with temperature, for any given value of E/p, and to the absolute dependence of the drift velocity on the temperature.

When taking measurements at 293°K the temperature as measured by the thermocouple within the drift tube slowly increased owing to the heating action of the filament. To minimize the temperature gradient across the drift space the filament was turned off at all times other than during the actual determination of f_n. Under most conditions the temperature as measured by this thermocouple rose by approximately 1.5°K, the maximum rise recorded being 2.5°K. Changes in the temperature of the bath surrounding the experimental tube were negligible. The best estimate of the temperature of the gas was taken to be the average of the two thermocouple readings, and this was the temperature on which corrections were based for variations in gas density from that corresponding to a temperature of 293°K.

When taking measurements at 77.6°K, the thermocouple in the drift tube indicated no change in temperature due to the heating action of the filament.

A temperature change of 3°K for gas at constant pressure is required to alter E/N by 1% at 293°K, and the change in W for a 1% change in E/N is generally less than 1%. Consequently, with the corrections that have been applied, it is considered that the error in the determination of E/N should be considerably less than 1%.

The variation of W with the temperature, at constant E/N, is greatest at the lowest values of E/N. As no correction was made for this effect, particular care was taken to ensure that the readings of W at the very lowest values of E/N were made when the gas temperature was within one degree of 293°K.

The measurements of W at 77.6°K are more susceptible to errors in the determination of the temperature, as it requires an error in the temperature determination of only 0.8°K to produce an error of 1% in the estimated value of E/N. Furthermore, the temperature as recorded by the thermocouple cannot be determined with as great an accuracy as at 293°K, errors of 0.5°K being possible. Consequently the overall experimental error of the drift velocity measurements at 77.6°K is expected to be

of the order of 2%. It is seen that at $E/p = 2$ the values of the drift velocity at 77·6°K in both hydrogen and nitrogen is 1% higher than the value at 293°K at the same value of E/p. It is not known whether this difference is a result of inaccuracies in the thermocouple calibration, an effect due to the heating action of the filament, or a genuine difference in the two sets of measurements due to the difference in the temperature. A likely explanation is that heat conduction from the leads to the electrodes, even though these leads were made of fine nichrome wire, is sufficient to raise the temperature of the gas above the temperature of the bath surrounding the experimental tube. It is also possible that the difference arises from too low an estimate of the effect of diffusion on the results at 77·6°K.

(e) Space Charge Repulsion

As the measured value of the drift velocity in hydrogen at $E/p = 0·005$ at 293°K was constant for values of the electron current which could be varied from 3×10^{-13} to 10^{-11} A, it is considered unlikely that errors due to the influence of space charge repulsion are present.

(f) Phase Errors of the A.C. Voltages

A critical requirement for accurate determinations of the drift velocity is that the phase of the a.c. signals applied to the first shutter be equal to the phase of the signals applied to the second shutter. Knowing that the capacity of each shutter is approximately 100 pF, it is possible to select the values of the resistances and capacitors of the R.C. network feeding the shutters so that any phase differences that do occur are less than 1°. A direct experimental check was also made to verify that such phase differences were not present.

As phase differences are generally a function of frequency, the existence of a phase shift between the first and second shutter would give rise to disagreement between the values of f_n/n for the current peaks of the current-frequency curves. As has been previously mentioned, no such disagreement has been observed.

Errors will also occur if the phase difference between the two a.c. signals applied to the two halves of a shutter is not exactly 180°. If such a phase error is small, the result is that the effective d.c. potential of the shutter, each time it is open, is slightly displaced from the correct d.c. potential required to maintain the uniform d.c. field. This displacement is alternately positive and negative for consecutive occasions that the shutter is open. As a consequence the resultant effects on successive electron pulses are compensating and the measured value of the drift velocity is unchanged. A slight broadening will occur, however, in the peaks of the current-frequency curves. A direct comparison of the phases of the voltages applied to the shutter failed to detect any error.

V. INFLUENCE OF GASEOUS IMPURITIES

The mass spectrographic analysis of samples taken from the gas after an experimental set of results had been completed confirmed that the only impurities likely to be present were hydrogen in nitrogen, nitrogen in hydrogen, and water vapour.

To determine the influence of hydrogen impurities on the drift velocity measurements in nitrogen, small quantities of hydrogen were added to nitrogen and the resulting change in the drift velocity noted. It was found that at least $0 \cdot 5\%$ of hydrogen had to be added to change the drift velocity by 1%, and the change in W was approximately proportional to the percentage of hydrogen added. Table 5 gives the percentage changes in W at $E/p = 0 \cdot 5$ that were observed when various percentages were added.

TABLE 5

CHANGE IN DRIFT VELOCITY IN NITROGEN WHEN HYDROGEN ADDED

Hydrogen (%)	$\frac{1}{2}$	1	$2 \cdot 5$	5	10
Increase in W (%)	1	2	6	10	16

Table 6 gives the percentage increase in the drift velocity that was observed at various values of E/p for a mixture of $2 \cdot 5\%$ hydrogen in nitrogen at $293°$K.

The table also gives the changes that would be expected in the drift velocity calculated using the theory of mixtures as developed by Bailey and Healey (1935). It is seen that good agreement is obtained between the theoretical predictions and

TABLE 6

CHANGE IN DRIFT VELOCITY FOR VARIOUS VALUES OF E/p

$2 \cdot 5\%$ hydrogen in nitrogen at $293°$K

E/p	20	5	2	1	0·5	0·2	0·1	0·05	0·03	0·018	0·005
Experimental increase (%)			1	3	6	4	5	2	0	−3	
Theoretical increase (%)	0	0	1	4	6	5	5	2	−1	−2	−2

the experimentally observed increases in the drift velocity. It is concluded that over the whole range of E/p for which the present results are taken, impurities of $0 \cdot 5\%$ or more of hydrogen are required to change the drift velocity results in nitrogen by 1%. The mass spectrographic analysis revealed that the percentage impurity of hydrogen was less than $0 \cdot 01\%$. It is evident that the resultant percentage change in the values of the drift velocity is below $0 \cdot 1\%$.

Similar experiments were conducted to determine the influence of small quantities of nitrogen on the drift velocity of electrons in hydrogen. In general it was found that a given percentage of nitrogen in hydrogen had much less effect in changing drift velocity values than the same percentage of hydrogen in nitrogen. Table 7 gives the percentage change in the drift velocity for a 10% mixture of nitrogen in hydrogen at $293°$K. A comparison with the values as predicted by the theory of mixtures again shows good agreement.

It is again evident from the results given in Table 7 that the final drift velocity results could not be significantly affected by the presence of impurities of nitrogen because a mass spectrographic analysis showed that the percentage of nitrogen present in samples of hydrogen was less than $0 \cdot 01 \%$.

In all experiments with mixtures of hydrogen and nitrogen it was found that the experimental results slowly varied with time until the gas mixture became uniform. A period of up to 60 hours was allowed for the gases to mix together. If a further period of 12 hours produced no further change in the results, the time allowed for the gases to mix together was considered to be adequate.

TABLE 7

CHANGE IN DRIFT VELOCITY FOR VARIOUS VALUES OF E/p

10% nitrogen in hydrogen at 293°K

E/p	10	2	0·5	0·1	0·08	0·05	0·01	0·005
Experimental increase (%)			—1	3	4	5	6	
Theoretical increase (%)	1	—1	0	3	4	4	6	7

Experiments have also been carried out to ascertain the influence of traces of water vapour on the values of the drift velocity of electrons in nitrogen. The results indicate that for a given percentage of water vapour impurity the percentage increase in W is over 100 times greater than for the same percentage of hydrogen impurity.

TABLE 8

EFFECT OF WATER VAPOUR ON DRIFT VELOCITY IN NITROGEN AT

293°K FOR $p = 250$ MM, $E/p = 0 \cdot 16$

Amount of Water Vapour Added (μ)	Percentage of Water Vapour	Increase in Measured Value of W (%)
40	0·02	6
5	0·002	0·7

Water vapour was introduced into the evacuated apparatus by connecting to the apparatus a cold trap containing a small quantity of ice. The amount of water vapour that is thus introduced is assumed to be the vapour pressure of ice corresponding to the temperature of the ice in the cold trap. This temperature was controlled by means of a cold bath of alcohol and measured by means of a thermo-couple embedded in the ice. Although it is possible that the estimate of the concentration of water vapour may be in error by as much as 20%, the results quoted in Table 8 show the marked effect of traces of water vapour on the value of the drift velocity.

The addition of water vapour also caused a change in the form of the current-frequency curves. The curves for the two experimental conditions of Table 8 are illustrated in Figures 6 and 7.
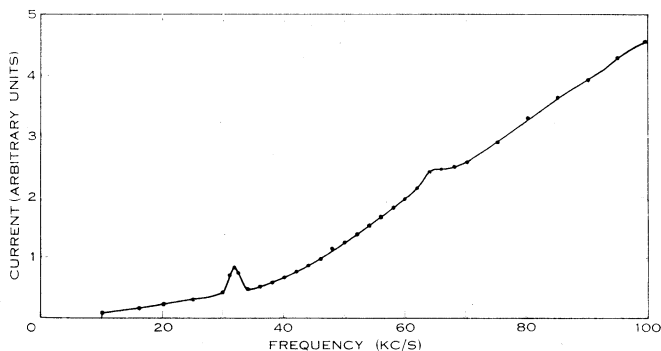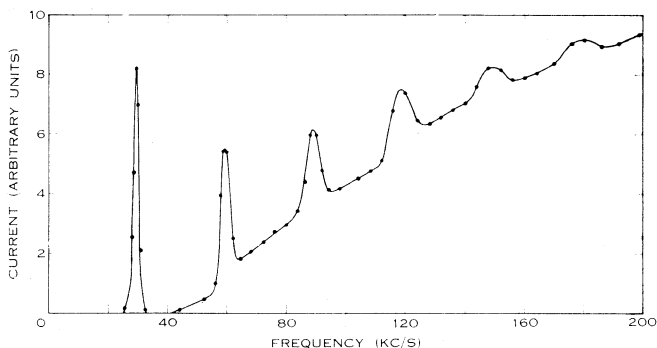

Fig. 6.—Variation of electrometer current with change of frequency when $0 \cdot 02\%$ of water vapour is present in nitrogen ($E/p = 0 \cdot 16$, $p = 250$, $T = 293°\mathrm{K}$).

It is seen that the normal series of current peaks is superimposed on a background current which increases with increase of frequency, the background current consisting of negative ions formed by attachment. At high frequencies more ions are transmitted by the shutter because the field between the shutter wires changes too rapidly for the ions to be collected and so the background current increases with frequency.

Fig. 7.—Variation of electrometer current with change of frequency when $0 \cdot 002\%$ of water vapour is present in nitrogen ($E/p = 0 \cdot 16$, $p = 250$, $T = 293°\mathrm{K}$).

The existence of the background current will slightly displace the positions of the maxima of the current-frequency curves. By subtracting the background current from the total current it may be shown that the presence of this current accounts for only $0 \cdot 1\%$ of the 6% increase in the value of the drift velocity, which is therefore a real increase in W due to the presence of water vapour impurity.

The existence of a background current of negative ions is a valuable criterion for ascertaining whether water vapour is present in the gas. It is seen that, for the

conditions of Figure 7, the amount of water vapour required to increase the value of the drift velocity by only $0 \cdot 7\%$ is still easily detectable by the presence of a background current. In all measurements that were taken in pure gas no background current could be detected and this is regarded as being the best indication that the present results are not in error by more than $0 \cdot 5\%$ due to the presence of water vapour. Furthermore, the measured value of the drift velocity for any one gas sample remained constant for 12 hr so that it is unlikely that errors were introduced by the outgassing of the experimental tube.

VI. FURTHER TEST OF EXPERIMENTAL ACCURACY

An additional experiment that has been conducted gives further evidence that the method of Bradbury and Nielsen is not prone to errors from factors such as errors in phase or field distortion from the shutter voltages.

TABLE 9
VELOCITY OF POSITIVE POTASSIUM IONS PRODUCED BY ACCELERATING VOLTAGES

Accelerating Voltage	30	40	50	60	70	80	90	100	150	200
Theoretical velocity $\times 10^{-5}$ (cm/s)	12·1	14·0	15·7	17·2	18·5	19·8	21·0	22·2	27·2	31·3
Experimental velocity $\times 10^{-5}$ (cm/s)	12·0	14·0	15·6	17·1	18·4	19·7	20·9	22·1	27·0	31·0

A similar shutter apparatus was used to measure the velocity of a collimated monoenergetic beam of positive potassium ions travelling in vacuum. The ions were initially accelerated through an accurately measured potential difference V before reaching the first shutter, and then travelled with constant velocity v in a region of field-free space between the shutters. The velocity could be calculated using the relation

$$\tfrac{1}{2}mv^2 = eV, \tag{2}$$

where m is the mass of the positive ion and e the electronic charge. The positive ions were produced from a filament of the type used by Blewett and Jones (1936).

The agreement which was obtained between theory and experiment, as is shown by the results given in Table 9, was within 1%.

VII. DISCUSSION OF RESULTS

The Best Estimate values of the results are now compared with the results of other investigations. When account is taken of the limits of the experimental accuracy of each investigation, the present results in nitrogen at room temperature agree with the results of Nielsen (1936), Comunetti and Huber (1960), Nagy, Nagy, and Desi (1960), and Pack and Phelps (1961). The results of Bortner, Hurst, and Stone (1957) and Bowe (1960) are up to 6% lower than the present results, while the results of

Klema and Allen (1950) and Colli and Facchini (1952) are generally higher than the present results.

The results in hydrogen at room temperature agree with the previous measurements of Bradbury and Nielsen (1936) and Pack and Phelps (1961) to within the experimental error. The only previous measurements of the drift velocity at liquid air temperatures is the investigation of Pack and Phelps, with which agreement is obtained.
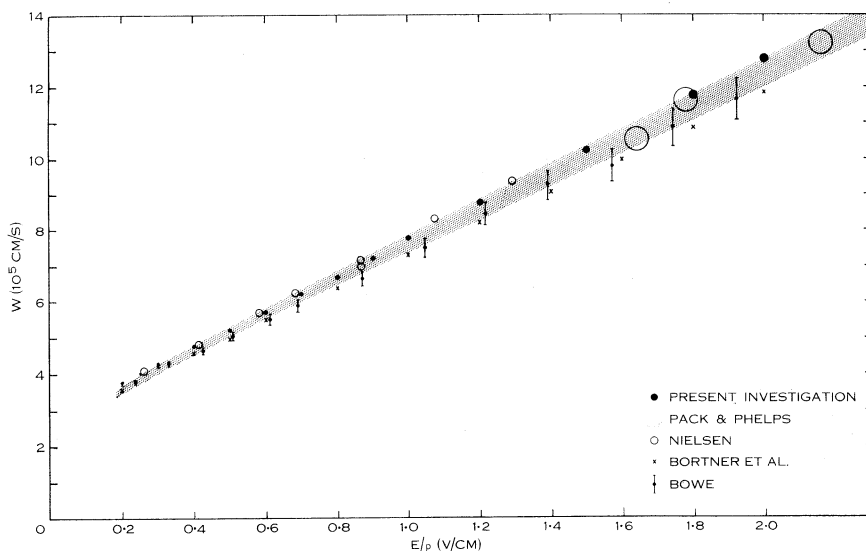

Fig. 8.—Comparison of drift velocity results in nitrogen at 293°K for $0 \cdot 2 < E/p < 2 \cdot 2$.

The most recent of the investigations is that of Pack and Phelps (1961) which gives results at four different gas temperatures and at values of E/p over a very wide range. However, as the graph on which the experimental results were plotted has a logarithmic scale, the width of the line passing through the experimental points corresponds to 7% of the value of the drift velocity. On their graph the experimental points are indicated by circles and show a scatter which (in some cases) is comparable with the width of the line.

The values of the drift velocity that have previously been most generally accepted are those of Bradbury and Nielsen (1936) and Nielsen (1936) who give values of the drift velocity at 293°K over a range of E/p from $0 \cdot 05$ to 20. The scatter of the experimental points indicates that the accuracy of their investigation was of the order of 4%.

A comparison of the results of various investigations is made graphically in Figure 8 for nitrogen at 293°K over the range $0 \cdot 2 < E/p < 2 \cdot 2$. The shaded area corresponds to the line on the graph of the results of Pack and Phelps. The experimental points of Nielsen and of Bortner, Hurst, and Stone are given, together with every third point of the investigation of Bowe. The solid circles represent the experimental points of the present investigation, the size of the circles indicating

the range $\pm 1\%$ of the measured value. All results have been corrected to apply for a gas density corresponding to a temperature of 293°K.

VIII. Acknowledgments

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