the IBM 704 at Avco and we thank the staff at that facility for their cooperation.

APPENDIX

The counterparts to Eqs. (1) and (2) for the $3p$ series atoms can be written as:

$$\epsilon_x = K_x + 2F^0(x,1s) + 2F^0(x,2s) + 2F^0(x,3s)$$
$$+ 6F^0(x,2p) - G^0(x,1s) - G^0(x,2s) - G^0(x,3s)$$
$$- G^0(x,2p) - 2/5G^2(x,2p)$$
$$+ qF^0(x,3p) - rG^0(x,3p) - sG^2(x,3p),$$

where q, r, and s are coefficients which are different for Eqs. (1) and (2) and are determined by the number, n,

of electrons in the $3p$ shell. For Eq. (1) they are:

n	q	r	s
1	1	$-1/6$	$-1/15$
2	2	$-2/6$	$-2/15$
3	3	$-3/6$	$-3/15$
4	4	$-4/6$	$-4/15$
5	5	$-5/6$	$-5/15$
6	6	-1	$-6/15$

and for Eq. (2) they are:

n	q	r	s
1	1	-1	0
2	2	-1	-0.2
3	3	-1	-0.4
4	4	-1	-0.3
5	5	-1	-0.32
6	6	-1	-0.4.

Temperature Variation of Ionic Mobilities in Hydrogen

Lorne M. Chanin
Honeywell Research Center, Hopkins, Minnesota
(Received March 6, 1961)

Measurements have been made of the temperature variation of the mobilities of positive ions in hydrogen over the range 77°–300°K. The zero-field mobility values are $\mu_0 = 12.3$ cm²/v sec (300°K), 13.3 (195°K), and 13.0 (77°K). The present results at 300°K are in agreement with the data of Lauer, Bradbury, and Mitchell at low E/p_0, and at high E/p_0 agree with Rose's measurements. Only a single ion species was observed in the present studies. Reasons are given which support the belief that the ion observed in these measurements was H_3^+.

INTRODUCTION

RESULTS of measurements of the mobilities of positive ions in hydrogen reported in the literature date back as early as 1932. Since then, the mobility of positive ions in hydrogen has been the subject of numerous experimental investigations. In spite of this, as a result of discrepancies between the various sets of experimental data, there has existed considerable uncertainty of the value of the ion mobility. In addition, the nature of the ion involved has been controversial, primarily as a result of the lack of suitable theoretical values with which to compare with experiment. The present studies were undertaken in an attempt to obtain reliable measurements of the ion mobilities in the major energy range of interest, i.e., at low values of the electric field to pressure ratio. In addition these studies were undertaken in order to obtain information concerning the temperature variation of the mobilities, and if possible to shed some light on the ionic species involved.

APPARATUS

The mobility tube used in the present studies has been described in detail previously[1]; therefore, only a brief description will be given here. The tube, which is shown schematically in Fig. 1, consists of a shielded discharge region in which a short-duration pulse is generated, a grid which admits the ions to the drift region, and a collector electrode to which the ions drift under the influence of an applied electric field. The motion of the ions in the drift region induces a current in a resistor in the external circuit. Following amplification, the resulting voltage waveform is applied to a synchroscope with a calibrated time base. The ion transit times are determined from the breaks in the waveforms which occur when the ions reach the collector.

As in previous studies[2] of the variation of the mobility with temperature, the mobility tube is immersed in a refrigerating bath either at 77°K (liquid nitrogen) or at 195°K (dry ice). The refrigerants are contained in a styrofoam chamber which surrounds the tube. In the low-temperature measurements several hours were permitted to elapse, before taking the measurements following the introduction of the gas into the tube, in order to allow the tube and the gas to achieve thermal equilibrium at the refrigerant temperature.

The gas samples used in these studies are introduced to the mobility tube by means of an ultra-high vacuum gas handling system[3]. Following extended bakeout at

[1] M. A. Biondi and L. M. Chanin, Phys. Rev. **94**, 910 (1954).
[2] L. M. Chanin and M. A. Biondi, Phys. Rev. **106**, 473 (1957).
[3] D. Alpert, J. Appl. Phys. **24**, 860 (1953).

350°C the system attains an ultimate vacuum $<10^{-8}$ mm Hg with a rate of rise of contamination pressure $<10^{-9}$ mm Hg/min when isolated from the pumps. The gas samples employed in these studies were Airco reagent grade with impurities reported not to exceed 0.0001 mole percent.

MEASUREMENTS

The measured values of mobility μ_0 versus the electric field, to pressure ratio are shown in Figs. 2-4. The mobility μ_0 refers to a standard gas density of 2.69×10^{19} atoms/cc, in keeping with previous usage, while the pressures at various temperatures are reduced to their corresponding values for 0°C ($p_0 = 273p/T$).

The experimental results obtained at 300°K are shown in Fig. 2. The data shown cover a pressure range from 0.65 to 1.84 mm Hg and a range of E/p_0 from 3 to 49. An average of the experimental data obtained by Mitchell[4] and Rose[5] is indicated by the labelled lines in Fig. 2. Also shown are the data of Bradbury,[6] Bennet,[7] and Lauer,[8] given for low values of E/p_0, which we assumed to apply at $E/p_0 = 0$. In Bradbury's measurements the predominant ion observed had a mobility of 7.6. In addition, the existence of an ion with a mobility of 12.3 was also reported. There is reason to believe that the low mobility ion reported by Bradbury and the value given by Bennett were affected by gaseous impurities. It will be noted that the
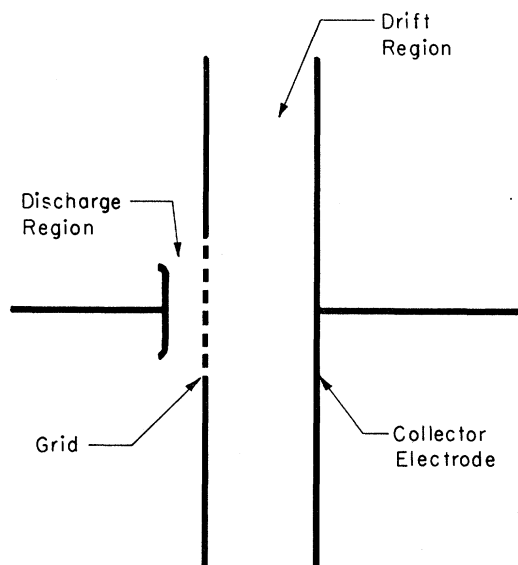

FIG. 1. Schematic arrangement of the electrodes in the ion mobility tube.

[4] J. H. Mitchell, quoted in A. M. Tyndall, *The Mobility of Positive Ions in Gases* (Cambridge University Press, New York, 1938).
[5] D. A. Rose, J. Appl. Phys. **31**, 643 (1960).
[6] N. E. Bradbury, Phys. Rev. **40**, 508 (1932).
[7] W. H. Bennett, Phys. Rev. **58**, 992 (1940).
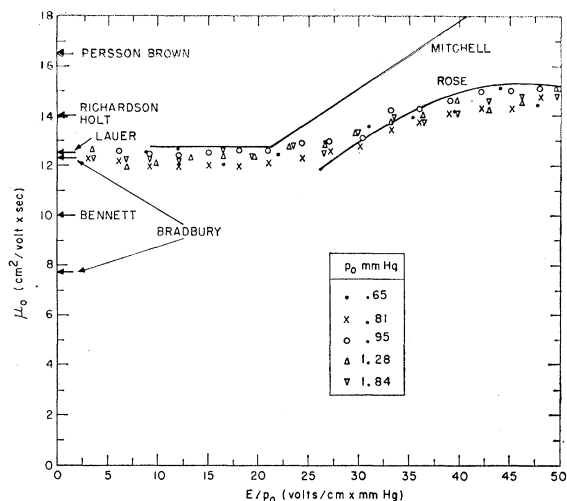[8] E. J. Lauer, J. Appl. Phys. **23**, 300 (1952).

FIG. 2. Normalized mobility μ_0 as a function of the ratio of drift field to reduced pressure at 300°K.

present results at low E/p_0 are in agreement with the value reported by Lauer and the high mobility ion reported by Bradbury and are also in fair agreement with Mitchell's low E/p_0 measurements.

In addition to previous results of direct measurements of the mobility, in Fig. 2 we show the values deduced from several of the recent[9] microwave measurements of the ambipolar diffusion coefficient in hydrogen afterglows. These values may be deduced by noting that under conditions of thermal equilibrium

$$D_a \simeq 2D_+, \qquad (1)$$

where D_a and D_+ are the ambipolar and ionic diffusion coefficients, respectively, and that

$$D_+/\mu_+ = kT_+/e = kT/e,$$

where μ_+ is the ionic mobility, k is Boltzmann's constant, and e is the ionic charge; T_+ and T are the ion and gas temperatures, respectively, and are assumed equal under thermal equilibrium conditions. From the measured values of $D_a p$ the corresponding mobilities are obtained. It will be noted that the microwave values lie considerably above the more reliable of the directly determined values. Rose has pointed out that the presence of higher diffusion modes in the discharge cavity, effect of gas heating during the discharge pulse, and its effect on the afterglow and the possibility that the diffusion may not be strictly ambipolar may account for the high mobility values deduced from the microwave measurements. The possibility exists, however, that the ion species in the microwave studies was not of the same type as observed in the direct measurements.

Figures 3 and 4 show the experimental results obtained at 195° and 77°K, respectively. It is to be noted that the zero-field mobility which at 300°K is approxi-

[9] K. B. Persson and S. C. Brown, Phys. Rev. **100**, 729 (1955); J. M. Richardson and R. B. Holt, Phys. Rev. **81**, 153 (1951).
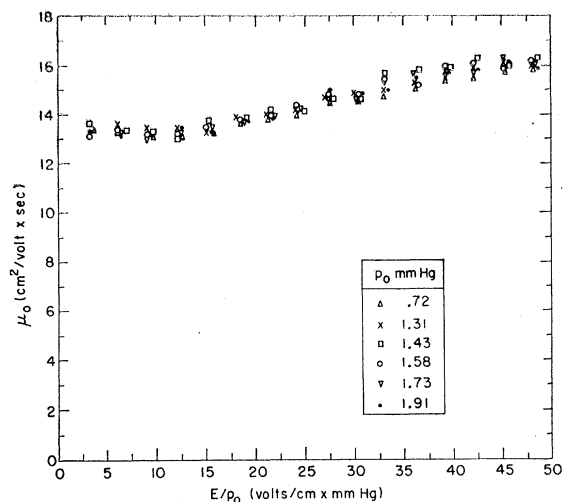
FIG. 3. Normalized mobility μ_0 as a function of the ratio of drift field to reduced pressure at 195°K.

mately 12.3 increases slowly with decreasing temperatures. The zero-field values at 195° and 77°K are, respectively, 13.3 and 13.

DISCUSSION

Some evidence of the internal consistency of the experimental data may be observed with reference to Figs. 2–4. At low E/p_0 in the thermal energy range the ion energy is controlled by the thermal motion of the gas molecules. With increasing E/p_0 the ions gain more energy from the field until, at sufficiently high E/p_0 the ion energy distribution will be controlled by the applied electric field. Hence at sufficiently high E/p_0 one should expect the mobilities to be independent of the gas temperature. The data shown in Figs. 2–4 roughly fulfill this condition, thus, at sufficiently high E/p_0 the plot of mobility versus E/p_0 at 77°K merge with those at 195° and 300°K.

It is to be noted from comparison of Figs. 2-4 that the range of E/p_0 for which the mobility is a constant is considerably greater at 77°K than at 195°K and at 300°K. Wannier[10] has shown that in the case of consant mean-free time between collisions the average energy $\bar{u}$ of the ions is simply

$$\bar{u} = Mv^2 + \tfrac{3}{2}kT. \tag{3}$$

where M is the mass, v the drift velocity of the ions. By using this expression the drift velocity may be calculated under conditions for which the contribution to the ion energy from the applied field equals the thermal energy. From the experimental measurements of the drift velocity versus E/p_0 the corresponding E/p_0 may be determined. The observed range of E/p_0 for which the mobility is a constant and the calculated range of E/p_0 are found to be in quite good agreement.

[10] G. Wannier, Phys. Rev. 83, 281 (1951).

In the present studies only one ion species was observed. Bradbury reported the existence of two ions; however, in view of the fact that his 7.6 value refers to ions $\approx 10^{-2}$ sec old these ions may not be hydrogen, as has previously been pointed out.[6,8] Rose reported the possible existence of a second ion species but only in the vicinity of $E/p_0 \sim 100$. In the present studies a second ion type could not have been detected if it had contributed only a few percent to the ion current or if it had the same mobility value within a few percent of that of the observed ion. No evidence was found in the present studies to indicate that the observed ion was changing its nature over the measured range of E/p_0 as has been reported by Varney[11] for the case of nitrogen and carbon monoxide.

ION IDENTITY

The products of ionization of hydrogen by electrons of controlled energies have been systematically investigated using mass spectrometric techniques.[12] From these studies it is known that the primary product of ionization in hydrogen is H_2^+ which first appears at 15.4 ev. For electron energies ~ 18 ev, low-energy H^+ ions are produced while energetic H^+ ions appear at ~ 28 ev. At low gas pressures the H_2^+ ion peak is dominant. For energies ~ 16 ev at high pressures, considerable numbers of H_3^+ ions are created by secondary processes, and if the ion has some kinetic energy H^+ also appears at high pressures. These products result from secondary processes described by
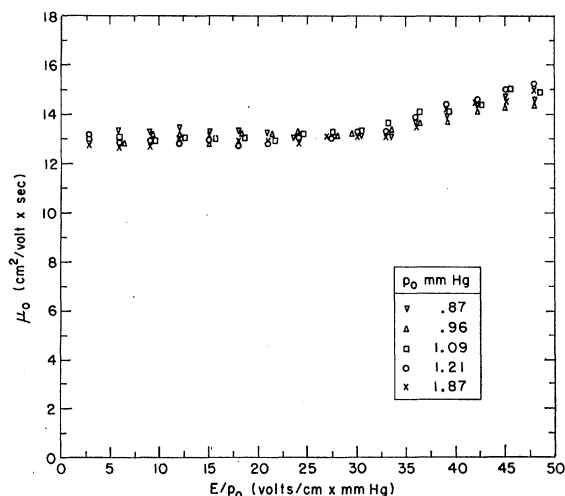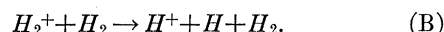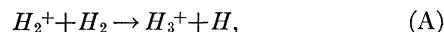
$$H_2^+ + H_2 \rightarrow H_3^+ + H, \tag{A}$$

$$H_2^+ + H_2 \rightarrow H^+ + H + H_2. \tag{B}$$

FIG. 4. Normalized mobility μ_0 as a function of the ratio of drift field to reduced pressure at 77°K.

[11] R. N. Varney, Phys. Rev. 89, 708 (1953).
[12] H. D. Smyth, Phys. Rev. 25, 452 (1925); W. Bleakney, ibid. 35, 1180 (1930); W. W. Lozier, ibid. 36, 1285, 1417 (1930); H. D. Hagstrum and J. T. Tate, ibid. 59, 354 (1941).

Reaction (B) occurs only on collision between ions and molecules in which the relative kinetic energy of impact exceeds 2.6 ev.

Mass spectrometric studies[12,13] of the relative ion current components as a function of gas pressure clearly indicate that at low pressures $\simeq 10^{-2}$ mm Hg roughly 80% of the observed ions were H_2^+. With increasing gas pressure the relative concentration of H^+ and H_3^+ was observed to increase while that of H_2^+ decreased. For pressures ~ 0.5 mm Hg, recent mass analysis[14] of the ionization products of electrodeless discharges indicate that H_3^+ ions constitute $\sim 80\%$ of the ions observed: Additional confirmation that H_3^+ is the dominant ion at these pressures has been obtained by Barnes, Martin, and McDaniel.[15] It thus seems clear that if we extrapolate the results of these studies to the conditions of the present experiment, the ion observed in the present work should be H_3^+.

In 1936, Eyring, Hirschfelder, and Taylor[16] using the theory of reaction rates investigated process (A) and derived a value of $2.07 \times 10^{-9} \kappa$ cm³/molecule/sec for the rate constant, in addition the dependence of the constant on temperature and mass was predicted. Subsequent experimental studies of Gutbier[17] and Stevenson and Schissler[18] have confirmed not only the predicted dependence but also the order of magnitude of the reaction rate. For low-energy ions this rate leads to a cross section $\sim 10^{-14}$ cm², which is considerably in excess of normal kinetic theory cross sections.

Recent energy calculations[19] of the linear H_3^+ ion system yield values for the endothermicity of the reaction $H_3^+ = 2H + H^+$ of 158 kcal/mole. As Field and Franklin[20] have pointed out this corresponds to an

$H_2^+ - H$ bond dissociation energy ~ 4.18 ev. This value is to be compared with the binding energy of H_2^+ of 4.48 ev.

In a recent publication, Varney,[21] with reference to Stevenson's[18] work, has drawn attention to the large value of the cross section for process (A) and the large probable value of the charge exchange cross section of H_3^+ ions moving in hydrogen. Varney has suggested that in view of the fact that the binding energy of H_2^+ and H_3^+ are very similar the charge-exchange mechanism is probably a proton exchange rather than the more usual electron exchange; moreover, the magnitude of the exchange cross section would have a pronounced effect in lowering the mobility value of H_3^+.

Mason and Vanderslice[22] have recently calculated the mobility of H^+, H_2^+, and H_3^+ in hydrogen. In these calculations the long-range ion-molecule force laws determined by the polarization and dispersion forces were calculated from theory. The more difficult short-range forces were estimated from analysis of scattering measurements of low-velocity ion beams in hydrogen obtained by Simons[23] and co-workers. Comparison of the present results and the results of previous investigations with the theoretical mobilities suggest that the ion observed was H_2^+ (experimental values $\sim 10\%$ below theoretical results).

From the preceding discussions, it is clear that in view of the neglect of the charge exchange interaction for H_3^+, such a comparison is quite misleading and that the ion observed in mobility studies is not H_2^+ but rather H_3^+ as Varney has previously pointed out. With such a large value for the cross section for process (A), it is understandable that the same ion was observed under the widely varying experimentsl conditions; e.g., in Lauer's experiments the gas pressures used were several hundred mm compared to pressures of approximately one mm in the present studies.

ACKNOWLEDGMENT

[13] T. R. Hogness and E. G. Lunn, Phys. Rev. 26, 44 (1925); G. P. Harwell, ibid. 29, 830 (1927); C. J. Brasefield, ibid. 31, 52 (1928); O. Luhr, ibid. 44, 459 (1933).

[14] I. B. Ortenburger and M. Hertzberg, J. Chem. Phys. 33, 579 (1960).

[15] W. S. Barnes, D. W. Martin, and E. W. McDaniel, Phys. Rev. Letters 6, 110 (1961).

[16] H. Eyring, J. O. Hirschfelder, and H. S. Taylor, J. Chem. Phys. 4, 479 (1936).

[17] H. Gutbier, Z. Naturforsch. 129, 499 (1957).

[18] D. P. Stevenson and D. O. Schissler, J. Chem. Phys. 23, 1353 (1955).

[19] R. S. Barker, J. C. Giddings, and H. Eyring, J. Chem. Phys. 23, 344 (1955).

[20] F. H. Field and J. L. Franklin, Electron Impact Phenomena (Academic Press, Inc., New York, 1957).

[21] R. N. Varney, Phys. Rev. Letters 5, 559 (1960).

[22] E. A. Mason and J. T. Vanderslice, Phys. Rev. 114, 497 (1959).

[23] J. H. Simons, C. M. Fontana, E. E. Muschlitz, Jr., and S. R. Jackson, J. Chem. Phys. 11, 307 (1943); J. H. Simons, C. M. Fontana, H. T. Francis, and L. G. Unger, ibid. 11, 312 (1943).