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Mobility of Mass-Analyzed H^+, H_3^+, and H_5^+ Ions in Hydrogen Gas*

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The mobilities of the positive ions H^+, H_3^+, and H_5^+ in H_2 gas have been measured, using the "four-gauze" electrical shutter method. The ions have been identified mass-spectrometrically. Measurements were made over a range of E/p_0 (E=electric field intensity, p_0=normalized pressure) from 5.5 to 100 V per cm×mm Hg and in a pressure range of from 0.5 to 1.6 mm Hg. The predominant ion is H_3^+. The mobility μ_0 corrected to 0°C for the H^+ ions was 14.4, for the H_3^+ ions 10.2 and for the H_5^+ ions 9.6 cm²/V×sec at E/p_0=10 V/cm×mm Hg. With increasing E/p_0, the mobility of the H^+ ions decreases, that of the H_3^+ ions increases to a maximum of 14.7 cm²/V sec at E/p_0=60 V/cm×mm Hg and then decreases, and that of the H_5^+ ions increases.

I. INTRODUCTION

PUBLISHED experimental values of the mobility of positive hydrogen ions in hydrogen gas range from 7.6 to 17.5 cm² per V×sec. Measurements of hydrogen ion mobilities have been made by Bradbury,[1] Bennett,[2] Mitchell,[3] Lauer,[4] and more recently by Rose,[5] Frommhold,[6] Jaeger and Otto,[7] Chanin,[8] and Sinnott.[9] The highest value of the mobility resulted from the measurement of the ambipolar diffusion coefficient in a hydrogen afterglow by Persson and Brown.[10] In all these experiments the ions have not been identified by mass spectrum analysis. In the present work, the mobilities of hydrogen ions in hydrogen gas have been measured over the range $7.5<E/p_0<100$ for the H^+ and H_3^+ ions and $5.5<E/p_0<32$ for the H_5^+ ions, where E is the electric field strength in the drift space and p_0 is the pressure of the gas in the tube reduced to the corresponding value at 0°C. Ions have been identified by a 90°-sector-type mass spectrometer.

II. EXPERIMENTAL METHOD

The "four-gauze" electrical shutter method developed by Tyndall, Starr, and Powell[3,11] was used for the measurement of the drift velocities of the ions. The experimental tube is identical to that used by Sinnott. The last or fourth grid was replaced by the stainless-steel-to-glass seal through which the tube was connected to the mass spectrometer. The seal serves as the first accelerating electrode of the ion gun of the mass spectrometer. The ions formed in the glow discharge drift through a 2-cm thermalizing space to the first shutter. An opposing electrical field between the shutter grids prevents entrance of the ions into the region between shutters. Only when a square-wave electrical pulse is applied between the shutters, which are 1 mm apart, can the ions enter the 1-cm drift space. These ions pass through the second shutter if the second square wave is applied to the second set of grids at precisely the arrival time of the ions there. Some of these ions next enter into the electrical accelerating field of the mass spectrometer through a pinhole of 2×10^{-3} cm radius in the platinum foil attached to the stainless-steel-to-glass seal. The electrical field is uniform throughout the drift tube. The mass spectrometer used was a standard 90°-sector-type instrument with the radius of curvature of the ion beam in the magnetic field of 4.5 cm. Pressure differentials between the tube and between different regions of the mass spectrometer

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were maintained using two ion pumps of 75 liter/sec (air pumping speed) and 200 liter/sec and an oil diffusion pump of 25 liter/sec. The differential pumping resulted, in a typical experimental case, in a pressure of the H_2 gas in the drift tube of 1.6 mm Hg, that in the region adjacent to the drift tube of 2×10^{-4} mm Hg, while the pressure in the magnetic analyzer was 3×10^{-6} mm Hg. The ion currents after the deflection by the magnetic field of the analyzer were measured by a Bendix magnetic electron multiplier and a vibrating reed electrometer and recorded with an XY recorder. Pressures in the drift tube were measured directly by an attached Pirani gauge and in other regions of the vacuum system by Veeco ionization gauges. The Pirani gauge was calibrated against a McLeod gauge. Temperature of the experimental gas was measured directly by a calibrated thermocouple. The ultimate pressure in the drift tube was 10^{-8} mm Hg after long degassing at 200°C. The gas to be studied was admitted through a liquid-nitrogen trap by means of an Alpert-type valve from a flask of highly pure gas obtainable commercially (Linde). The positions of the mass peaks were determined by magnetic scanning at a constant electric accelerating voltage of 500 V. In the measurements of relative abundances of various ions at different values of E/p_0, both shutters were open. The mobility data for the H^+ and H_3^+ ions were obtained at temperature of 30–32°C and for the H_5^+ ion at 40°C and over a range of pressure from 0.5–1.6 mm Hg.

With the electrical shutters open, the positions of the mass peaks were established by magnetic scanning. Magnetic-flux-density measurements for the calibration of the mass spectrometer were obtained using a Hall-effect device (Bell, Inc.) the output of which was displayed on the X axis of the XY recorder. Then after adjusting the mass spectrometer onto one of the ion peaks, the electrical square-wave pulses were applied to the grids and the times of flight of the ions in the 1-cm drift space were measured.

III. RESULTS AND DISCUSSION

Typical data points of the drift velocities of the H^+, H_3^+ and H_5^+ ions in hydrogen gas are shown in Fig. 1 plotted as function of E/p_0. Figure 2 shows the mobilities of the H^+, H_3^+, and H_5^+ ions as a function of E/p_0. Mobility is defined conventionally as

$$\mu_0=(v/760(E/p_0)).$$

Zero-field mobilities of Bradbury, Bennett, Mitchell, Lauer, Chanin, Sinnott, and Persson and Brown are indicated by arrows in Fig. 2. These results are shown adjusted to 0°C. The value of $\mu_0=16.6\pm1.2$ cm²/V sec was derived by Rose from the Persson and Brown measurement of the ambipolar diffusion coefficient in the hydrogen afterglow.

Three positive hydrogen ions, H^+, H_3^+, and H_5^+ were observed. The small mass peaks of two and four were identified as the D^+ ion and H_2D^+, respectively, due to the anticipated deuterium impurity in the hydrogen gas. The relative abundance of the H^+, H_3^+, and H_5^+ ions varied with E/p_0. Thus, at $E/p_0=6.45$, the ratios were: $I_{H_5^+}/I_T=25\%$, $I_{H_3^+}/I_T=74\%$ and $I_{H^+}/I_T=1\%$

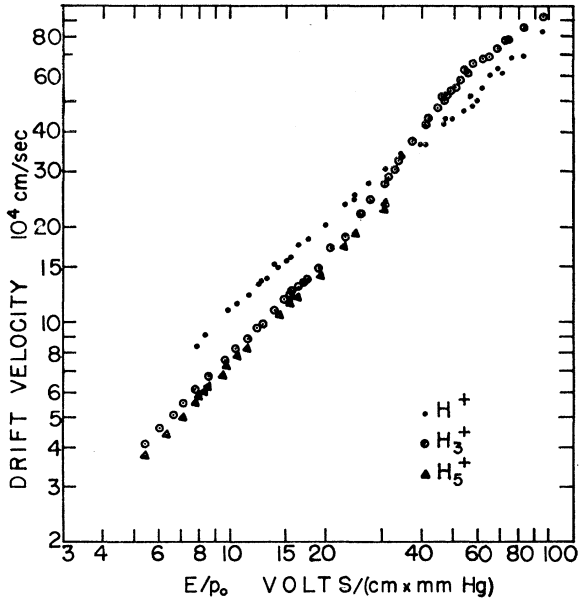

FIG. 1. Log-log plot of drift velocity of the H^+, H_3^+, and H_5^+ ions in hydrogen gas versus E/p_0. The data for the H^+ and H_3^+ ions were obtained at gas temperature of 30–32°C and for the H_5^+ ions at 40°C.

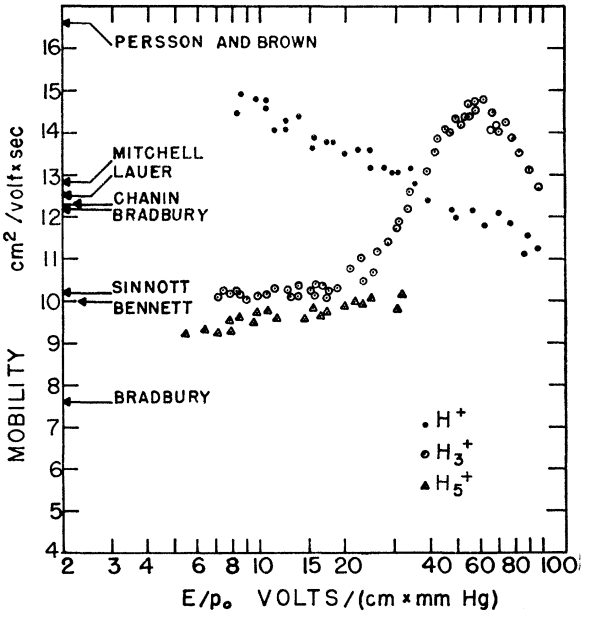

FIG. 2. Reduced mobility (μ_0) of the H^+, H_3^+, and H_5^+ ions in hydrogen gas as a function of E/p_0. The data for the H^+ and H_3^+ ions were obtained at gas temperature of 30–32°C and for the H_5^+ ions at 40°C. Zero-field mobilities of Bradbury, Bennett, Mitchell, Lauer, Chanin, Sinnott, and Persson and Brown are also shown.

and at $E/p_0=25.6$ the ratios changed to: $I_{H_5^+}/I_T=0.5\%$, $I_{H_3^+}/I_T=95\%$ and $I_{H^+}/I_T=4.5\%$. The proton current did not exceed ten percent of the total current I_T at the high values of E/p_0. Dawson and Tickner[12] and Kirchner[13] have identified the H_5^+ ion. From the electron impact ion source it was deduced that the tertiary H_5^+ ion is formed in three-body collisions of the H_3^+ ion with the hydrogen molecules.[14] The H_5^+ ion current decreases rapidly with increasing E/p_0 in the drift space. Therefore, the binding energy of the H_5^+ ions is very small. The H_3^+ ion has a high binding energy. Christoffersen *et al.*[15] have calculated the dissociation energy ($D=8.3$ eV) of the equilateral triangle model of the H_3^+ into $H^+ + H + H$. Bradbury observed two ions in hydrogen gas. His measurements were taken at atmospheric pressure. He found the stable ion to be the ion of low mobility. This could be the mobility of the H_5^+ ion. Mason and Vanderslice[16] have calculated quantum mechanically the zero-field mobility of the H^+, H_2^+, and H_3^+ ions in hydrogen gas. Their values are 18.3, 13.9, and 22.0 cm^2/V sec, respectively, for a temperature of 300°K. The result of this work, of Persson and Brown and of Mason and Vanderslice are in reasonable agreement for the mobility of the protons. For H_3^+ the experimental value is much lower than the theoretical value. If the proposal of Varney[17] is correct that H_3^+ may be subject to proton exchange in passing through H_2 gas, the mobility would in all likelihood be greatly reduced and may in fact account for the observed low value. It would seem necessary to add the further hypothesis that, at values below E/p_0 of 18, H_3^+ ions in an encounter with H_2 have a good chance of either sticking together to form H_5^+ or exchanging a proton and thereby slowing the effective motion of the H_3^+. As E/p_0 is allowed to grow about 18, both H_5^+ formation and proton exchange fall off severely. The abundance of H_5^+ is almost undetectable at E/p_0 of 25, and the mobility of H_3^+ climbs rapidly to the peak at E/p_0 of 60, presumably with decrease of proton transfer, striving toward the high value predicted for it by Mason and Vanderslice.

The growths of H^+ ions in abundance with increasing E/p_0 is not specifically explainable. The implied possibilities are on the one hand that it is created in increasing abundance in the drift space as E/p_0 increases or on the other hand that it has a short life and vanishes in the long drift times associated with low E/p_0. The declining mobility with E/p_0 suggests that changes in flight occur, such as creation of H^+ by breakup of H_3^+ in flight (see Ref. 14). These alternatives do not seem to be resolved by the present experiment.

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