The Ionization Potential of Molecular Hydrogen

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A description is given of a mass spectrograph designed to work with gases at very low pressures. The metal parts are made entirely of tantalum and tungsten enclosed in an all glass system which may be baked out quite thoroughly, making it possible to work with gases at pressures of the order of 10^{-6} mm. The apparatus has been applied to the study of the ionization potential of molecular hydrogen yielding a value of 15.37 ± 0.03 volts. A discussion of all the previous measurements of this quantity is given.

INTRODUCTION

THE ionization potentials of molecules and in particular that of molecu-I lar hydrogen have been of considerable interest for the last twenty years, and its measurement has been the object of more than twenty experiments. At first it was believed that a stable H_2^+ ion did not exist and the efforts were directed toward learning the nature of the mechanism of ionization and how the energy was distributed between the various components. Now we know that as the velocity of the impinging electrons is increased from zero, the first ion formed in pure molecular hydrogen is the stable H₂⁺ configuration which may be changed subsequently by collisions with other molecules. The minimum energy required to produce this ion by electron impact from hydrogen in the normal state has lately become of importance because of its relation to the host of facts now known about the potential energy curves, vibrational levels, heats of dissociation and band spectra of this molecule and the limitations imposed by the Franck-Condon principle. Probably all the physicists who have worked in this field now agree that this ionizing potential lies in the neighborhood of 16 volts. Considering the number of different determinations scattered over a period of several years and the accuracy claimed for them, the values obtained are surprisingly discordant. In Table I will be found a list of all the values of any importance known to the writer.

Smyth¹ after a critical survey of all the best values rejected the author's recent determination (and justifiably so) but hoped the experiment would be repeated using argon as the calibrating gas. Kallmann and Rosen² on the other hand have given full credence to this value in their report. This experiment has now been repeated using an entirely new setup and it is the object of this paper to present the results. The author hopes he is not adding to the confusion by contributing a value which lies outside the range of all the other observations!

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¹ Smyth, Rev. Mod. Phys. 3, 347 (1931).

² Kallmann and Rosen, Phys. Zeits. 32, 534 (1931).

I. P. (volts)	Observer ³	Reference
1. P. (volts) 15.8 15.7 17.1 16.5 \pm 0.5 16.9 15.9 17.1 \pm 0.2 15.6 \pm 0.1 16.0 16.0 16.0 16.0 15.8 15.9 16.7 15.8 15.7 16.0 16.0 16.5 15.4 \pm 0.1 15.4 \pm 0.1	Doserver ³ Davis and Goucher Bishop Franck, Knipping, and Krüger Found Mohler and Foote Horton and Davies Compton and Olmstead Krüger Boucher Foote and Mohler Mohler, Foote, and Kurth Olmstead Mackay Horton and Davies Olson and Glockler Mackay Hogness and Lunn Smyth Hogness and Lunn Dorsch and Kallmann Langmuir and Jones Vencov Bleakney	Reference Phys. Rev. 10, 101 (1917). Phys. Rev. 10, 244 (1917). Ber. d. D. phys. Ges. 21, 728 (1919). Phys. Rev. 16, 41 (1920). Bur. Stan. Bull. 16, 669 (1920). Proc. Roy. Soc. A97, 23 (1920). Phys. Rev. 17, 45 (1921). Ann. d. Physik 64, 288 (1921). Phys. Rev. 19, 189 (1922). Origin of Spectra, p. 68 Phys. Rev. 19, 414 (1922). Phil. Mag. 46, 828 (1923). Phil. Mag. 46, 828 (1923). Phil. Mag. 46, 828 (1923). Proc. Nat. Acad. Sci. 9, 122 (1923). Phys. Rev. 25, 452 (1923). Phys. Rev. 26, 44 (1925). Zeits. f. Physik 44, 565 (1927). Phys. Rev. 31, 357 (1928). C. R. 189, 27 (1929). Phys. Rev. 35, 1180 (1930). Phys. Rev. 35, 1180 (1930).
15.37 ± 0.03	Bleakney	This paper

TABLE I. Observed I. P. for molecular hydrogen.

Apparatus

The apparatus employed was in the form of a mass spectrograph to which reference has already been made⁴ but one which has never been described in detail. The basic principles are the same as the one previously used by the author⁵ with the exception of the analyzer. A large water-cooled solenoid was made in the Palmer Laboratory shops one meter in length and 5 inches bore capable of producing a field of 1500 gauss continuously without the introduction of any iron in the magnetic circuit. With such a field it was possible to employ the semicircular type of analyzer as first introduced by Dempster.⁶ An isometric drawing of the metal parts of the vacuum tube is shown in Fig. 1. Electrons from the filament F are accelerated between the first two diaphragms of the electron gun G and pass between the plates A and B as shown by the dotted lines. They are finally collected on the inclined plate P which is maintained about 100 volts positive with respect to the rest of the trap T in order to prevent the escape of secondary electrons. The electron beam is kept accurately lined up with the apparatus by the longitudinal magnetic field H. The positive ions formed along the electron path are accelerated through the two slits S_1 and S_2 by a small field between A and B and a stronger one between B and C. The ions then travel on the arc of a circle due to the influence of the magnetic field H. The radius r of the circle is

³ The values listed in this table were reported, in many cases, merely as critical potentials and it was only later that the true explanation became apparent.

⁴ Bleakney, Phys. Rev. 39, 536 (1932); 40, 130 (1932).

⁵ Bleakney, Phys. Rev. 34, 157 (1929).

⁶ Dempster, Phil. Mag. 31, 438 (1916).

determined by the relation,

$$m/e = r^2 H^2/2V$$

where V is the velocity expressed in equivalent volts which the ion has acquired before passing through S_2 . Obviously the value of r may be determined by adjusting V such that ions having a particular value of m/e will pass through the third slit S_3 and fall upon the plate K which is connected to a Compton electrometer having a sensitivity of 5000 mm per volt. When several different types of ions are present they may be passed in succession before the slit S_3 by varying the accelerating potential V. The plate L may also be connected to the electrometer and serves to measure the total number of ions in a particular beam when the potential V is adjusted so that the totality of the beam falls upon it. The whole apparatus within the vacuum tube is made of the two metals tantalum and tungsten with Pyrex glass insulation. The tube is entirely free of wax and grease joints and is permanently mounted within a furnace. The furnace itself is mounted inside the water-



Fig. 1. Isometric drawing of the apparatus with sections cut away to show the interior. All dimensions are to scale except the widths of the slits which are 1.0, 0.2, and 0.5 mm for S_1 , S_2 and S_3 respectively.

cooled solenoid so that the tube may be baked out at any time without disturbing anything. With this apparatus it is possible to study ionizing potentials with pressures ranging from 10^{-4} to 10^{-7} mm Hg.

PROCEDURE AND RESULTS

After the tube had been evacuated and baked until the residual pressure was less than 10^{-7} mm Hg as measured by using the tube itself as an ionization gauge, a mixture of hydrogen and argon was admitted and allowed to flow continuously out through the pumps. The hydrogen was admitted through a palladium tube and the argon, which had been purified in a misch metal arc, was allowed to leak through a fine capillary. The pressure of the argon in the reservoir as well as the temperature of the palladium tube could be controlled and hence the partial pressures of the two gases in the ionizing

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chamber could be varied at will. For a given steady mixture the analyzer was set to catch the H_2^+ ion and a run was made studying the intensity of this ion as a function of the electron velocity. Immediately thereafter the field between *B* and *C* was changed so that the intensity of the A⁺ ions could be submitted to a like study, everything else remaining as nearly constant as possible. In the region *AB* the paths of the ions are bent slightly before enter-



Fig. 2. Typical ionization potential curves showing the positive ion current as a function of the electron velocity (uncorrected).

ing S_1 due to the magnetic field and since the electric field between A and B is held constant throughout it follows that the H₂⁺ ions will be deflected more than the heavier A^+ . Hence in order to enter the slit S_1 the H_2^+ and A^+ ions must start from different points. The electron velocity will not be the same at these two points due to the potential drop in the filament. However this discrepancy will be reversed in sign when the filament current is reversed and the mean should be free of any such error. The shift observed on reversing the filament current was about 0.2 volts. Eight different runs were made to determine the difference between the ionizing potentials of H_2^+ and A^+ . Each of these runs was checked by varying the electron velocity in the opposite direction making really sixteen runs in all. Of the eight values four were made with the filament current reversed so that on averaging corresponding pairs four independent values of the difference were obtained. They were 0.40, 0.25, 0.35, and 0.30. In every case argon showed the higher I.P. In Fig. 2 is shown a typical run. Assuming the value for argon to be 15.69 the I.P. for H_2^+ is

$$I.P. = 15.37 \pm 0.03$$
 volts

where the probable error is calculated from the internal consistency of the data. Measurements taken under a variety of conditions representing changes

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in pressure of one-hundred fold, in electron current of tenfold, and in magnetic field of twofold failed to show any consistent variations in the ionization potential. In all cases the relative pressures were adjusted so that the intensities of the two ion peaks were of the same order of magnitude.

DISCUSSION

The results of this experiment agree very satisfactorily with those previously reported by the author.⁷ There seems to be no obvious systematic error in this method although it differs from all the other work. In many of the older experiments the effect of velocity distribution of electrons and contact potential was unknown. Usually the apparatus was calibrated by admitting a gas whose I.P. was known. This gas was then removed before admitting the hydrogen and it is possible that the contact potential changed at the same time. This would not account for the results obtained by Dorsch and Kallmann, Hogness and Lunn, Smith, and Mackay however since in these experiments the two gases were mixed together. In these cases the discrepancy may be entirely due to the sensitivity of the apparatus. A study of the potential energy curves in the light of the Franck-Condon theory shows that the most probable excitation is one to a higher vibrational state involving a total energy change of about 15.9 volts and the probability of transitions on either side of this value falls off. This probability is even appreciable at 18 volts7 where the ion is just able to dissociate and it is believed that this experiment shows that this range may extend as low as 15.4 volts or lower. It may be well to point out that these results offer no contradiction to those of Harnwell⁸ which showed that $H_2^++A \rightarrow H_2^+A^+$ because the H_2^+ ion may have any energy from 15.4 to 17.9 volts and most of the hydrogen ions will have energies above the I.P. of argon. The theoretical minimum should be that energy required to transform the normal molecule from its lowest vibrational state to the corresponding lowest vibrational state of the ion assuming no change in rotation energy. This ionization potential has been calculated many times, both from band spectra and theory, with varying degrees of accuracy. Perhaps the best values are those calculated by Birge⁹ from Richardson's data on the band spectra and a later value given by Richardson and Davidson.¹⁰ These were 15.34 and 15.381 volts respectively. The agreement with the result of this experiment, 15.37, seems to indicate that transitions by electron impact from the ground level of normal hydrogen to the ground level of the molecular ion are possible.

In measuring the difference between the I.P.'s of H₂ and A it is perhaps well to point out that the latter has two I.P.'s differing by 0.18 volts according as the argon ion is left in the ${}^{2}P_{1\frac{1}{2}}$ or the ${}^{2}P_{\frac{1}{2}}$ state. It seems safe to assume however that the minimum observed is the lower of these two, cor-

⁷ Bleakney, Phys. Rev. 35, 1180 (1930).

⁸ Harnwell, Phys. Rev. 29, 830 (1927).

⁹ Birge, Proc. Nat. Acad. Sci. 14, 14 (1928).

¹⁰ Richardson and Davidson, Proc. Roy. Soc. A123, 466 (1929); Richardson, The Faraday Society, *Molecular Spectra and Molecular Structure*, Sept. 1929, p. 686.

responding to an I.P. of 15.69 volts. The slight "foot" at the end of the argon curve in Fig. 2 is probably due partly to the two I.P.'s and partly to the velocity distribution of the electrons. In helium which has only one I.P. to contend with the foot is less pronounced. The effect is quite marked in the case of H_2^+ and is probably explained by excitation to the higher vibration levels of the molecular ion as the electron velocity is increased.

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