

## A Search for Isotopes of Hydrogen and Helium

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The well-known triatomic hydrogen ion ( $\text{H}^1\text{H}^1\text{H}^1$ )<sup>+</sup> of mass 3 is formed by electron impact at a rate proportional to the square of the pressure if the pressure is very low. The isotopic molecular ion ( $\text{H}^1\text{H}^2$ )<sup>+</sup>, also of mass 3, would be expected to vary linearly with pressure. These two facts constitute a method for distinguishing between the two with a mass spectrograph whose resolving power is insufficient to separate them by magnetic analysis. The method becomes successful only when the working pressures are very low. With a mass spectrograph designed for low pressure work evidence was found which amply confirms the existence of an isotope of hydrogen of mass 2 and also gives a fair estimate of the abundance. In a sample of ordinary commercial electrolytic hydrogen the data indicate an abundance ratio

$$\text{H}^2/\text{H}^1 = 1/30000 \pm 20\%.$$

The same ratio for a sample of hydrogen which had been concentrated by Urey, Brickwedde and Murphy came out to be

$$\text{H}^2/\text{H}^1 = 1/1050 \pm 5\%.$$

An effort was made to detect a difference in mass between the ions ( $\text{H}^1\text{H}^1\text{H}^1$ )<sup>+</sup> and ( $\text{H}^1\text{H}^2$ )<sup>+</sup> without success. Considering the resolving power of the apparatus this failure was interpreted as meaning that the packing fraction of  $\text{H}^2$  is greater than  $4 \times 10^{-3}$  i.e., the atomic weight is greater than 2.008. A search was also made for isotopes 3 and 5 of helium but none were found. It is concluded that their abundance must be less than one part in 50,000.

### INTRODUCTION

THE hydrogen and helium atoms play such fundamental roles in all physics that any new properties or characteristics of their nuclei are of wide interest. There have been indications that two or more isotopes of these elements may exist and several attempts have been made from time to time to find them experimentally. The first positive evidence for the existence of an isotope of hydrogen of mass 2 has been obtained recently by Urey, Brickwedde and Murphy<sup>1</sup> whose paper also gives a review of previous work and a bibliography of the subject which need not be repeated here. Their photographs of the Balmer spectrum under very high dispersion reveal weak satellite lines attributable to hydrogen atoms of mass 2. These lines were enhanced in a sample of hydrogen in which enrichment of the heavy isotope had been attempted by evaporation near the triple point. Further evidence for the existence of an isotope in hydrogen may be found in Allison's interpretation of his experiments on optical rotation<sup>2</sup> but his method is as yet little

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<sup>1</sup> H. C. Urey, F. G. Brickwedde and G. M. Murphy, *Phys. Rev.* **40**, 1 (1932); also *Phys. Rev.* **39**, 164 (1932) and **39**, 864 (1932).

<sup>2</sup> F. Allison, *Jour. Ind. Eng. Chem.* **4**, 9 (1932).

understood. The importance of the problem seemed to warrant an independent investigation from a different angle and accordingly a careful re-examination of the hydrogen and helium ions was undertaken with a mass spectrograph.

There are many complications which arise in the magnetic analysis of hydrogen ions because of the various primary and secondary combinations involved. Let us assume that a rare isotope of mass 2 does exist and let us enumerate the possibilities when the ions are formed at a very low pressure by electron impact. It is well known<sup>3</sup> that under these conditions monatomic, diatomic and triatomic ions are produced. Hence we should expect the various combinations listed in Table I. The column labeled  $f(p)$  gives the intensity or number of ions as a function of pressure when  $p$  is so small that

TABLE I. Possible ions resulting from a mixture of two hydrogen isotopes in which  $H^1$  is much more abundant than  $H^2$ .

	Ion	$m/e$	$f(p)$	Intensity
1.	$(H^1)^+$	1	$a_1p + b_1p^2$	weak
2.	$(H^1H^1)^+$	2	$a^2p$	v. strong
3.	$(H^2)^+$	2	$a_2p + b_2p^2$	v. weak
4.	$(H^1H^1H^1)^+$	3	$b_4p^2$	weak
5.	$(H^1H^2)^+$	3	$a_5p$	weak
6.	$(H^2H^2)^+$	4	$a_6p$	v.v. weak
7.	$(H^1H^1H^2)^+$	4	$b_5p^2$	v.v. weak
8.	$(H^1H^2H^2)^+$	5	$b_6p^2$	v.v. weak
9.	$(H^2H^2H^2)^+$	6	$b_7p^2$	v.v. weak

secondary reactions are small compared with primary ones. In general the primary processes will vary linearly with pressure while secondary ones will be proportional to the square. Of the configurations listed in Table I it is to be expected that 6, 7, 8 and 9 will be too weak for observation. Number 1 is of no interest in this particular case and 3 will be completely masked by 2. Since 2 is a linear function of pressure and since it is very strong it serves as a good index of the pressure. There are left 4 and 5, two ions of comparable abundance but different functions of pressure and it is in this direction that the following studies were made. In the case of helium no such complications arise.

#### EXPERIMENTAL PROCEDURE

The apparatus used in this experiment has been described<sup>4</sup> in a previous number of this journal and some preliminary results have also been reported.<sup>5,6</sup> The flow method was used in every case, the gases streaming into the tube through fine capillaries or a palladium tube and out through diffusion pumps. The lighter the atom the faster will it leak through the capillary but presumably the same selective effect will occur in the diffusion pumps so that the relative concentrations of isotopes in the ionization chamber will

<sup>3</sup> H. D. Smyth, Rev. Mod. Phys. **3**, 347 (1931).

<sup>4</sup> W. Bleakney, Phys. Rev. **40**, 496 (1932).

<sup>5</sup> W. Bleakney, Phys. Rev. **39**, 536 (1932) (Letter).

<sup>6</sup> W. Bleakney, Phys. Rev. **40**, 130 (1932) (Abstract).

remain unchanged after equilibrium has once been established. No difference in the results on hydrogen were observed when the palladium tube was substituted for the fine capillary.

Through the kindness of Professor Urey and Dr. Murphy a sample of the residue of hydrogen evaporated near the triple point by Dr. Brickwedde at the Bureau of Standards was provided. The details of the preparation of this hydrogen have been described in their paper.<sup>1</sup> This particular sample was designated by them "Sample III." Ordinary commercial electrolytic hydrogen was used for the rest of the work.

The procedure in the case of hydrogen was to measure the total number of ions of mass 3 reaching the collector, per unit electron current, as a function

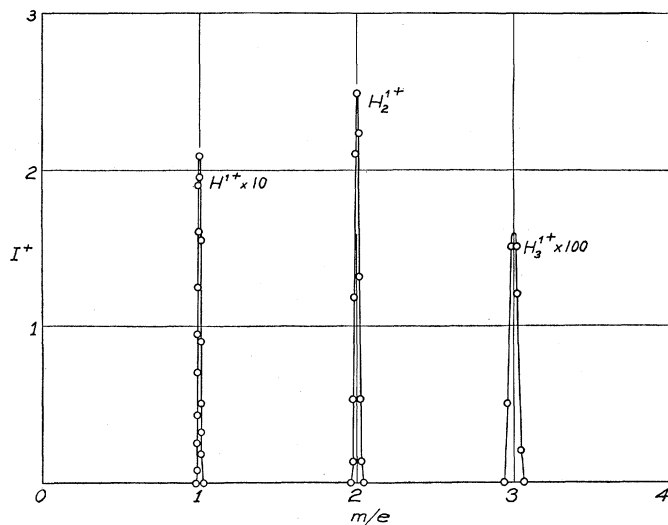


Fig. 1. A typical  $e/m$  analysis curve for ordinary hydrogen.  $p \approx 10^{-5}$  mm Hg.  $H = 400$  gauss.  $V_a = 60$  volts electron velocity.

of the pressure. The pressure itself could be measured in two ways. The first method consisted in observing the intensity of the ion peak of mass 2 which is proportional to  $p$ . In the second method the tube was used as an ionization gauge by observing the total positive ion current per unit electron current. The two methods gave substantially the same results. At the low pressures used the McLeod gauge could not be read with any accuracy. After baking the tube the residual pressure of foreign gases was always in the neighborhood of  $10^{-8}$  mm. The working pressures ranged from  $10^{-4}$  to  $10^{-6}$  mm.

#### RESULTS FOR HYDROGEN

Some idea of the resolving power of the apparatus may be had from Fig. 1 which shows the three typical peaks obtained in ordinary hydrogen with a magnetic field of 400 gauss and a pressure of about  $10^{-5}$  mm. The electron velocity was 60 volts. At higher magnetic fields the peaks become somewhat sharper. Fig. 2 represents the number  $I$  of ions of mass 3 as a function of the number of ions of mass 2. Both ordinate and abscissa are plotted in the same

arbitrary units. Curve I was observed for ordinary hydrogen and curve III for Brickwedde's concentrated sample. The difference between these two curves is given by the straight line II.

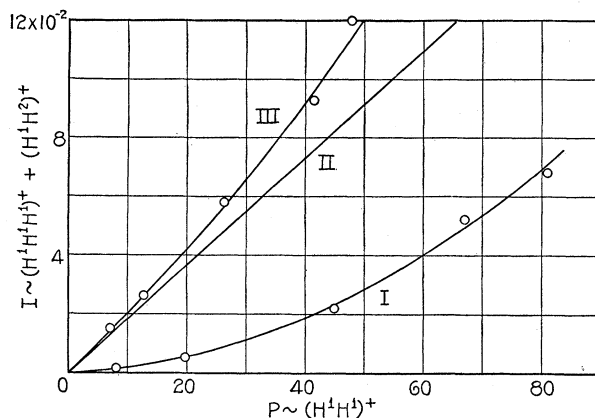


Fig. 2. Total number of ions  $(\text{H}^1\text{H}^1\text{H}^1)^+ + (\text{H}^1\text{H}^2)^+$  of mass 3 as a function of the number  $(\text{H}^1\text{H}^1)^+$  of mass 2. Curve I, ordinary commercial electrolytic hydrogen. Curve III Brickwedde's concentrated sample. Curve II, difference.

These data are interpreted by the author in the following manner. As indicated in Table I we should expect the number of ions of mass 3 to be given by

$$I = ap + bp^2. \quad (1)$$

Now it is significant that curves I and III may be fitted by Eq. (1) using a different value for the constant  $a$  but the same value for  $b$  in each case. The circles represent the experimental points while the curves are plotted from the following equations.

$$\text{Curve I} \quad I_{\text{I}} = (6.6p - p^2) \times 10^{-5} \quad (2)$$

$$\text{Curve III} \quad I_{\text{III}} = (190.0p - p^2) \times 10^{-5} \quad (3)$$

$$\text{Curve II} \quad I_{\text{II}} = I_{\text{III}} - I_{\text{I}} = 183.4 \times 10^{-5}p. \quad (4)$$

The left-hand member of Eq. (4) is interpreted as the difference between the numbers of isotopic ions  $(\text{H}^1\text{H}^2)^+$  in the two samples. Since  $p$  is actually measured in terms of the number of  $(\text{H}^1\text{H}^1)^+$  ions it is evident that the slope of curve II gives the increase due to the concentration process.

$$\text{H}^1\text{H}^2/\text{H}^1\text{H}^1 = 1/546. \quad (5)$$

Here we assume of course that the probabilities of ionization of the two types are the same. The total concentration of the  $\text{H}^1\text{H}^2$  molecules is given by the coefficient  $a$  of Eq. (1). For curve III this is

$$\text{H}^1\text{H}^2/\text{H}^1\text{H}^1 = 1.90 \times 10^{-3} = 1/526 \quad (6)$$

and for ordinary hydrogen

$$\text{H}^1 \text{H}^2 / \text{H}^1 \text{H}^1 = 6.6 \times 10^{-5} = 1/15100. \quad (7)$$

The probable error in these two results is estimated to be 5 percent and 20 percent respectively. No attempt was made to treat the data by the method of least squares in detail since neither the ordinate nor the abscissa is known precisely and the probable error of each observation varies from point to point. The curves were therefore fitted in a rather arbitrary way. If we write the ratio of numbers of atoms instead of molecules we have

$$\text{H}^1 / \text{H}^2 = 1050 \pm 5\% \quad (8)$$

for the concentrated sample and

$$\text{H}^1 / \text{H}^2 = 30,000 \pm 20\% \quad (9)$$

for ordinary hydrogen. It will be noticed that there is quite a marked discrepancy between these results and those first reported by Urey, Brickwedde and Murphy,<sup>1</sup> but they have largely succeeded in accounting for the difference<sup>7</sup> by considering the relative absorption of strong and weak lines in their discharge tube.

In order to show the results in a more striking manner it is illuminating to divide Eq. (1) by the pressure and so obtain

$$I/p = a + bp \quad (10)$$

an equation of a straight line whose intercept  $a$  gives the abundance of the isotope sought. Curves I and III of Fig. 3 plotted in this manner represent the same data as are shown in Fig. 2. This method of presenting the data improves one's confidence in the evidence for the existence of the isotope in ordinary hydrogen but on the same scale the points for the concentrated sample appear scattered over a considerable range. However a little consideration will probably convince the reader that the probable error chosen is not too small. The curves I and III are plotted from Eqs. (2) and (3).

It is of importance to point out that the triatomic ion  $(\text{H}^1\text{H}^1\text{H}^1)^+$  is not only a function of the pressure but also of the geometry of the apparatus and the fields applied. The coefficient  $b$  of Eq. (1) is related to the intensity of this ion and is given by the slope of the curves in Fig. 3. The relative number of isotopic molecules, however, should be independent of these conditions. Curve IV was taken with an altered set of electric and magnetic fields and it is evident that the slope  $b$  has been greatly increased while the intercept remains unchanged within the experimental error. The fact that curves I and IV have exactly the same intercept is not a coincidence. Since their probable errors overlap they were *made* to coincide by the author in fitting the curves.

Some data for another sample of hydrogen are shown by curve V in Fig. 3. This sample was prepared by Professor Urey by a diffusion method and represents a concentration of the lighter isotope. The data are admittedly rather inaccurate but the results seem to indicate less of the heavier isotope

<sup>7</sup> H. C. Urey, F. G. Brickwedde and G. M. Murphy, Phys. Rev. **40**, 464 (1932).

than is to be found in ordinary hydrogen. Professor Urey estimated the concentration of  $\text{H}^1\text{H}^2$  in this sample to be about one tenth of that in ordinary hydrogen, a result which is not inconsistent with the somewhat higher one obtained here when account is taken of the rather large probable error involved in locating the intercept of curve V.

Kallmann and Lasareff<sup>8</sup> have attempted to verify the existence of the  $\text{H}^2$  isotope by seeking for the  $(\text{H}^1\text{H}^1\text{H}^2)^+$  ion of mass 4, but were unable to find it.

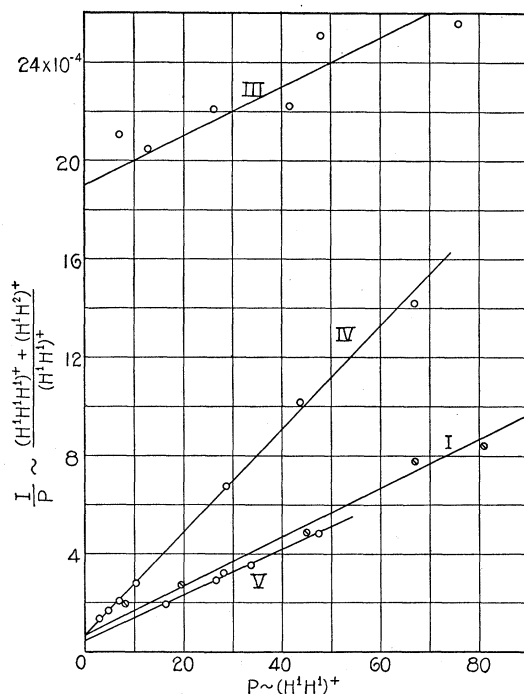


Fig. 3.  $I/p$  plotted as a function of  $p$ . Curve III, Brickwedde's concentrated sample. Curves I and IV, ordinary commercial electrolytic hydrogen each taken under a different set of fields. Curve V, sample of hydrogen enriched in  $\text{H}^1$  by diffusion process.

Perhaps the probability for its formation is very small. They then tried the method of this experiment but at the lowest pressures possible in their apparatus ( $5 \times 10^{-5}$ ) the ratio of ions of mass 3 to those of mass 2 was 1:4000 for ordinary and concentrated samples alike. The conclusion they reach is that their concentrated sample is at most one tenth as good as the one used in this work. If this is true then there is probably no contradiction between the two experiments.

An accurate determination of the mass of the new isotope is of the greatest importance. Unfortunately the mass spectrograph employed has not a high dispersion on the mass scale. Nevertheless a trial was made to determine if possible a lower limit for the packing fraction. First ordinary hydrogen was admitted and the shape of the peak corresponding to ions of mass 3 was ex-

<sup>8</sup> H. Kallmann and W. Lasareff, *Naturwiss.* **20**, 206 (1932).

aminated very carefully. The pressure was such that this peak was made up almost entirely of  $(\text{H}^1\text{H}^1\text{H}^1)^+$ . Then a mixture of the two samples was admitted at such a pressure that  $(\text{H}^1\text{H}^1\text{H}^1)^+$  and  $(\text{H}^1\text{H}^2)^+$  were present in equal numbers and again the shape of the peak was examined. If the two ions are of different weight one would expect the peak in the latter case to appear somewhat broadened. No such broadening could be detected. It is estimated from these measurements that the packing fraction of  $\text{H}^2$  lies between  $4 \times 10^{-3}$  and  $12 \times 10^{-3}$ ,

$$\text{or } 2.024 > W > 2.008$$

where  $W$  represents the atomic weight.\*

It may be well to point out that all the results of this paper simply point to the conclusion that a small number of normal molecules of mass 3 does exist in hydrogen. Conrad<sup>9</sup> has found evidence for the formation of neutral  $\text{H}_3$  molecules in a discharge tube but it has been shown<sup>10</sup> on quantum mechanical grounds that three normal H atoms cannot combine to form a stable triatomic molecule. Hence if a neutral triatomic molecule exists it must be in an excited state in which case the ion would be formed as the result of a secondary or tertiary process and would not be a linear function of the pressure. Even without considering the weight of the spectroscopic evidence<sup>11</sup> the most reasonable assumption which accounts for the results of this experiment is the presence of  $\text{H}^1\text{H}^2$  molecules in hydrogen.

#### RESULTS FOR HELIUM

Helium purified in a misch-metal arc was admitted to the tube and a search made for isotopes 3 and 5. None were found. It is believed that a concentration of one in 50,000 or less could have been detected. This negative result agrees with that of Kallmann and Lasareff<sup>8</sup> but is a test not as discriminating as theirs.

The author is indebted to Professor Urey and Drs. Brickwedde and Murphy for the samples of hydrogen which made this experiment possible. He is also grateful to the members of the Palmer Laboratory staff for their kindly interest and timely suggestions.

\* The author has just recently learned through private communication that Dr. K. T. Bainbridge has succeeded in measuring the atomic weight of  $\text{H}^2$  with his mass spectrograph. His result is  $W = 2.0135$ .

<sup>9</sup> R. Conrad, *Zeits. f. Physik* **75**, 504 (1932).

<sup>10</sup> W. Heitler and F. London, *Zeits. f. Physik* **44**, 455 (1927).

<sup>11</sup> The existence of the  $\text{H}_\alpha^2$  line has been confirmed by Shenstone and Turner using a grating in this laboratory and some of the "sample III" hydrogen.