AUGUST 15, 1933 PHYSICAL REVIEW VOLUME 44

The Relative Abundance of Hydrogen Isotopes

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(Received June 30, 1933)

Samples of rain water collected at Princeton were decomposed by repeated passage over iron turnings heated to 510°C. The hydrogen formed was analyzed with a mass-spectrograph to determine the abundance ratio $H^2:H^1$. The first fraction of hydrogen to be liberated from a particular sample of the water yielded a value given by $H^2:H^1=1:6500$ while the last fraction gave $1:4500$. Another sample was prepared in which the decomposition was carried to completion and all of the hydrogen collected. The abundance found in this sample was $1:5000$. It is believed that this last figure represents a close approximation to the true abundance ratio for natural hydrogen. The value $1:30{,}000$ previously reported by Bleakney for electrolytic hydrogen may be in agreement with these measurements when account is taken of the separation introduced by the electrolysis. A fairly extensive bibliography is given of recent work on the hydrogen isotopes.

INTRODUCTION

SINCE the discovery more than a year ago of a hydrogen isotope of mass 2 many attempts have been made to determine its true abundance in nature by estimating the relative numbers of H^1 and H^2 to be found in natural hydrogen. Large discrepancies exist, however, among the results so far obtained. From his observations on the magneto-optical effect Allison[1] believed that hydrogen had two isotopes but Urey, Brickwedde and Murphy[2] secured the first positive and quantitative evidence for the existence of an isotope of mass 2 and at that time they gave for the abundance ratio the value $H^2:H^1=1:4000$. This was in agreement with that predicted by Birge and Menzel[3] to account for the discrepancy between the chemical atomic weight and Aston's mass determinations. Bleakney[4] shortly after confirmed their discovery by an independent method but found a much smaller abundance for H^2. Even when Urey and Bleakney studied by their respective methods the same sample of hydrogen enriched by evaporation near the triple point they failed to agree on the relative amounts of H^1 and H^2 present. Urey, Brickwedde and Murphy[5] subsequently suggested a plausible explanation for this difference when they pointed out that the error could be attributed to unequal absorption in their discharge tube thus enhancing the H^2 lines at the expense of the H^1 spectrum. Meanwhile Bainbridge[6] had succeeded in making some excellent measurements of the mass of the new isotope. Bleakney's result for the abundance, $H^2:H^1=1:30{,}000$, was checked by the work of Hardy, Barker and Dennison[7] in which they found $1:35{,}000$, and later by Tate and Smith[8] when they reported a value of the order of $1:30{,}000$. Also Rank[9] succeeded in photographing the $H\gamma$ line and concluded that the abundance must be roughly of this order of magnitude.

The early work of Stern and Volmer,[10] however, indicated that H^2 cannot exist to the extent of one part in 100,000 while Menzel[11] and Unsöld[12] reached the same conclusion for the abundance of H^2 in the sun. Kallmann and

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[1] F. Allison, J. Ind. Eng. Chem. **4**, 9 (1932); J. Chem. Ed. **10**, 7 (1933).

[2] H. C. Urey, F. G. Brickwedde and G. M. Murphy, Phys. Rev. **40**, 1 (1932), **39**, 164 (1932) and **39**, 864 (1932).

[3] R. T. Birge and D. H. Menzel, Phys. Rev. **37**, 1669 (1931).

[4] W. Bleakney, Phys. Rev. **41**, 32 (1932).

[5] H. C. Urey, F. G. Brickwedde and G. M. Murphy, Phys. Rev. **40**, 464 (1932).

[6] K. T. Bainbridge, Phys. Rev. **41**, 115 (1932), **42**, 1 (1932) and **44**, 57 (1933).

[7] J. D. Hardy, E. F. Barker and D. M. Dennison, Phys. Rev. **42**, 279 (1932).

[8] J. T. Tate and P. T. Smith, Phys. Rev. **43**, 672 (1933).

[9] D. H. Rank, Phys. Rev. **42**, 446 (1932).

[10] O. Stern and M. Volmer, Ann. d. Physik **59**, 225 (1919).

[11] D. H. Menzel, Pub. Ast. Soc. of the Pac. **44**, 41 (1932).

[12] A. Unsöld, Naturwiss. **20**, 936 (1932).

Lasareff[13] made an attempt to find this elusive isotope and concluded it did not exist to the extent of one part in 10^6, basing their result on the extreme rarity of the $(H^1H^1H^2)^+$ ion as compared to the ordinary triatomic ion. This result is difficult to understand since Bainbridge[6] was able to photograph the triatomic ion of mass 4 with ease which proves that this ion is readily formed. Later, Kallmann and Lasareff[14] reported the detection of H^2 in some enriched samples of hydrogen.

The wide discrepancies among the various observations began to be understandable when Washburn and Urey[15] discovered the electrolytic method of separating the isotopes. Most of the researches so far mentioned have been carried out with electrolytic hydrogen, commercial or otherwise, and the hydrogen collected was therefore enriched in the lighter isotope by an amount depending on the age of the cell from which it came. By the electrolytic method Lewis[16] and Macdonald[17] obtained a very high degree of separation and concluded from their observations that the natural abundance for H^2 was about 1 : 6500. However, shortly after the publication of this communication Lewis and Cornish[18] expressed the opinion that this value was entirely too high.

At this point it might be well to complete the bibliography of the widely scattered references dealing with this isotope even though some of the work may not have a direct bearing on the subject of this paper.* On the theoretical side have appeared papers by Eyring,[19] Eyring and Sherman,[20] Urey and Rittenburg,[21] and Polanyi.[22] Other methods of concentration have been tried by Newell and Ficklen,[23] Washburn and Smith,[24] Taylor, Gould and Bleakney,[25] Lewis and Cornish,[18] and Cremer and Polanyi.[26] Bradley and Urey[27] have studied the concentrations in natural hydrogen from several different sources. Meissner and Steiner[28] measured directly the variation of the vapor pressure of hydrogen with concentration of the heavier isotope. Ashley[29] and Lewis[30] have observed the band spectrum of the heavy isotope and deduced a spin of unity for the H^2 nucleus. Ballard and White[31] have photographed and measured several members of the Lyman series and Williams and Gibbs[32] have reported some work on the fine structure of the spectrum of the heavy isotope. Lukanow and Schütze[33] have obtained spectra by the parabola method of the negative ion H^{2-}. Recently, also, the H^2 atom has been used as a new projectile in disintegration studies by Lewis, Livingston and Lawrence.[34]

A knowledge of the true abundance of the two

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[13] H. Kallmann and W. Lasareff, Naturwiss. **20**, 206 (1932).

[14] H. Kallmann and W. Lasareff, Naturwiss. **20**, 472 (1932).

[15] E. W. Washburn and H. C. Urey, Proc. Nat. Acad. Sci. **18**, 496 (1932).

[16] G. N. Lewis, J. Am. Chem. Soc. **55**, 1297 (1933).

[17] G. N. Lewis and R. T. Macdonald, J. Chem. Phys. **1**, 341 (1933).

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* See also the following references which were either overlooked or were published after this paper was written: E. W. Washburn, E. R. Smith and M. Frandsen, J. Chem. Phys. **1**, 288 (1933); H. L. Johnston and D. H. Dawson, Naturwiss. **21**, 495 (1933); G. N. Lewis and F. H. Spedding, Phys. Rev. **43**, 967 (1933); G. N. Lewis and R. T. Macdonald, J. Am. Chem. Soc. **55**, 3057 (1933); F. H. Spedding, C. D. Shane and N. S. Grace, Phys. Rev. **44**, 58 (1933); H. C. Urey, G. M. Murphy and F. G. Brickwedde, J. Chem. Phys. **1**, 512 (1933); J. Kendall, J. Am. Chem. Soc. **55**, 2612 (1933).

[19] H. Eyring, Proc. Nat. Acad. Sci. **19**, 78 (1933).

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[21] H. C. Urey and D. Rittenburg, J. Chem. Phys. **1**, 137 (1933).

[22] M. Polanyi, Naturwiss. **21**, 316 (1933).

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[26] E. Cremer and M. Polanyi, Zeits. f. physik. Chemie **B19**, 443 (1932).

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[28] W. Meissner and K. Steiner, Zeits. f. Physik **79**, 601 (1932).

[29] Muriel F. Ashley, Phys. Rev. **43**, 770 (1933).

[30] G. N. Lewis and Muriel F. Ashley, Phys. Rev. **43**, 837 (1933).

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[32] R. C. Williams and R. C. Gibbs, June Meeting, Am. Phys. Soc., Chicago, 1933.

[33] H. Lukanow and W. Schütze, Zeits. f. Physik **82**, 610 (1933).

[34] G. N. Lewis, M. S. Livingston and E. O. Lawrence, June Meeting, Am. Phys. Soc., Chicago, 1933. Also Phys. Rev. **44**, 55, 56 (1933).

isotopes in natural hydrogen is of fundamental importance and the discordant results already reported leave much to be desired. Before the question is settled the abundance must be measured in a variety of natural sources of hydrogen by a trustworthy method which introduces no change in the concentration during the process. The present work was undertaken as a first step toward this objective.

PREPARATION OF THE SAMPLES

All of the present work was done on samples of rain water collected at Princeton and purified by distillation from alkaline permanganate in an all-Pyrex still. The water was decomposed by repeated passage over iron turnings heated to 510°C. Fig. 1 is a diagram of the apparatus used for the decomposition. *A* and *B* are small traps which may be surrounded by liquid air. *D* is a connecting tube packed with iron turnings, wound with resistance wire, and insulated with a heavy layer of asbestos. In order to obtain fairly pure iron free from carbon the turnings were prepared from a piece of Norway iron. *F* leads to a mercury diffusion pump backed by an oil pump. *E* is a three-way stopcock leading to an automatic Sprengel pump.

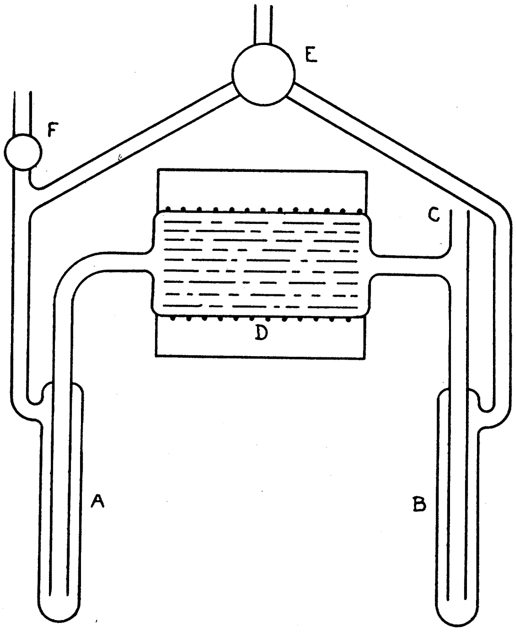

FIG. 1. Diagram of decomposition apparatus.

In the first experiment 0.3 cc of water was placed in *B* through the opening *C* after which tube *C* was sealed off. *B* was cooled in liquid air and the entire system evacuated through *F*. Stopcock *F* was then closed, stopcock *E* turned in such a position that the Sprengel pump exhausted the system through *A*, and the liquid air removed from *B* and placed around *A*. In this way some of the water vapor passing over the iron turnings at 510° was decomposed, the undecomposed portion frozen out at *A*, and the hydrogen formed removed and collected by the Sprengel pump. After all the water had evaporated from *B*, stopcock *E* was turned to connect the Sprengel pump with *B* which was again chilled while *A* was allowed to warm up to room temperature. This process of distilling the water back and forth over the hot iron was repeated until all of the water in the system was decomposed. We designate as sample I the first 30 cc of hydrogen collected and sample II the last 30 cc. In the second experiment 0.05 cc of water was decomposed as before except that all of the hydrogen formed was collected in one sample which we have called sample III.

METHOD OF MEASUREMENT

The instrument used to determine the relative numbers of the isotopes was a mass-spectrograph which has already been described by Bleakney[35] in a previous number of this journal. In order to distinguish between the many possible combinations of two isotopes to form monatomic, diatomic and triatomic hydrogen ions it is necessary to determine the e/m ratio and to study the intensity as a function of pressure. This procedure has been described by Bleakney[4] in detail in his first work on hydrogen isotopes. Briefly the method is to measure the number of $(H^1H^1)^+$ ions in order to determine the pressure and then find the intensity of the peak corresponding to ions of mass 3 which consists of the two kinds $(H^1H^2)^+$ and $(H^1H^1H^1)^+$. They are proportional to the first and second powers of the pressure respectively. Hence if we let p be the intensity of the $(H^1H^1)^+$ ion (always much stronger than any other) and let I be the number of ions of mass 3 we have $I=ap+bp^2$ or $I/p=a+bp$, which is the equation of a straight line whose intercept a is the ratio

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[35] W. Bleakney, Phys. Rev. **40**, 496 (1932).

$H^1H^2 : H^1H^1$. The ratio $H^2 : H^1$ is of course just half this value.

The hydrogen was admitted to the positive ray apparatus through a fine capillary leak while a rapid diffusion pump exhausted this chamber at such a rate that the pressure maintained there was of the order of 10^{-5} mm Hg. This pressure could be regulated by adjusting the pressure of the source. Sufficient time was given for equilibrium to be sensibly established before any readings were taken.

RESULTS

The curves for I/p plotted as a function of p for the three samples are shown in Fig. 2. Sample II, the last fraction to be liberated in the first experiment, shows a higher concentration of the heavy isotope than sample I and we conclude that the method of preparation is a selective one. Sample III in which the dissociation was carried to completion falls directly between the other two, as expected, and furnishes an excellent check on the reliability of the measurements. Taking the intercept of curve C we obtain for the relative abundance of the isotopes in rain water

$$H^2 : H^1 = 1 : 5000$$

with perhaps a probable error of ten percent. This value is about six times as great as the one previously reported by Bleakney.[4] The authors feel confident, however, that the discrepancy is due to a real difference in the samples tested and is not to be ascribed to errors of measurement. As a further check a sample of ordinary commercial electrolytic hydrogen was examined and the results are shown by curve IV which gives a result of about 1 : 25,000. This agrees with the earlier work of Bleakney. The fractionation factor of 5 for separation by the electrolytic method reported by Lewis and Macdonald[17] would seem to account almost perfectly for these results, but it is surprising that the samples of commercial hydrogen used by various observers should yield such a low concentration since this would imply that they all came from comparatively new cells. It would seem quite likely that if there were any selective reaction in the method of preparing the samples of hydrogen for this experiment it would be in a direction tending to decrease the concentration of the heavy isotope because of its lower zero point energy, and hence we believe the abundance found is certainly not too low. We hope to continue these experiments during the next year.

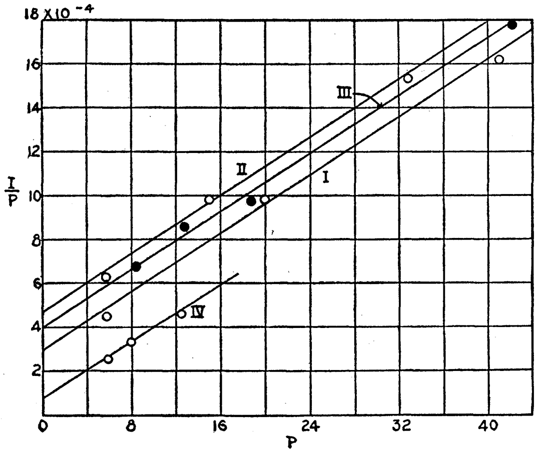

FIG. 2. The ratio I/p plotted as a function of p. The intercept on the vertical axis gives the ratio $H^1H^2 : H^1H^1$. Curves I and II represent the first and last fractions decomposed and curve III represents a sample completely decomposed. Curve IV represents a sample of commercial electrolytic hydrogen.