Mass-Spectrograph Determination of the Relative Abundance of Heavy Hydrogen in a Sample

The method of diffusion through palladium has been employed by Harris, Jost and Pearse¹ to effect the separation of the hydrogen isotopes. The increase of concentration of the heavy hydrogen was determined spectroscopically, and it was reported that under the conditions of the experiment approximately a tenfold enrichment was obtained, with a resulting concentration of about one percent deuterium. The spectroscopic method has been subjected to criticism and it was proposed that a test of the enriched sample be made with the mass-spectrograph. The method of Bleakney² was not applicable as the massspectrograph employed here3 is designed to operate at pressures of the order of 0.5 mm in the discharge tube with further aging in a drift space; and under these conditions 95 percent or more of all the ions obtained are triatomic. It seemed however that the triatomic ion of mass 4 (H1H1H2+) observed by Bainbridge,4 could be used to determine the concentration of heavy hydrogen where the relative percentage was small.

The triatomic ion in light hydrogen is formed by a reaction between the initial molecular ion and a neutral molecule as follows:

$$H^{1}H^{1+} + H^{1}H^{1} \rightarrow H^{1}H^{1+} + H^{1}$$
.

In mixtures of heavy and light hydrogen the following reactions should occur:

$$H^{1}H^{2+} + H^{1}H^{1} \rightarrow H^{1}H^{1}H^{2+} + H^{1},$$
 (1)

 $_{\pi}H^{1}H^{1}H^{2+}+H^{1}$ (a)

$$H^{1}H^{1+} + H^{1}H^{2}$$
 (2)
 $H^{1}H^{1}H^{1+} + H^{2}$ (b).

If f is the fraction of H² atoms relative to the total number of atoms, then 2f is the fraction of H1H2 molecules relative to the total, if f is small. Consequently, reaction number 1 above should yield an intensity of H1H1H2+ ions of 2f relative to $H^1H^1H^{1+}$, and reaction number 2 should yield a relative intensity of f, making a total of 3f.

This reasoning involves the assumption that reactions 2(a) and 2(b) are equally probable, which may not be entirely justified; but any departure from this assumption should lie within the experimental error. It is also required that the ions should be aged sufficiently and f should be small enough so that there is no measurable number of H²H²⁺ ions present.

A series of runs on a sample of the enriched hydrogen gave an average of about 1.5 percent of mass 4 ions relative to mass 3. This would indicate a relative concentration of hydrogen atoms of about 0.5 percent. A redetermination of the density of the original water used by Harris, Jost and Pearse was made by Dr. E. S. Gilfillan of the chemistry department and it was found that the concentration of heavy hydrogen was about 0.13 percent. The mass-spectrograph results thus indicate a fourfold enrichment by passage through palladium instead of 8 to 10 fold as previously reported.

The mass-spectrograph employing aged hydrogen ions, as was done in this experiment, furnishes a direct and simple method of determining the relative concentration of heavy hydrogen, providing the assumptions involved are justified. No ions of mass 5 or 6 could be observed owing to the small concentration of heavy hydrogen, but a complete study of the nature of aged ions in various mixtures of the hydrogen isotopes would yield interesting information concerning the atomic processes involved in the formation of the triatomic ions.

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George Eastman Research Laboratories, Massachusetts Institute of Technology, May 8, 1934.

¹ Harris, Jost and Pearse, Proc. Nat. Acad. Sci. 19, 991 (1933)

² W. Bleakney, Phys. Rev. 44, 256 (1933).
 ³ O. Luhr, Phys. Rev. 44, 459 (1933).
 ⁴ K. T. Bainbridge, Phys. Rev. 42, 1 (1932).

The Ultraviolet Absorption of Acetylene and Ethylene

For some time we have been investigating the far ultraviolet absorption of various simple hydrocarbons. We find, in the case of acetylene, a rich absorption spectrum which extends from 1520A to 1050A. The absorption is very strong and most of the bands appear with a pressure of only 0.001 mm of acetylene in the spectrograph, the light path being about 1.5 meters.

They can be conveniently divided into two classes. Class I contains bands possessing P, Q and R branches. They appear as narrow absorption doublets at low pressures. They have a sharp head and are shaded towards the red. The bands of Class II show a single head, and therefore contain only more diffuse P and R branches.

On account of the complexity of the spectrum some difficulty was experienced in analyzing it. Recently it has been enormously clarified by the use of the heavy hydrogen isotope. A comparison of the spectrum of light acetylene with that of heavy acetylene (C₂HD) immediately reveals the fundamental band of each electronic transition by its small isotopic shift which is due only to the change in zero point energy. In this way two Rydberg series were found, each containing more than ten terms. They have roughly the same limit and are given fairly well by the following formulas:

I
$$\nu_0^n = 92,000 - R/(n-0.95)^2,$$

II $\nu_0^n = 92,000 - R/(n-1.5)^2$
 $n = 3, 4, 5, \text{ etc.}$

The bands of class I fall into the first series and those of class II into the second. The first member of the second