Triatomic Ions in Mixtures of the Hydrogen Isotopes

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(Received January 4, 1935)

A mass spectrograph analysis has been made of aged ions in mixtures of hydrogen and deuterium. The concentration of deuterium was varied from 84 percent to less than one percent. After drifting through 5 cm of gas at about 0.5 mm pressure, the ions were found to be over 95 percent triatomic; that is, H_3^+, H_2D^+, HD_2^+ and D_3^+. Measurement of the relative intensities of the triatomic ion peaks indicates a slightly greater number of H_3^+ and D_3^+ ions compared to H_2D^+ and HD_2^+ than would be expected from probability considerations if the H and D atoms behaved exactly alike. This tendency for like atoms to group together may be accounted for by taking cognizance of the proper equilibrium constant for the different types of diatomic molecules in the gas mixtures employed. There is no evidence of further preferential grouping in the formation of the triatomic ions from the primary molecular ions. The relative heights of the triatomic ion peaks may be used to determine the abundance of the isotopes in a sample of gas.

INTRODUCTION

IF ions produced by a glow discharge in ordinary hydrogen at relatively high pressures are allowed to age by drifting at low speed through some cm of gas, it is found that the primary diatomic ions change over almost completely to triatomic ions of molecular weight three. The number of protons is comparatively small; so it is easily possible to attain a condition where 95 percent or more of all the ions present are triatomic. As would be expected, the same phenomenon occurs in mixtures of the hydrogen isotopes, only there the triatomic ions may have molecular weights of 3, 4, 5 and 6 depending on the combination of light and heavy hydrogen atoms which have formed a particular ion. These ions have been observed by several experimenters,[1, 2] and the triatomic ion, H_2D^+, of mass 4 has been employed by Luhr and Harris[3] to determine the concentration of deuterium in a sample of hydrogen where the percentage of deuterium is small. The purpose of this paper is to apply the method of Luhr and Harris to the general case for any concentrations of deuterium and protium. From measurement of the ratio of the intensities of the triatomic ion peaks it should be possible to determine the relative concentrations of the isotopes in the sample of gas and to find out something about the atomic processes involved in the formation of the triatomic ions.

APPARATUS AND METHOD

The sample of gas to be analyzed was prepared by the decomposition of water on a tungsten filament heated to about 1000°C. This method has been described by A. and L. Farkas and P. Harteck,[4] and furnishes a very convenient means of obtaining hydrogen from water where a small quantity is desired. For the samples containing the largest concentrations of deuterium a drop of heavy water (specific gravity, 1.1054; 95 percent deuterium or better) was pumped back and forth across the tungsten filament by condensing in liquid air traps until the water was nearly all decomposed. Despite all reasonable precautions the concentration of deuterium had dropped to about 84 percent by the time it was analyzed in the mass spectrograph. The gas was not pumped off after passing through the mass spectrograph but was circulated through the apparatus and was diluted as desired by the addition of tank hydrogen. This latter procedure was possibly undesirable as the various molecules in the gas may not have attained equilibrium. However, the results were the same when the diluted gas was prepared by decomposing a mixture of light and heavy water; so it seems likely that the glow discharge or the presence of catalysts such as nickel[5] in the system resulted in approximate equilibrium.

The mass spectrograph and discharge tube have been described previously.[6] A glow discharge

* Experimental work performed at Massachusetts Institute of Technology.

[1] K. T. Bainbridge, Phys. Rev. **42**, 1 (1932).

[2] W. Bleakney and A. J. Gould, Phys. Rev. **45**, 281 (1934).

[3] O. Luhr and L. Harris, Phys. Rev. **45**, 843 (1934).

[4] A. and L. Farkas and P. Harteck, Proc. Roy. Soc. **A144**, 467 (1934).

[5] Gould, Bleakney, Taylor, J. Chem. Phys. **2**, 362 (1934).

[6] O. Luhr, Phys. Rev. **44**, 459 (1933).

was maintained between water-cooled aluminum electrodes. Some of the ions passed through a grid and were aged by drifting through 5 cm of gas at about 0.5 mm pressure, under the action of a field of about a volt per cm. They then entered a Dempster-type mass spectrograph through a 0.01 mm slit, and the current to the collector was measured as a function of the magnetic field strength, the electric accelerating field being kept constant. The defining slits of the apparatus having been previously adjusted for work requiring high resolution, heights of the ion peaks were only approximately proportional to the intensity of the ion beams. No serious error was introduced, however, when the intensities were of the same order of magnitude. As would be expected, the smaller peaks were relatively too large when the ratio of the heights was of the order of a hundred, and in such cases more consistent results were obtained by the use of areas under the peaks.

EXPERIMENTAL RESULTS

Figs. 1 to 4 show typical mass spectrograph curves for various concentrations of the isotopes. Fig. 1 shows results for the highest concentration of deuterium obtained—about 84 percent. Figs. 2 and 3 show results when the deuterium has been diluted by the addition of tank hydrogen. Fig. 4 is a typical result obtained when the sample of hydrogen was prepared by decomposition of water containing 0.60 percent deuterium. This water was obtained from the chemistry department of M. I. T.

Two effects should be noted here. First, it was found that when tank hydrogen was added to the sample, dilution did not occur in the expected ratio; that is, there was a tendency for the deuterium to remain when the excess gas was pumped off. This effect was probably due to the difference in diffusion rates. For example, the percentage of deuterium found in Fig. 3 should have been one-fourth that found in Fig. 2. Actually, it was slightly less than one-third. Second, there was a tendency for the concentration of deuterium to decrease with time as the gas containing high percentages of deuterium was circulated through the system. Likewise, it was difficult to rid the apparatus of deuterium once it had been used. This effect presumably resulted from adsorbed gas on the walls.

DISCUSSION OF RESULTS

If it is assumed that the H and D atoms behave exactly alike in the formation of triatomic ions, straight probability gives the results shown
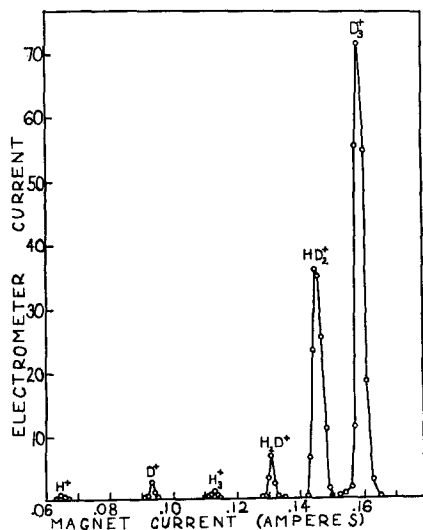

FIG. 1. Aged ions in a mixture of the hydrogen isotopes containing about 84 percent deuterium.
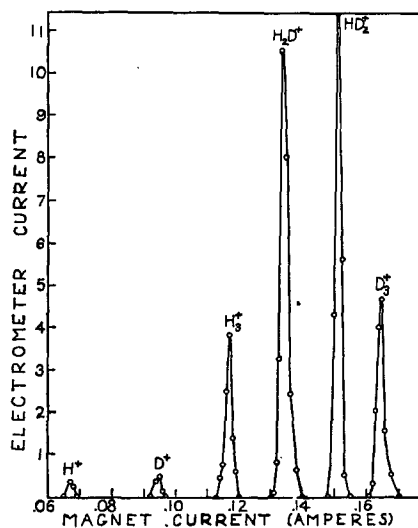

FIG. 2. Aged ions in a mixture containing nearly equal parts of hydrogen and deuterium.
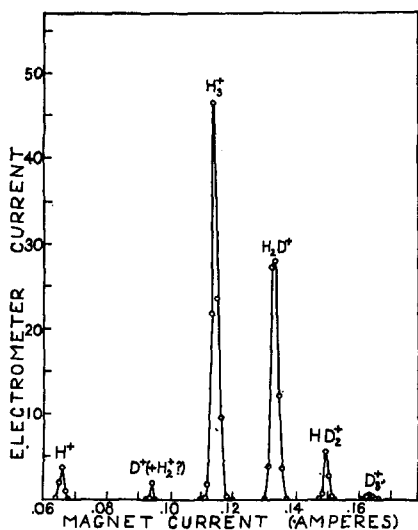
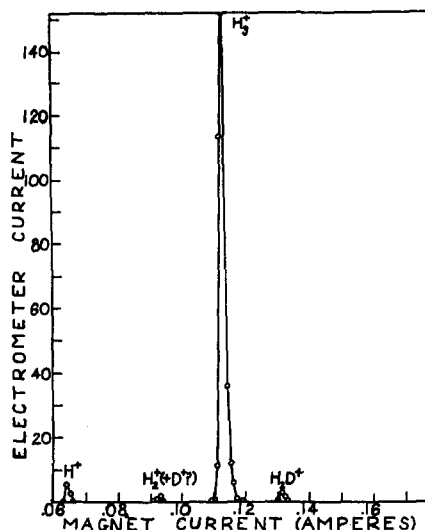FIG. 3. Aged ions in a mixture containing about 16 percent
deuterium.

FIG. 4. Aged ions in hydrogen containing about 0.6 percent
deuterium.

in Table I for the relative intensities of the ions.
The relative heights of the ion peaks bear simple
relationships to the ratio of atomic hydrogen and
deuterium ($H_3^+/H_2D^+ = h/3d$, etc.), and the per-
centages h and d should be the same when de-
termined from any pair of peaks. Such calcula-
tions indicated, however, that the intensities of
the H_3^+ and D_3^+ ions were too large relative to
H_2D^+ and HD_2^+. For example, in Fig. 2 the ratio
of atomic abundance, h/d, determined from
H_3^+/H_2D^+ is 1.08, while from HD_2^+/D_3^+ it is
0.83. Intermediate values of 0.93 and 0.92 are
obtained from the ratios H_3^+/D_3^+ and $H_2D^+/$
HD_2^+. The average of all possible combina-
tions is 0.92. These results are typical of some
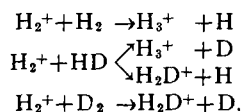fifteen runs.

It was next supposed that the molecules H_2,
HD and D_2 had reached a state of equilibrium
at approximately room temperature, and the
equilibrium constant K, defined by:

TABLE I. *Relative intensities of triatomic ions from ordinary
probability, where h and d are the percentages of atomic
hydrogen and deuterium, respectively.* $(h+d=100.)$

Ion	Molecular weight	Relative intensity
H_3^+	3	h^3
H_2D^+	4	$3h^2d$
HD_2^+	5	$3hd^2$
D_3^+	6	d^3

$$K = (HD)^2/[(H_2)(D_2)]$$

had the value[7] 3.28 instead of the straight
probability value, 4. It was finally assumed that
there was no further preferential grouping when
the primary molecular ions combined with
neutral molecules to form triatomic ions, by
such reactions as:

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$
$$H_2^+ + HD \begin{cases} \nearrow H_3^+ + D \\ \searrow H_2D^+ + H \end{cases}$$
$$H_2^+ + D_2 \rightarrow H_2D^+ + D.$$

Similar reactions were assumed for the HD^+
and D_2^+ ions. The results themselves furnish the
only proof that this last assumption is valid.

The ratios of the heights of the peaks no
longer bear simple relations to the atomic ratio
h/d, but the results are most easily obtained by
graphical methods. Table II was prepared show-
ing the ratios of the triatomic ion peaks for
various percentages of atomic hydrogen (h)
and atomic deuterium (d). This was done by
first calculating the percentage of H_2, HD and
D_2 molecules present for the various atomic
percentages and then adding up the probabilities
of formation of the several triatomic ions, taking

[7] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933);
Urey, Rittenberg and Bleakney, J. Chem. Phys. **2**, 48 (1934).

TABLE II. *Ratios of triatomic ion intensities for various percentages of atomic hydrogen (h) and deuterium (d).* $K = 3.28$.

h (%)	d (%)	H_3^+/H_2D^+	H_3^+/HD_2^+	H_3^+/D_3^+	H_2D^+/HD_2^+	H_2D^+/D_3^+	HD_2^+/D_3^+
0	100	——	——	0	——	0	0
5	95	0.0199	0.00112	0.000176	0.0562	0.00882	0.157
10	90	0.0423	0.00501	0.00164	0.118	0.0389	0.328
20	80	0.0948	0.0250	0.0181	0.263	0.191	0.723
30	70	0.1560	0.0688	0.0850	0.441	0.543	1.234
40	60	0.240	0.1620	0.308	0.675	1.29	1.90
50	50	0.357	0.357	1.000	1.000	2.80	2.80
60	40	0.526	0.777	3.25	1.48	6.17	4.17
70	30	0.810	1.840	11.76	2.27	14.53	6.42
80	20	1.380	5.25	55.3	3.80	40.0	10.52
90	10	3.050	25.7	610	8.44	199.5	23.65
95	5	6.37	113.6	5700	17.80	892	50.2
100	0	∞	∞	∞	——	——	——

into account all possible reactions similar to those indicated above. The ratios of these probabilities are then the ratio of the triatomic ion intensities.

From the values given in Table II, curves were plotted with the ratios of the triatomic ion intensities as functions of h or d. These curves were used to determine h and d from the mass spectrograph curves such as those shown in Figs. 1 to 3, assuming the heights of the peaks were proportional to the intensities of the ions. Within the limits of experimental error, the results were then consistent when calculated from the ratio of any pair of peaks, and the fractions of atomic hydrogen or deuterium could be determined in all cases with an estimated error of less than five percent. For example, the average value of h, determined from all possible peak ratios in Fig. 1, is (15.7 ± 0.3) percent; from Fig. 2, (48.5 ± 0.4) percent; and from Fig. 3, (83.7 ± 0.4) percent. The probable errors are calculated from Peter's approximation formula,[8] and may be too small as the individual observations are not completely independent. There was no independent method available for checking the results, but their consistency is believed to furnish sufficient proof of their validity.

In order to make the method outlined above more readily usable for other workers who might wish to analyze mixtures of the isotopes, an attempt was made to devise simple empirical relations to express the results of Table II. The following equations expressing h/d or d/h as a function of the peak ratios, were found to give the correct results to within about one percent over the range of the table:

[8] F. W. Mellor, *Higher Mathematics*, p. 524, London, 1929.

$$h/d = \alpha(3 - 0.13\alpha^{-\frac{1}{3}}), \qquad (1)$$

For $\beta < 1$: $h/d = 0.93\beta + 0.07\beta^2 \qquad$ (a),

For $\beta > 1$: $d/h = 0.93\beta^{-1} + 0.07\beta^{-2} \qquad$ (b), $\qquad (2)$

$$d/h = \gamma^{-1}(3 - 0.13\gamma^{\frac{1}{3}}), \qquad (3)$$

where $\alpha = H_3^+/H_2D^+$, $\beta = H_2D^+/HD_2^+$, $\gamma = HD_2^+/D_3^+$. Since only three of the six peak ratios shown in Table II are independent, three equations suffice to calculate h/d from any experimental results. The equations, of course, like the table, only apply when the equilibrium constant, K, has a value close to 3.28.

In practice, when the atomic percentages of hydrogen or deuterium are less than 5 or over 95, the straight probability relations given in Table I may be used with negligible error. This results from the fact that some of the peaks become too weak to measure, and the values of Table II approach those given by straight probability for the ratios remaining. In Fig. 4, for example, all but the H_3^+ and H_2D^+ peaks were too weak to be measured, and simple probability gave the average percentage of atomic deuterium from six runs as (0.60 ± 0.03), in agreement with the density measurements on the water used in preparation of the sample.

CONCLUSION

The results of this experiment indicate that a mass spectrograph analysis of the triatomic ions in mixtures of hydrogen and deuterium may be used to determine the abundance of the isotopes in a sample. Simple probability considerations suffice when less than five percent of either atomic hydrogen or deuterium is present, but when the ratio of the two is more nearly equal to unity, the molecular equilibrium constant must be taken into account. The consistency of the results themselves indicates that the formation of triatomic ions from the primary molecular ions is purely a chance phenomenon to a good degree of approximation. That is, there is no preferential clustering of particular atoms in the formation of the triatomic ions.

The writer wishes to express his gratitude to Dr. A. McKellar, Dr. C. A. Bradley and Professor Louis Harris, all of M. I. T., who kindly supplied the samples of heavy water. He wishes especially to thank Professor V. Rojansky of Union College for his aid and helpful discussions on the theoretical aspects of this paper.