

THE
PHYSICAL REVIEW

A HYDROGEN ISOTOPE OF MASS 2 AND ITS CONCENTRATION*

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(Received February 16, 1932)

ABSTRACT

In a recent paper Birge and Menzel pointed out that if hydrogen had an isotope with mass number two present to the extent of one part in 4500, it would explain the discrepancy which exists between the atomic weights of hydrogen as determined chemically and with the mass spectrograph, when reduced to the same standard. Systematic arrangements of atomic nuclei require the existence of isotopes of hydrogen H^2 and H^3 and helium He^5 to give them a completed appearance when they are extrapolated to the limit of nuclei with small proton and electron numbers. An isotope of hydrogen with mass number two has been found present to the extent of one part in about 4000 in ordinary hydrogen; no evidence for H^3 was obtained. The vapor pressures of pure crystals containing only a single species of the isotopic molecules H^1H^1 , H^1H^2 , H^1H^3 were calculated after postulating: (1) that the rotational and vibrational energies of the molecules are the same in the solid and gaseous states; (2) that in the Debye theory of the solid state, the Θ 's are inversely proportional to the square roots of the molecular masses; (3) that the free energy of the gas is given by the free energy equation of an ideal monatomic gas; and (4) that there is a zero point lattice energy equal to $(9/8)R\Theta$ per mole. The calculated vapor pressures of the three isotopic molecules in equilibrium with their solids at the triple point for ordinary hydrogen are in the ratio $p_{11}:p_{12}:p_{13}=1:0.37:0.29$. The isotope was concentrated in three samples of gas by evaporating large quantities of liquid hydrogen and collecting the gas which evaporated from the last two or three cc. Sample I was collected from the end portion of six liters evaporated at atmospheric pressure and samples II and III from four liters, each, evaporated at a pressure only a few millimeters above the triple point.

These samples and ordinary hydrogen were investigated for the visible, atomic Balmer series spectra of H^2 and H^3 from a hydrogen discharge tube run in the condition favorable for the enhancement of the atomic spectrum and for the repression of the molecular spectrum, using the second order of a 21 foot grating with a dispersion of 1.31A per mm. When with ordinary hydrogen, the times of exposure required to just record the strong H^1 lines were increased 4000 times, very faint lines appeared at the calculated positions for the H^2 lines accompanying $H^1\beta$, $H^1\gamma$ and $H^1\delta$ on the short wavelength side and separated from them by between 1 and 2A. These lines do not agree in wave-length with any known molecular lines and they do not appear on the plates taken with the discharge tube operating under conditions favorable for the production of a strong molecular spectrum and the repression of the atomic spectrum. With or-

* Publication Approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

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dinary hydrogen they were so weak that it was difficult to be sure that they were not irregular ghosts of the strongly overexposed atomic lines. Samples II and III evaporated near the triple point show these lines and another near $H^{1\alpha}$ greatly enhanced relative to the H^1 lines over those with ordinary hydrogen showing that these new lines are not ghosts, and that a considerable increase in the concentration of the isotope had been effected. With sample I, evaporated at the boiling point, no appreciable increase in concentration was detected. The new lines agree in wave-length with those calculated for an H^2 isotope.

The H^2 lines are broad as is to be expected for close unresolved doublets, but they are not as broad and diffuse as the H^1 lines, probably due to the smaller Doppler broadening. The $H^{2\alpha}$ line is resolved into a close doublet with a separation that agrees within the accuracy of the measurements with the observed separation for $H^{1\alpha}$.

Relative abundances were estimated by comparing the times required to just record photographically the corresponding H^1 and H^2 lines. The relative abundance of H^2 and H^1 in natural hydrogen is estimated to be about 1:4000 and in the concentrated samples about five times as great.

THE possibility of the existence of isotopes of hydrogen has been discussed for a number of years. Older discussions involved Prout's hypothesis and dealt with the question as to whether hydrogen consisted of a mixture of isotopes, one having an atomic weight exactly one, and another or others with integral values, in such proportions as to give an average atomic weight of 1.008. The result of an exact determination in 1927 with the mass spectrograph by Aston¹ of the atomic weight of the hydrogen isotope of mass-number one not only proved that it is not integrally equal to unity but the agreement with the chemically determined value was so close that it was considered unlikely that hydrogen had more than the single isotope of mass-number one. The discovery of the oxygen isotopes by Giauque and Johnston² in 1929 showed that the chemical standard of atomic weights was not the same as that used by Aston and that agreement between the chemical determinations and Aston's values should not be expected. When the atomic weights of hydrogen as determined chemically and by the mass spectrograph are reduced to a common standard, the previous apparent agreement is destroyed and they differ. Birge and Menzel³ showed that this discrepancy could be explained by the presence of an isotope of hydrogen of mass-number two, present to the extent of one part in 4500.

Quite independently of such a quantitative basis of prediction as is furnished by the agreement or disagreement of the atomic weights determined chemically and with the mass spectrograph, one may be led by other lines of reasoning to expect heavier isotopes of hydrogen and helium, as well, even though the atomic weights reduced to a common standard do agree, for it is only necessary to assume that they are so rare that they can not be detected

¹ F. W. Aston, Proc. Roy. Soc. (London) **A115**, 487 (1927).

² W. F. Giauque and H. L. Johnston, J. Am. Chem. Soc. **51**, 1436 and 3528 (1929).

³ R. T. Birge and D. H. Menzel, Phys. Rev. **37**, 1669 (1931); F. Allison (J. Ind. Eng. Chem. **4**, 9 (1932)) interprets two minima observed by his magneto-optical effect in water solutions of acids as due to two isotopes of hydrogen having mass numbers of 1 and 2. Whatever weight can be given to this method of detecting the *number* of isotopes of an element, certainly without some understanding of its dependence on mass the method gives no evidence in regard to the *masses* of the isotopes.

by atomic weight determinations within the limits of the experimental accuracy. The recent discoveries of rare isotopes emphasize that it may be impossible ever to disprove the existence of any nuclear species. Recent systematic arrangements of nuclear species⁴ lead one to expect isotopes of hydrogen of masses 2 and 3 and an isotope of helium of mass 5. Beck leaves a place in his tables for H^3 and He^5 . Johnston has question marks in his table for H^2 , H^3 , He^5 and Li^5 . Urey makes no definite predictions but presents a proton-electron plot which shows the regularities very well, the three isotopes, H^2 , H^3 , and He^5 being required to give this plot a completed appearance.

METHODS OF CONCENTRATION

Birge and Menzel³ remark that the discovery of a hydrogen isotope of higher mass-number by the methods of molecular spectra would be difficult though not impossible. The maximum abundance of an isotope of mass-number 2 which can be expected is that given by Birge and Menzel for if any isotope of higher mass number were present the abundance of the isotopes would all necessarily be less. It seemed essential to find some way of concentrating the heavier isotopes if they were to be detected by spectroscopic methods. Any of the various methods used for concentrating isotopes should be more effective in the case of these isotopes of hydrogen because of the large ratio of masses. Of these methods, that of fractional distillation should give the largest supply with the least effort. This method has been tried in a number of cases⁵ but with little success except in the case of neon.⁶

The vapor pressures of the molecules H^1H^1 , H^1H^2 , H^1H^3 in equilibrium with their pure solids can be calculated if the following postulates are made: (1) the rotational and vibrational energies of the molecules are the same in the solid and gaseous states and thus need not be considered in the calculations of vapor pressures; (2) the free energy⁷ of the solids can be calculated from the Debye theory of the solid state, assuming that the Θ 's of the three solids are inversely proportional to the square roots of the molecular weights; (3) the free energy of the gas is given by the free energy equation of an ideal monatomic gas.

At equilibrium, the free energy of the gas is equal to the free energy of the solid, and since all the quantities may be evaluated, we may calculate the vapor pressures of the isotopic molecules. The free energy and entropy of hydrogen gas are given by the following expressions:

⁴ H. L. Johnston, *J. Am. Chem. Soc.* **53**, 2866 (1931); Harold C. Urey, *J. Am. Chem. Soc.* **53**, 2872 (1931); Guido Beck, *Z. Physik* **47**, 407 (1928); Henry A. Barton, *Phys. Rev.* **35**, 408 (1930).

⁵ F. A. Lindemann and F. W. Aston, *Phil. Mag.* (6) **37**, 523 (1919); F. A. Lindemann, *Phil. Mag.* (6) **38**, 173 (1919); H. G. Grimm, *Zeits. f. phys. Chem.* **B2**, 181 (1929); H. G. Grimm and L. Braun, *Zeits. f. phys. Chem.* **B2**, 200 (1929); P. Harteck and H. Striebel, *Zeits. f. anorg. allgem. Chem.* **194**, 299 (1930).

⁶ W. H. Keesom and H. van Dijk, *Proc. Acad. Sci. Amsterdam* **34**, 42 (1931); H. van Dijk, *Physics* **11**, 203 (1931).

⁷ The "free energy" as used here refers to this term as defined by Lewis. See Lewis and Randall, *Thermodynamics*, McGraw-Hill, 1923, New York.

$$F_g = E_g + RT - TS_g \quad (1)$$

$$S_g = \frac{3}{2} R \ln M + \frac{5}{2} R \ln T - R \ln P + C + R \ln R \quad (2)$$

where M is the molecular weight, P is the pressure in atmospheres, R is the gas constant in cal. per mole per degree and C is the Sackur-Tetrode constant and equals -11.053 cal. per degree⁸ and

$$E_g = \frac{3}{2} RT + \chi. \quad (3)$$

χ is the heat of vaporization at absolute zero from a hypothetical solid hydrogen without zero point energy, which for convenience is chosen as the standard reference energy state to which the internal energies of the solid and gaseous phases are referred. χ is assumed to be the same for the isotopic molecules. The differences between the values of the internal energy of the gas at the triple point of hydrogen (13.95°K) as calculated by Eq. (3) and by the more exact equations for a degenerate gas are negligibly small.

The free energy of solid hydrogen is given by:⁹

$$F_s = E' + T\Phi(M, T) + PV. \quad (4)$$

Because of the small volume of solid hydrogen the PV term may be neglected without serious error. The quantity E' is the zero point energy (Nullpunktsenergie) and must be included.¹⁰ The function $\Phi(M, T)$ may be obtained from the Debye theory of specific heats.⁹

Solving these equations for $\ln P$ after equating (1) and (4) and dividing through by RT , we have:

$$\ln P = \frac{E'}{RT} + \frac{\Phi}{R} + \frac{3}{2} \ln M + \frac{5}{2} \ln T + \frac{C}{R} + \ln R - \frac{5}{2} - \frac{\chi}{RT}. \quad (5)$$

The only terms on the right of (5) which depend on the mass are the 1st, 2nd, and 3rd, since χ has been assumed to be the same for isotopic molecules. If we indicate the two molecules H^1H^1 and H^1H^2 by subscripts we have the ratio of their vapor pressures given by:

$$\ln P_{11}/P_{12} = \frac{1}{RT} (E'_{11} - E'_{12}) + \frac{1}{R} (\Phi_{11} - \Phi_{12}) + \frac{3}{2} \ln M_{11}/M_{12}. \quad (6)$$

The quantity $\Phi(M, T)$ is a function of $h\nu/kT$, where ν is the characteristic frequency for the solid state; $h\nu/k$ for ordinary hydrogen as determined by Simon and Lange is 91.¹¹ Since the characteristic frequency ν is inversely proportional to the square root of the molecular weight, the argument of Φ may be determined for the isotopic molecules and the value of Φ taken from the

⁸ R. T. Birge, *Rev. Mod. Phys.* **1**, 65 (1929).

⁹ *Handbuch der Physik*, Vol. X, p. 360-361, Julius Springer, 1926 Berlin.

¹⁰ R. W. James, I. Waller and D. R. Hartree, *Proc. Roy. Soc.* **A118**, 334 (1928).

¹¹ Franz Simon and Fritz Lange, *Zeits. f. Physik* **15**, 312 (1923).

tables.¹² The calculation of the ratio P_{11}/P_{12} is made for the temperature 13.95°K, the triple point for ordinary hydrogen. The ratio P_{11}/P_{13} is calculated in a similar way.

The numerical values for $h\nu/k$ and Φ are:

Molecule	M	$h\nu/k$	Φ
H ¹ H ¹	2	91	- 0.1339
H ¹ H ²	3	74.29	- 0.2251
H ¹ H ³	4	64.36	- 0.3364

The value of the zero point energy is $9/8h\nu$ per molecule¹³ and may be easily calculated for the isotopic molecules. The values of E' thus become $(9/8)R(h\nu)/k$; or $(9/8)R\Theta$. Substituting the numerical values in (6), we get:

$$P_{11}/P_{12} = 2.688, \quad P_{11}/P_{13} = 3.354.$$

If the calculation is carried through assuming that the zero point energy is zero, it is found that on this basis the *heavier* isotopic molecules should have the higher vapor pressures which is contrary to experience not only with the hydrogen isotopes but with all other isotopes.

This calculation of the ratios of the vapor pressures has been made for the solid state. A similar calculation cannot be made for the liquid state since the theory is inadequate. It seems reasonable to expect that differences between the vapor pressures of the isotopes should persist beyond the melting point and that a fractionation of the liquid solution should be possible.

The Rayleigh distillation formula integrated for ideal solutions is:

$$\left(\frac{1 - N_0}{1 - N}\right)^{\alpha/(1-\alpha)} \left(\frac{N}{N_0}\right)^{1/(1-\alpha)} = \frac{W_0}{W} \quad (7)$$

where N and N_0 are the mole fractions of the less volatile constituent left in the still and in the original sample respectively and W and W_0 are the moles of both constituents left in the still and in the original sample respectively, and α is the distribution coefficient equal to the ratio of the vapor pressure of the less volatile constituent to that of the more volatile constituents. If N_0 and N are small as compared to 1 as is the case for the distillation of these isotopes of hydrogen, this formula reduces to:

$$\left(\frac{N}{N_0}\right)^{1/(1-\alpha)} = \frac{W_0}{W}. \quad (8)$$

¹² Handbuch der Physik, Vol. X, p. 364-70, Julius Springer, 1926, Berlin.

¹³ The mean zero point energy per degree of freedom is

$$\frac{\int_0^{\nu_{\max}} \frac{h\nu}{2} \nu^2 d\nu}{\int_0^{\nu_{\max}} \nu^2 d\nu} = \frac{3}{8} h\nu_{\max}$$

for $3N$ degrees of freedom, this gives $9/8 N h\nu$. Lindemann (Phil. Mag. **38**, 173 (1919) showed that in order to make the calculated vapor pressures of the isotopes of lead at its boiling point equal to each other, as was found by experiment to be true, it was necessary to make the internal energy of isotopic, pure crystals at 0°K equal to $9/8 h\nu$.

This formula has been used in estimating the increased concentrations expected.

If we assume that the mole fraction of H^2 is $1/4500$ in the original hydrogen, that $\alpha = 1/2.688$ and that $W_0/W = 4000$, we secure about 4 mole percent as the value of N . Since we have not secured such high concentrations, we conclude that either the ratio of vapor pressures of the solids is quite different from those of the liquids at the same temperature, or that some of the assumptions made in regard to the solids are not sufficiently exact.¹⁴ We have made this calculation in order to see whether the separation by fractionation was likely to be effective.

PREPARATION OF THE CONCENTRATED HYDROGEN SAMPLES

Each of the different samples of hydrogen, which were later examined spectroscopically, was prepared from liquid hydrogen made by circulating about 400 cubic feet of free gas through a liquefier of the ordinary Hampson type in which, after precooling with liquid air boiling at reduced pressure, it was expanded from a pressure of about 2500 pounds per square inch to atmospheric pressure. As the liquid hydrogen was obtained it was collected in storage containers from which it was transferred to an unsilvered triple walled flask of about 1600 cm³ capacity in which the concentration of the isotope was effected. After filling the flask, the liquid hydrogen was allowed to evaporate until only about 1/3 or 1/4 remained, when the flask was refilled and the procedure was repeated until all the liquid had been transferred. The flask was connected by vacuum tight joints to the glass bulbs in which the hydrogen gas evaporating from the last two or three cubic centimeters of liquid was collected. These bulbs were connected to a Hyvac pump for exhaustion and flushing out previous to the collection of the final concentrate. Proper precautions were taken to prevent the entry of air into the system while the samples were being collected. This method of evaporation is somewhat less efficient than the method assumed in the calculation above and accounts, at least in part, for the lower efficiency observed.

Sample I was collected from the end portion of six liters of liquid hydrogen evaporated at atmospheric pressure, and samples II and III, each, from four liters evaporated at a pressure only a few millimeters above the triple point. The process of liquefaction could have had only a small effect in changing the relative concentrations of the isotopes since no appreciable increase in the concentration of the isotopic molecule H^1H^2 over that in ordinary hydrogen was detected for sample I obtained from six liters of liquid hydrogen evaporated at atmospheric pressure.

¹⁴ Professor K. F. Herzfeld has called to our attention the possibility that the rotational states of the unsymmetrical molecules, H^1H^2 and H^1H^3 , may not be the same as those of the gas, even though this is true for the symmetrical molecules. The center of mass of the unsymmetrical molecules does not coincide with the midpoint of the line of nuclei so that the rotation would take place in such a way that the H^1 atom would encounter the fields of force of other molecules to a greater extent thus changing the rotational levels in an unpredictable way.

SPECTRUM ANALYSIS

It is possible to detect the hydrogen isotopes from the positions of the atomic lines, since the Balmer lines of any heavier isotopes will be displaced to the violet side of the H¹ Balmer lines. Assuming that the masses of the isotopic hydrogen nuclei of mass-numbers 2 and 3 are exactly twice and three times the mass of the proton, the calculated wave-lengths of the isotopic lines and the observed wave-lengths of the H¹ lines are:

	α	β	γ	δ
H ¹	6562.793	4861.326	4340.467	4101.738
H ²	6561.000	4860.000	4339.282	4100.619
H ³	6560.400	4859.56 ₆	4338.882	4100.239.

The second order of a 21 foot grating with a dispersion of 1.3A per mm was used to analyze the spectrum from a Wood hydrogen discharge tube run in his so-called black stage.¹⁵ This tube was 1 cm in diameter and was excited by a current of about 1 ampere at 3000 to 4000 volts; the radiation was sufficiently intense to record the H¹ β and H¹ γ lines in about 1 sec., though the lines were broad and unresolved under these conditions. By greatly decreasing the current and increasing the exposure time to about 16 sec., it was possible to resolve the H¹ β line into a doublet, but a simple calculation showed that the time of exposure necessary to record the isotope lines under conditions necessary to resolve them would be prohibitively long. We therefore worked with the high current density in order to decrease the exposure time.

The usual method of securing clean atomic hydrogen spectra by flowing moist hydrogen through the tube was not used, as the samples were limited in amount. They were not moistened by saturation with ordinary water since we did not wish to contaminate them with ordinary hydrogen from the water. The sample of hydrogen was contained in a glass bulb with two stop-cocks attached in series so that a small sample of hydrogen (about 2 cc) could be admitted to the discharge tube at one time. The stop-cock grease was a disadvantage since it was probably the source of the cyanogen bands in our tube which was troublesome when working with H δ . The hydrogen gas was either, not moistened at all, in which case the molecular spectrum was rather strong, or, it was moistened by attaching near the electrodes small side tubes containing copper oxide or, by admitting oxygen gas in small amounts. The copper oxide in the side tubes was reduced by atomic hydrogen diffusing in from the discharge tube and water was formed. When oxygen was used, some of the oxygen bands and lines appeared which, however, caused no trouble. None of these methods of suppressing the molecular spectrum was as effective as the flowing stream of moist hydrogen gas and at times the molecular spectrum became intense in spite of all our efforts to keep the tube in a good black stage.

Before working on the evaporated samples of hydrogen, ordinary hydrogen was tried first in order to overcome any difficulties in the method of ex-

¹⁵ R. W. Wood, Proc. Roy. Soc. (London) **97**, 455 (1920); **102**, 1 (1923); Phil. Mag. **42**, 729 (1921); **44**, 538 (1922).

citation. The sample of hydrogen evaporated at the boiling point (Sample I) was next investigated, but no isotopes present in the estimated concentrations could be found, though faint lines appeared at the calculated positions for H^2 lines. Returning then to ordinary hydrogen, these same lines were found with about the same intensity as in sample I. It was difficult to be certain that these lines were not irregular ghosts. All other lines near the Balmer lines could be accounted for as known molecular lines. Turning then to sample II, evaporated near the triple point, the H^2 lines were found greatly enhanced relative to the H^1 lines thus showing that an appreciable increased concentration of the H^2 isotope had been secured and that the lines could not be ghosts since their intensity varied relative to the known symmetrical ghosts. Sample III was investigated subsequently and found to have a higher concentration of H^2 than sample II.

The measurements on ordinary hydrogen will be discussed first. A great many plates were taken with ordinary hydrogen with the tube in the black stage and one with the tube in the white stage. (Copper oxide was blown into the discharge tube to produce an intense molecular spectrum.) In Table I we give the measurements made on plates (34*t*, 35*t*) showing the $H\beta$ and $H\gamma$ regions with the tube in the white stage, and measurements made on plates (36*t*, 37*t*) with the tube in the black stage. The times of exposure and currents through the tube were the same for all these plates. For comparison we give the wave-lengths given by Gale, Monk and Lee,¹⁶ and by Finkelburg¹⁷ for the molecular spectrum in these regions and the calculated wave-lengths of the Balmer lines of H^2 and H^3 . The positions of the H^1 lines were secured by taking the means of the positions of the symmetrical ghosts and all the lines were measured relative to the standard iron lines.

TABLE I.

		35 <i>t</i>	37 <i>t</i>	Gale, Monk and Lee ¹⁶	Finkelburg ¹⁷
$H^1\beta$	4861.326	4861.322 4860.892 4860.636 4860.104	4861.320 — 4860.633 —	4861.328 4860.806 — 4860.108	— — 4860.620 4860.134
$H^2\beta$	4860.000	—	4859.975	—	—
$H^3\beta$	4859.566	—	—	—	—
		34 <i>t</i>	36 <i>t</i>		
$H^1\gamma$	4340.467	4340.465 4340.084 4339.847 4339.568	4340.486 — 4339.879 4339.599	4340.470 — 4339.817 4339.534	4340.466 4340.154 4339.845 4339.538
$H^2\gamma$	4339.282	—	4339.318	—	—
$H^3\gamma$	4338.8 ₈₂	—	—	—	—

The discrepancies between our values and those of the other authors are rather large. In view of the fact that the molecular lines on our plates were so

¹⁶ H. G. Gale, G. S. Monk and K. O. Lee, *Astrophys. J.* **67**, 89 (1928).

¹⁷ W. Finkelburg, *Zeits. f. Physik* **52**, 27 (1928).

weak that the measurements of their positions were very difficult, the agreement obtained was considered satisfactory. The $H^2\gamma$ line appeared as a slight irregularity on a microphotometer curve of the plate 34*t* but could not be measured with the comparator. The measurements on other plates taken of the atomic spectrum of ordinary hydrogen run very much the same, sometimes with other observed molecular lines on them. The average displacements of the H^2 lines from all plates taken with ordinary hydrogen are given in Table II.

The measurements of plates taken with the hydrogen of sample I under the same conditions as with ordinary hydrogen run very much the same as those for ordinary hydrogen. It was impossible by visual observation to be certain of any difference between the intensity of the H^2 lines on the plates

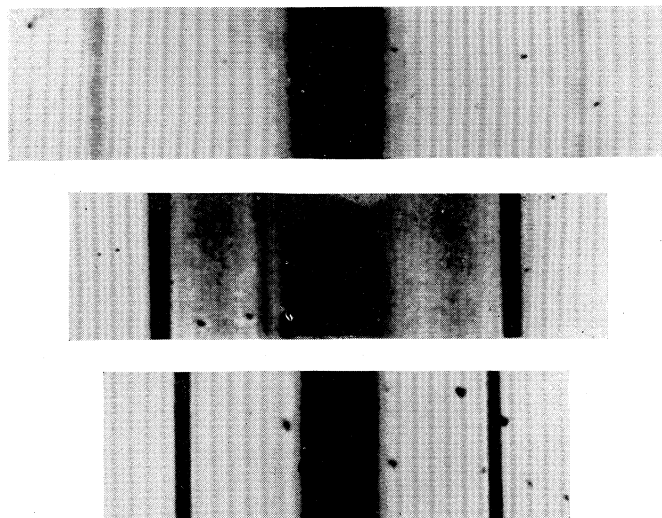


Fig. 1. Enlargement of the $H\alpha$, $H\beta$ and $H\gamma$ lines. The faint lines appearing on the high frequency side of the heavily over-exposed H^1 lines are the lines due to H^2 . The symmetrical pair of lines in each case are ghosts.

for ordinary hydrogen and for sample I, although there were fewer molecular lines on sample I plates than on ordinary hydrogen plates. From this it was concluded that there was no appreciable increase in the concentration of the isotope H^2 in sample I evaporated from six liters of liquid hydrogen at atmospheric pressure over that in ordinary hydrogen and that at 20°K , the vapor pressures of the H^1H^1 and H^1H^2 isotopic molecules must be nearly, if not actually equal. The mean wave-length displacements of the H^2 lines from the H^1 lines on these plates are given in Table II. The agreement with the calculated displacements is better than in the case of ordinary hydrogen. This may indicate a greater ease of measurement due to an increased photographic density of the H^2 lines on sample I plates from which it might be concluded that there was a slight increase in the concentration of the heavier isotope.

When observations were made on samples II and III evaporated just above the triple point, the H^2 lines stood out so clearly from the background that there was no longer any possibility of confusing them with the molecular lines and no further measurements of the molecular lines were made. The measurement of the positions of the H^2 lines on these plates relative to the ghosts of the H^1 lines could be made with ease. The mean displacements listed in Table II for samples II and III are the most reliable ones obtained.

A mercury line falls at 4339.23, while the calculated wave-length of $H^2\gamma$

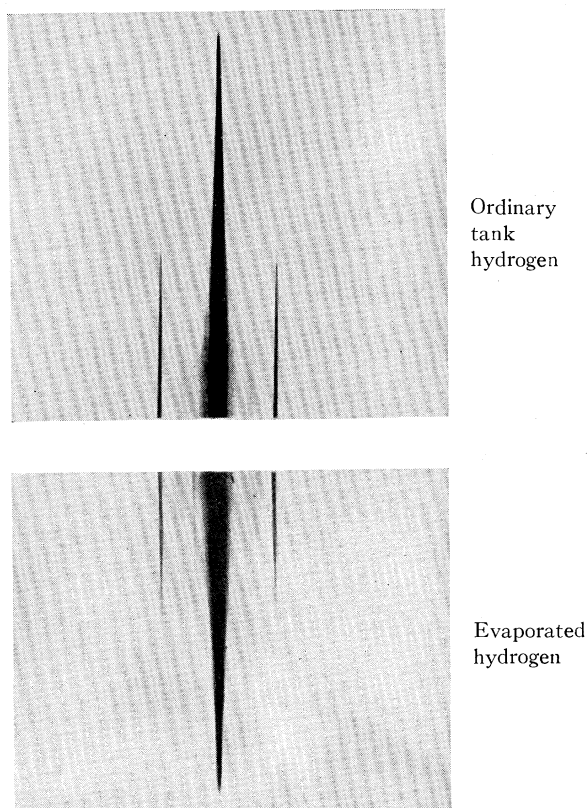


Fig. 2. The $H\beta$ lines for ordinary tank hydrogen, and sample II of the evaporated hydrogen. Although the intensity of the main line is about the same for both exposures, the $H^2\beta$ line is considerably more intense in the second case showing the increased concentration.

is 4339.282. Mercury got into our discharge tube due to various efforts we made to depress the molecular spectrum in the stationary gas. This occurred while we were working with samples II and III. On some plates this mercury line appears as a very faint black edge on the broad atomic line. In other cases, it was more intense and appeared as a very sharp line.

Fig. 1 shows enlarged prints of plates taken with sample II of the $H^1\alpha$, $H^1\beta$, and $H^1\gamma$ lines with the isotope lines appearing as faint companions on the high frequency side of the H^1 lines. The pair of symmetrical lines in each

case are the ghosts. Fig. 2 shows the $H\beta$ lines for ordinary tank hydrogen and for the evaporated hydrogen, sample II, the condition of the discharge and the time of exposure being approximately the same. The isotope H^2 line for sample II is considerably more intense than for ordinary hydrogen, showing that a considerable increase in the concentration of this isotope was affected by evaporation near the triple point. Similar plates have been obtained for $H\gamma$. The $H^2\alpha$ line was obtained only with samples II and III.

TABLE II.¹⁸

	$H\alpha$	$H\beta$	$H\gamma$	$H\delta$
Calcd. displacement	1.793	1.326	1.185	1.119
Obs.				
Ordinary hydrogen	—	1.346	1.206	1.145
Sample I	—	1.330	1.199	1.103
Samples II and III	1.791	1.313	1.176	1.088

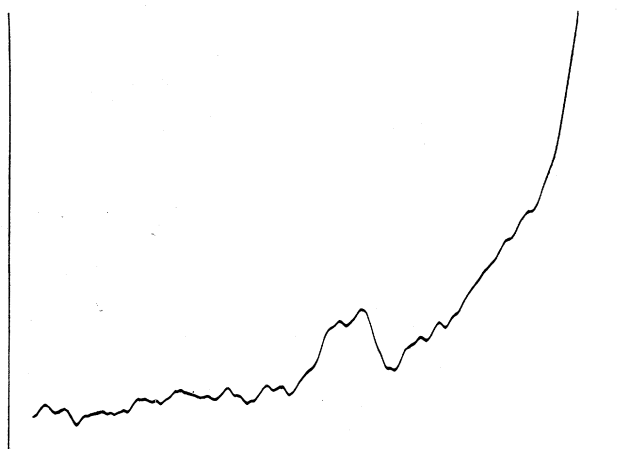


Fig. 3. Microphotometer curve of $H^2\alpha$ showing the doublet separation which is from 0.10 to 0.12A.

The lines of H^2 are broad as is to be expected if they consist of close unresolved doublets, but they are not so broad and diffuse as the lines of H^1 probably due to less Doppler broadening.¹⁹ The $H^2\alpha$ line is just resolved into a close doublet on two plates. Visual settings on these lines with the comparator were difficult. One plate measured in this way gave a doublet separation of 0.16A. Microphotometer curves also show the doublet separation and the

¹⁸ In the letter to the Physical Review 39, 164 (1932) the wave-length displacement of the $H\alpha$ line from sample II was given as 1.820. An error was made in the calculation of this displacement. The correct value for the one plate measured at that time is 1.778A. No measurements of plates with the mercury line near $H^2\gamma$ of more than slight intensity are included in this table. No plate of sample III showing the $H^2\gamma$ line is included for this reason.

¹⁹ The abstract of this paper in the Bulletin of the American Physical Society states that the lines of H^2 have about the same breadth as the main lines. More careful study of our plates showed that the H^2 lines are distinctly narrower than the H^1 lines.

separation secured in this way is from 0.10 to 0.12A. These latter figures are the more reliable and agree with the observed separation of the H^{α} line of 0.135A, being somewhat lower than the value for the well resolved line as is to be expected for partially resolved lines. Fig. 3 shows a microphotometer curve of this line. By itself it is not entirely convincing because of the irregularities due to grain size of the plate. That the resolution is real is proven by visual observation of the plate.

RELATIVE ABUNDANCE

When using ordinary hydrogen, the $H^2\beta$ line appears as a rather sharp line lying in a clear part of the plate between the region of halation from the main line and the main line itself. As the time of exposure is increased, the irradiated region and the region of halation build up the diffuse background of the plate so rapidly that the H^2 line does not become more distinct. However, in the case of sample II and sample III, the H^2 lines come out with a very much greater distinctness so that it is possible to secure these lines without bad halation from the main line. Thus there is no doubt that there has been a very distinct increase in concentration of the H^2 isotope relative to the H^1 isotope in the process of evaporation. It is difficult, however, to give an exact estimate of the relative abundance from the intensity of spectral lines which lie so close together with one so much more intense than the other. Moreover, a comparison of exposure times is not entirely satisfactory because we note that the H^2 lines are distinctly sharper than the H^1 lines so that if the same amounts of energy were emitted by the two varieties of atoms, the H^2 lines should appear to be the more intense, since this energy would fall in a narrower region on the plate. Comparison of the relative intensities of the ghosts of the H^1 lines and the H^2 lines meets with this same difficulty for the ghosts are distinctly more diffuse than the H^2 lines. The best that can be done, therefore, is to give rather rough estimates of the relative abundance judging from times of exposure.

In the case of ordinary hydrogen, it was found that when the discharge tube was running with such an intensity that the H^1 lines could be recorded within one second, that it required somewhat more than an hour to just detect the H^2 lines. It is, therefore, estimated that the relative abundance of the isotopes in ordinary hydrogen is about 1 in 4000 or less. We believe that the estimate of Birge and Menzel based on the atomic weights is consistent with our observations and that their estimate is probably the more reliable.

In the case of sample II, the $H^2\beta$ and $H^2\gamma$ lines could be photographed in ten minutes and the corresponding H^1 lines in one second. From this it is estimated that the relative abundance of H^2 in sample II was 1 in 600, but this, it is believed, is too high because in this case the discharge tube was running better than before and it should have been possible to photograph the H^1 lines in less than a second. Again, the intensities of the ghost lines produced by the grating used are about 1/200th of the intensities of the main lines and the H^2 lines have an intensity equal to about 1/4th of that of the ghost lines as determined by relative exposure times of 1 to 4. This gives a

ratio of about 1 in 800. This is about the best estimate that we were able to make of the relative intensities in this sample. Sample III contains H^2 in larger amounts than sample II, perhaps as much as 1 part in 500 to 600.²⁰

Fig. 4 shows microphotometer curves of the $H\beta$ lines from three samples of hydrogen. The plates were selected so that the densities of the ghost lines were as nearly alike as possible. Visual comparison of the plates shows that the variations in the densities of the ghost lines are such that the intensities

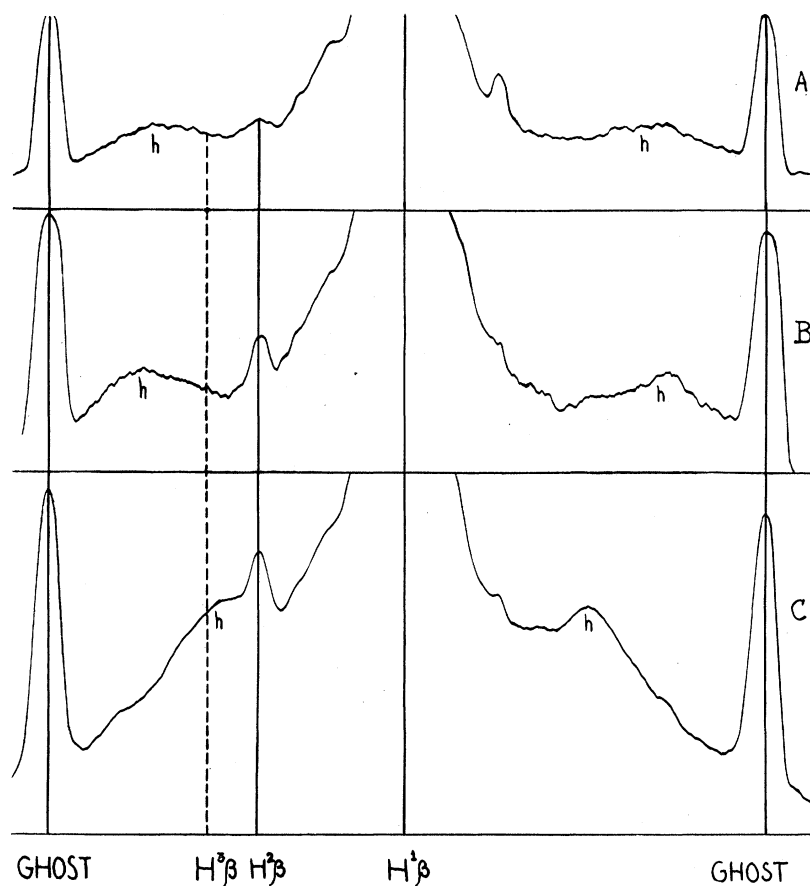


Fig. 4. Microphotometer curves of $H\beta$ for (A) ordinary hydrogen (B) Sample II (C) Sample III. The calculated position of $H^2\beta$ is indicated although there is no evidence for its existence from these curves. The h 's indicate regions of halation.

are in the order $A > B > C$. The heights of the microphotometric curves of the ghosts in Fig. 4 would not seem to substantiate this statement. The ghost

²⁰ Walker Bleakney (Bull. Am. Phys. Soc., Boston meeting) has found that the relative abundance in sample III is $1:1100 \pm 10$ percent. This was determined after this paper was written. We have not revised our estimate since it was our best judgment based on our exposure times, but we believe his estimate to be better than ours since his method is the more reliable.

curves of *B* and *C* are higher than that of *A* because of a more continuous background in *A* due partly to the different distribution of the halation. The fourth order ghosts on the plates are not complicated in this way and visually have the intensity order $A > B > C$. The line to the right of the main H^1 line with an intensity in *A* greater than in either *B* or *C* is a molecular line. The increase in the intensity of the $H^2\beta$ line for samples II and III as recorded by curves *B* and *C* over that for ordinary hydrogen, Curve *A*, can easily be seen.

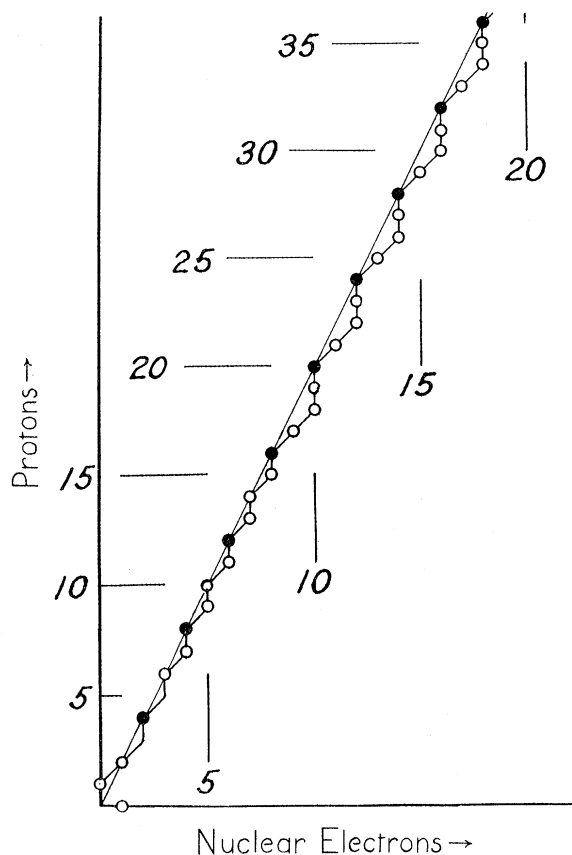


Fig. 5. The proton-electron plot of atomic nuclei.

This shows that the concentration of the H^2 isotope was markedly increased by evaporation at the triple point. The heights of the curves above the estimated continuous backgrounds are in the ratio $A:B:C=4:16:17$, thus substantiating the estimates of increased concentration from exposure times.

A SYSTEM OF ATOMIC NUCLEI

It is of interest to see how the H^2 nucleus fits into a system of atomic nuclei. Periodic systems have been proposed by several authors and are largely equivalent. The simple proton-electron plot shows regularities in a

very good way and the accompanying figure (Fig. 5) shows the regularities up to A^{36} . The figure suggests that H^3 and He^5 should exist. No evidence for H^3 has as yet been found, but further concentration (see below) may yet show that this nuclear species exists. It should be possible to concentrate He^5 by the distillation of liquid helium, and this method may show that this nucleus also exists.

OTHER METHODS FOR CONCENTRATING THE HEAVIER ISOTOPES OF HYDROGEN

It seems entirely feasible to construct a fractionating column that will greatly increase the efficiency of the distillation method for separating these isotopes. This method has the distinct advantage that it is capable of producing large samples. On the other hand, it requires rather large volumes of gas, so that after the isotope has been concentrated in small volumes by the fractional distillation and rectification of liquid hydrogen, further concentration may be better carried out using diffusion methods. Stern and Vollmer²¹ used such a method in an attempt to find isotopes of hydrogen and oxygen, working on the hypothesis that the non-integral atomic weight of hydrogen might be due to a higher isotope. They report that a heavier hydrogen isotope is not present to the extent of 1 part in 100,000. Their negative result emphasizes the difficulties of diffusion methods which for success require carefully controlled conditions. Such an apparatus as has been described by Hertz²² should be very effective for the separation of the hydrogen isotopes. Work is in progress on the construction of such an apparatus for further concentration beyond the state that we can reach with distillation methods.

The authors take pleasure in acknowledging their indebtedness to the Physics Department of Columbia University for the grating and other facilities used in this work and for its cooperation. We are also indebted to the Chemistry Department of New York University and, to Mr. R. L. Garman in particular, for the microphotometer curves.

²¹ O. Stern and M. Vollmer, *Ann. d. Physik* (4) 59, 225 (1919).

²² G. Hertz, *Zeits. f. Physik* 19, 35 (1923).

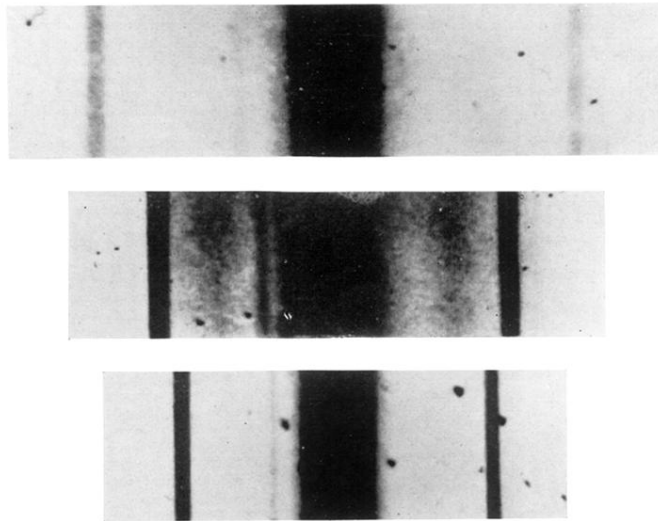


Fig. 1. Enlargement of the $H\alpha$, $H\beta$ and $H\gamma$ lines. The faint lines appearing on the high frequency side of the heavily over-exposed H^1 lines are the lines due to H^2 . The symmetrical pair of lines in each case are ghosts.

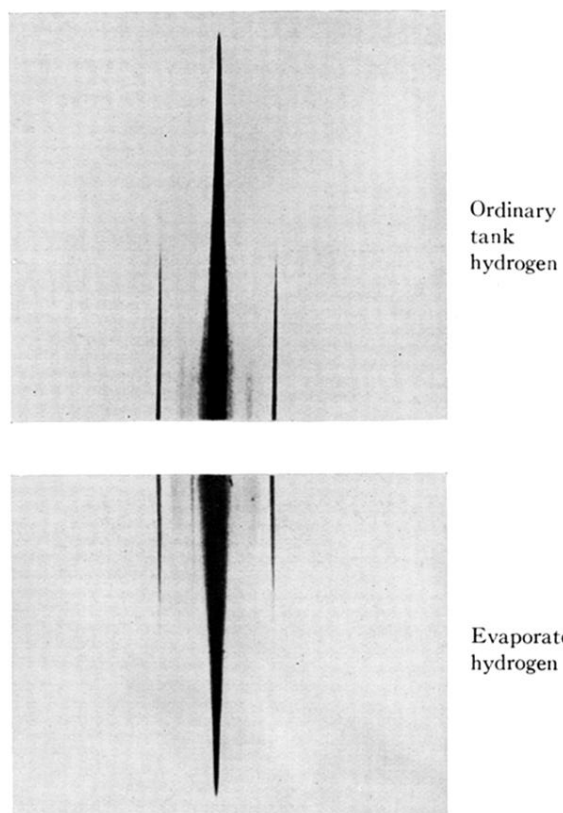


Fig. 2. The $H\beta$ lines for ordinary tank hydrogen, and sample II of the evaporated hydrogen. Although the intensity of the main line is about the same for both exposures, the $H^2\beta$ line is considerably more intense in the second case showing the increased concentration.