Studies on Concentrating the Hydrogen Isotope H^2 by the Electolysis of Water. Part I.

(With 2 Plates and 5 Text-Figures)

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Introduction

The first quantitative evidence for the existence of a hydrogen isotope of mass 2, was secured by UREY, BRICKWEDDE and MURPHY[1] and they gave for the abundance ratio of H^2 to H^1 in natural hydrogen, the value $H^2 : H^1 = 1 : 4000$. These results were obtained by an observation along Balmer lines. Since then many investigations have been conducted to determine the true value of the abundance ratio in natural hydrogen. The most provable one of value at present is the one recently obtained by BLEAKNEY and GOULD:[2] $H^2 : H^1 = 1 : 5000$.

In spite of the very small amount of H^2 present in ordinary hydrogen, it is very promising to fractionate H^2 and H^1 completely, because the mass of H^2 is twice as large as that of H^1 and therefore the difference of properties between them is expected to be far greater than between any other pair of isotopes. UREY, BRICKWEDDE and MURPHY[1] first obtained a sample which contained H^2 about five times as great as natural hydrogen by evaporating liquid hydrogen at a pressure which was only a few millimeters above the triple point. Soon after this work the possibility of fractionating H^2 and H^1 by the electrolysis of water was suggested by WASHBURN and UREY.[2] According to their theory, in the process of electrolysis of water there are two causes for excluding one isotope from the other: (1) the effect of a possible little difference between the normal

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electrode potentials of H^1 and H^2 (2) the effect due to the diffusion process of two species of ions and also discharged ions in the mechanism of formation of hydrogen molecules at the cathode. And they confirmed their expectation by finding the definite increase in the abundance ratio in the residual solution obtained by the electrolysis of water to produce oxygen for industrial purposes. By virtue of this method brilliant success in fractionating H^2 and H^1 to a considerable degree was recently achieved by LEWIS and MACDONALD.[4] In their experiment, water was made conductive by adding NaOH and nickel plates were used as electrodes. The solution was carefully cooled to avoid the loss of water caused by evaporation. Reducing twenty liters of water obtained from the industrial electrolytic cell used about four years to one-half of cubic centimeter by electrolysis, they could obtain water which has a specific gravity of 1.073 and contained H^2 and H^1 in ratio: $H^2 : H^1 = 2 : 1$. From their results they also estimated the ratio of the percentage loss of H^2 to that of H^1 at 0.20. Another important work of research is that of WASHBURN, SMITH and FRANDSEN.[5] In their experiment, water having an initial specific gravity of 1.000034 was made conductive by adding sulphric acid, and the solution (0.01 N) was electrolyzed by using an anode of right platinum and a gold-plated copper cathod covered with platinum black. They measured the variation of the density of water caused by continued electrolysis, and gave curves illustrating the efficiency of the fractionation.

Since it is very provable that H^2 may offer very powerful aids to researches in all branches of physics and chemistry, especially in nuclear physics, our laboratory immediately took up the study on the electrolysis method, soon after the announcement of the success of LEWIS and MACDONALD arrived here. In the following papers, the experiments and results obtained are given.

Methods and Results of the Experiment.

In order to determine the abundance ratio of H^2 to H^1 in water, the following three methods will be used: (1) Density measurement

(2) Positive ray method (3) Spectroscopic method. In the present experiment, the spectroscopic method was adopted, and the abundance ratio was determined by comparing the intensities of the H_β lines of H^1 and H^2 with each other.

According to the theory of line spectra, the position of the H^2 Balmer lines is to be shifted a little to the violet side of the corresponding H^1 Balmer lines. These separations were first measured by UREY, BRICKWEDDE and MURPHY.[1] They photographed the spectrum of light from a Wood hydrogen discharge tube in the second order of a 21 foot grating having dispersion of 1.3 A. per mm., and obtained the following results.

	H_α	H_β	H_γ	H_δ
separations in A.U.	1.791	1.313	1.176	1.088

Moreover, besides the above small separated distance between the Balmer lines of H^1 and H^2, the broadening of H^1 lines caused by over exposure cannot be avoided, therefore a spectrograph having large dispersion and resolving power must be used to detect the H^2 line from the H^1 line. The author therefore used a large glass prism

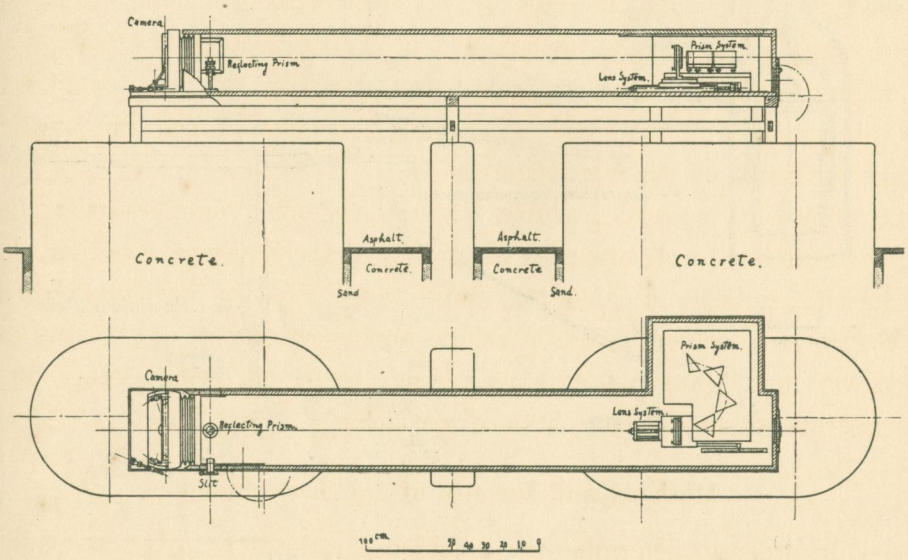


Fig. 1.

spectrograph of Littrow mounting constructed in our laboratory. The details of the design are shown in Fig. 1.

The optical train consists of one achromatic lens of 10 cm. aperture and 300 cm. focal length made by Hilger & Co. (No. E 263), a 60° prism and a 30° prism each of which is 13.0 cm. length of face × 7.6 cm. in height by Hilger & Co. (No. E 245) and two 60° prism by Kōgaku Kōgyō & Co., which are similar in size to the above ones.

The slit is Hilger's No. F 31. The dark slide is Hilger's No. E 295.

The light that enters through the slit is reflected along the camera case by a right-angled prism of 1.4 cm. length of reflecting face × 1 cm. in height, is collimated by the lens; passes through the train of the prisms; is reflected back by the 30° prism the reflecting face of which is coated with tin-mercury amalgam; and retraces its path through the lens, an image of the spectrum being focussed on the photographic plate. The prism system is placed on a stand

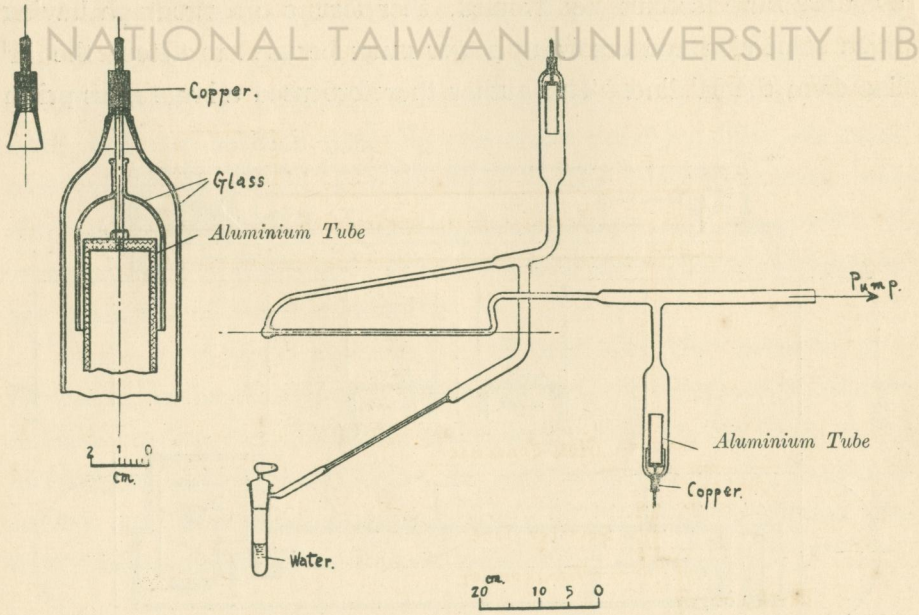


Fig. 2.

fixed to the bottom of a case of the spectrograph. The lens is mounted on a carriage which can be moved along a slide by a screw, its position being defined by a scale and an index, and its position can be accurately adjusted for the focusing purpose. The case is made of well seasoned Japan cypress. The spectrograph is settled on concrete bases separated by a layer of sand from the ground floor to avoid the disturbance caused by the shock.

This spectrograph gives a very fine image of the spectrum. The dispersion is 1.4 A./mm. at the H_β line, so the separation of H^1_β and H^2_β lines on a photographic plate is about 1 mm.

The discharge tube used is the type designed by R. W. WOOD and shown in Fig. 2.

The main part of the tube is 0.8 cm. in inner diameter. Alminium cylinders of 2.5 cm. in diameter and 10 cm. in length are used as electrodes, and each of them is fixed to a copper lead jointed to a glass tube of 4 cm. in diameter as shown in Fig. 2b. The discharge tube is connected through a capillary to a small vessel in which samples of water are put in, and also to a Cenco Hyvac pump as shown in Fig. 2a.

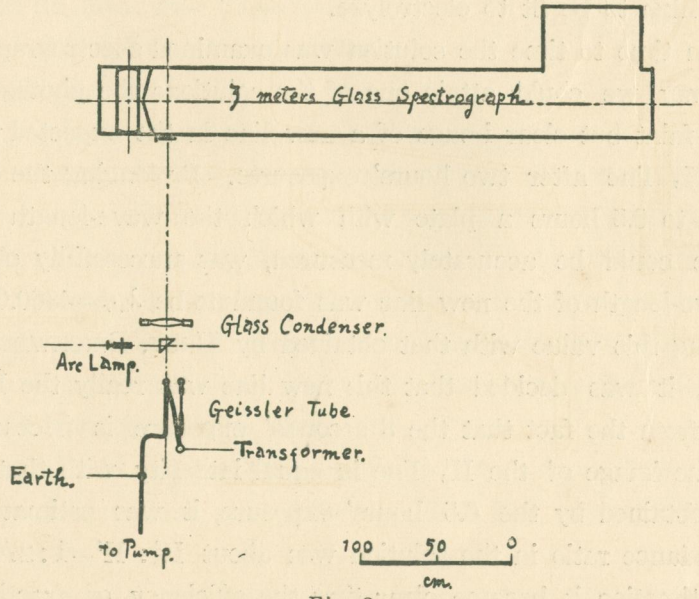


Fig. 3.

The tube is excited by a current of about 80 ma., using a 5 kw. X-ray transformer with one pole earthed. During the excitation, water vapour was continuously run through the tube.

The whole arrangement for the spectroscopic work is shown in Fig. 3.

The photographic plate used was the Ilford special rapid panchromatic plate (thin glass).

The emission of the discharge tube gave very pure atomic spectrum of hydrogen and was so intense that the image of the H^1_β line could be clearly detected on the plate by 5 seconds' exposure.

To concentrate H^2 by the electrolysis of water the following method was first tried. Fifteen liters of ordinary distilled water was made conductive by adding 5% NaOH, and was poured into twenty cells, which were provided with electrodes of iron plates and connected in series in a D.C. 100 volts circuit. The cells were cooled from the out-side by water. The current of electrolysis was about 6 amperes. The electrolysis of water was continued, collecting the solution in the smaller number of cells when it reduced in quantity, and distilling the solution when the concentration of NaOH in it rose too high to be fit to electrolyze.

From time to time the solution was examined spectrographically. In this way we could attain one of the solutions the photograph of which a faint but clear image of a new line in the expected position of the H^2_β line after two hours' exposures. Prolonging the time of exposure to 6.5 hours a plate with which the wave-length of the new line could be accurately measured, was successfully obtained. The wave-length of the new line was found to be $\lambda_{air}=4860.03$ A.U. Comparing this value with that obtained by UREY, BRICKWEDDE and MURPHY, it was decided that this new line was really the H^2_β line. Judging from the fact that the 8 seconds' exposure is necessary to obtain the image of the H^1_β line in equal intensity with that of the H^2_β line obtained by the 6.5 hours' exposure, it was estimated that the abundance ratio in the solution was about $H^2 : H^1 = 1 : 2700$. By rough estimation it became clear that the efficiency of fractionation

was worse than that of LEWIS and MACDONALD's method.

Next, to improve the efficiency of fractionation the following method was tried. The electrolyser used was the one shown in Fig. 4.

An outer glass tube (a) was 3 cm. in inner diameter and 35 cm. in length. A hole of about 1 cm. in diameter was made on the upper part of the outer tube. An inner glass tube (b) was 10 mm. in diameter and was so constructed as to cool the solution by the stream of cooling water through it. The electrodes were made by rolling a sheet of iron shown in Fig. 4b in a cylindrical form, and they were placed in contact with an outer tube and an inner one respectively. The capacity of the electrolyser was about 100 cc.

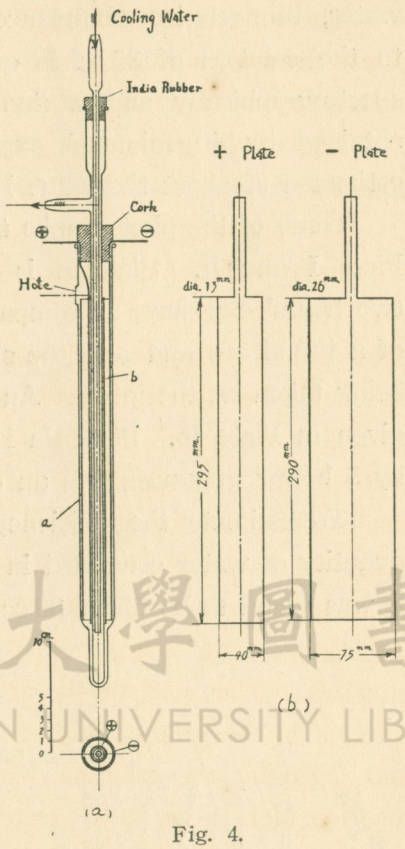


Fig. 4.

A certain great quantity of distilled water can be reduced to a small quantity of 30 cc. by this arrangement of electrolysis in the following way: 100 cc. of the distilled water is at first made conductive by resolving 10 g. of NaOH and then introduced into the cell; then the cell was operated upon with a current of 8 amperes being supplied with the distilled water through the hole twice a day till the volume reached its initial 100 cc. In such a way the solution was reduced to the quantity of 30 cc.

The solution was so well cooled by this arrangement that the decrease of its volume was almost equal to that expected by the law of electrolysis.

To know the efficiency of the fractionation, 280 cc. of distilled

water, the relative abundance being $H^2 : H^1 = 1 : 2700$, was reduced to the solution of 35 cc. in quantities. This solution was examined spectrographically and a fine photograph of the H_β^2 line could be obtained by 40 minutes' exposure. The relative abundance was estimated at about the value $H^2 : H^1 = 1 : 400$.

Some of the photographs taken with this solution are shown in Plate I and II. Plate Ia is a reproduction of a plate obtained by two hours' exposure, as comparison spectra the Fe and Ni spectra of a Pfund arc and also the spectra of the hydrogen discharge tube being taken on the plate. An enlarged reproduction of the plate is given in Plate Ib. Plate IIa is a reproduction of a plate obtained by 5 hours' exposure, and an enlarged one is given in Plate IIb.

To estimate the efficiency of fractionation of H^2 and H^1, the quantity of water contained in the final solution must be known and it was found to be about 30 cc. Therefore the value of

$$\frac{R}{R_0} : \frac{V_0}{V}$$

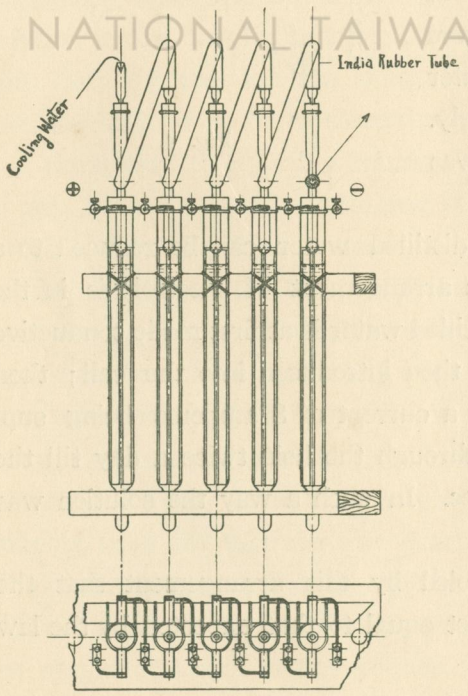
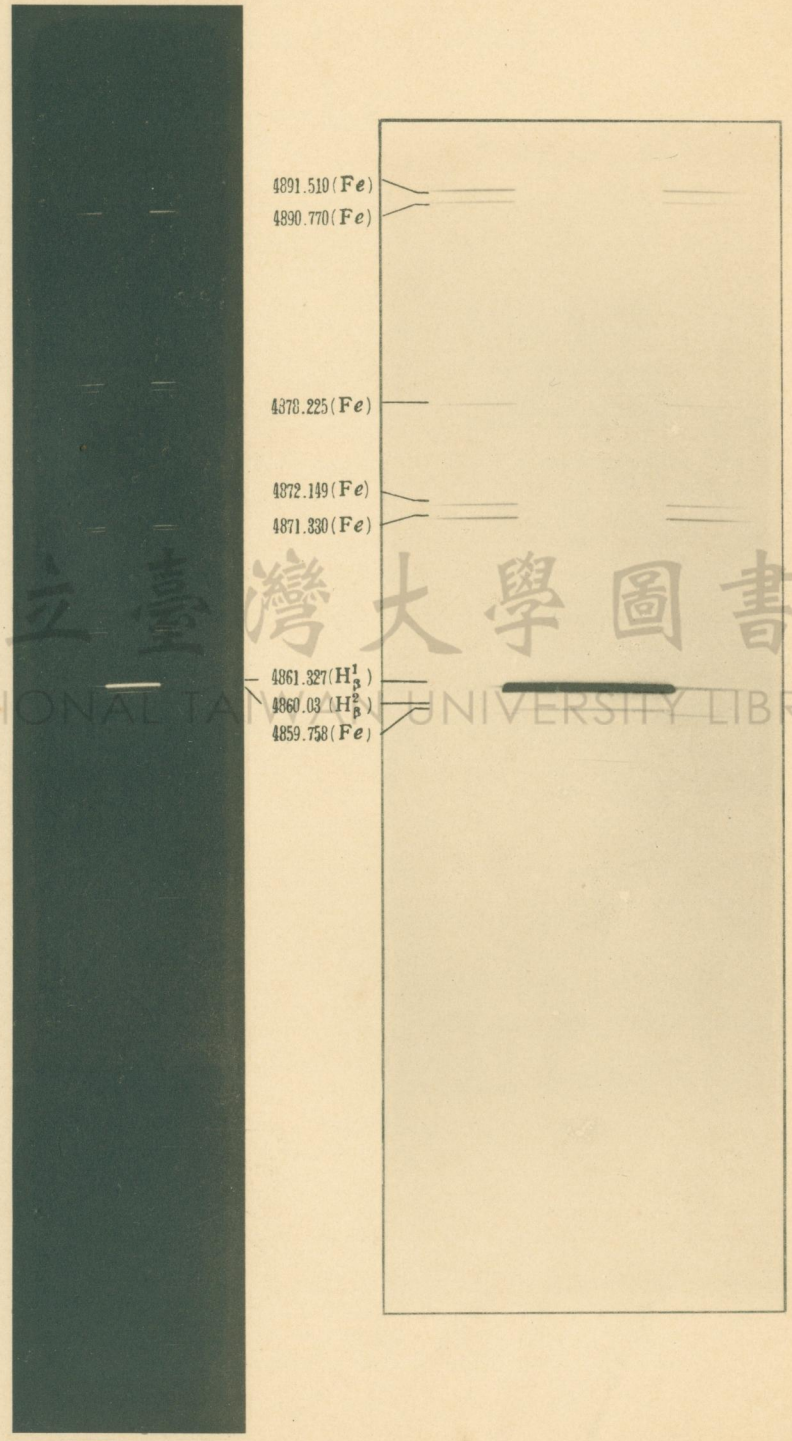


Fig. 5.

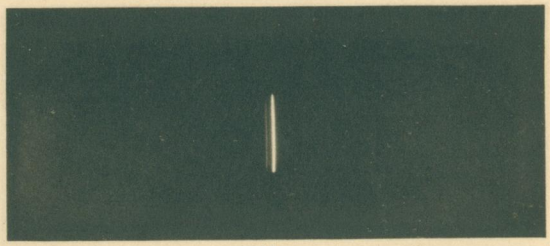
was about 0.7, where R_0 and R, indicating the initial and final value of the abundance ratio $H^2 : H^1$, and V_0 and V, that of the volume of water. Thus the efficiency of fractionation was nearly as good as that of LEWIS and MACDONALD.

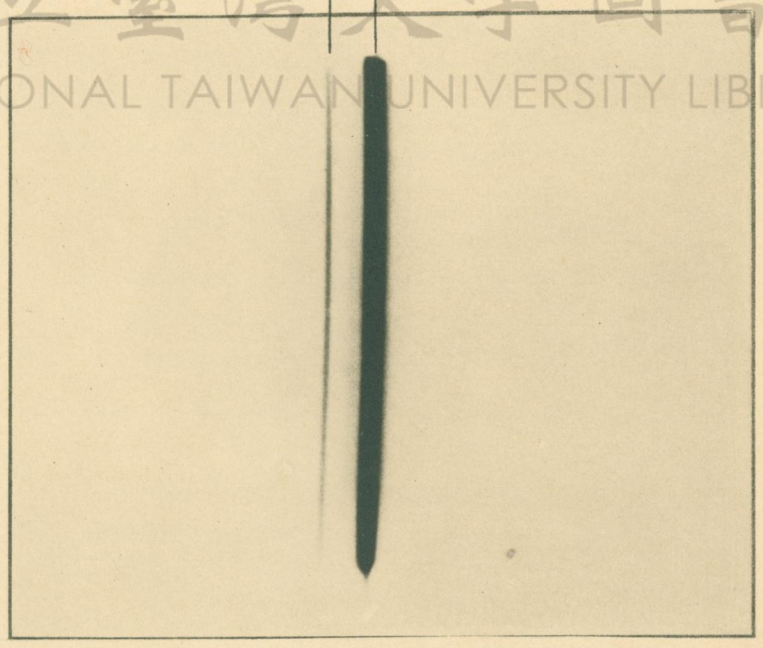
By connecting the cells in such a way as shown in Fig. 5, they are conveniently used to concentrate H^2.

To operate them with a current of 8 amperes, about 45 of them were connected in series in a D.C. 120 volts circuit. In



(a)





(b)

our laboratory, with these devices the experiments on the subject are being continued, the details of which will be published shortly.

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Literatures

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