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## Concentration of $H^2$ Isotope

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A method is described of producing any desired concentration of the isotope of hydrogen,  $H^2$ , by electrolysis. Starting with twenty liters of water from an old commercial electrolytic cell and electrolyzing in four stages until only one-half of a cubic centimeter of water remained, this water had the specific gravity 1.073. Having shown that no large accumulation of the heavy isotopes of oxygen occurs and assuming that the density varies

linearly with the fraction of  $H^2$ ,  $2/3$  of the hydrogen in this water is  $H^2$ . It is shown that a further reduction of volume to one-quarter will give 99 percent  $H^2$ . In our electrolyses the percentage loss of  $H^1$  is to the percentage loss of  $H^2$  in the ratio of five to one. By two methods we have found 1 in 6500, as a provisional value for the concentration of  $H^2$  in ordinary water.

SINCE the announcement<sup>1</sup> of our success in attaining a high concentration of hydrogen isotope has aroused some curiosity as to the methods that were employed, we shall describe here our procedure, although we should have liked first to have made a more scientific analysis of the various steps in the process, and although it seems probable that better methods of preparing the isotope will shortly be available. The fact is, the difference in properties between the two isotopes of hydrogen is so much greater than between any other pair of isotopes that in spite of the very small amount of  $H^2$  present in ordinary hydrogen, several methods will lead to an almost complete separation of  $H^2$  from  $H^1$ , as we have convinced ourselves by a number of preliminary experiments.

Being engaged some months ago in the separation of the isotopes of oxygen, we found it possible to follow small changes in the ratio of the isotopes in water by careful measurements of the density. By finding the temperature at

which a 10 cc float will neither sink nor rise in ordinary pure water, and then finding the temperature at which this buoyancy balance is again established in a new sample of water, the specific gravity of that sample may be obtained with an accuracy of one part per million. At about 16°C a change of one part per million in density corresponds to a change of 0.006° in the temperature of the buoyancy balance. Of course, all the water samples must be carefully distilled and freed from dissolved air.

While we were engaged in the slow process of concentrating the oxygen isotopes we realized how much more interesting and important it would be to obtain the isotope of hydrogen which was discovered last year by Urey, Brickwedde and Murphy.<sup>2</sup> Since the concentration of  $H^2$  in ordinary hydrogen has been recently estimated to be only about one part in thirty thousand, or less, it seemed hopeless to attempt such a separation unless a fractionating process could be

<sup>1</sup> Lewis, J. Am. Chem. Soc. 55, 1297 (1933).

<sup>2</sup> Urey, Brickwedde and Murphy, Phys. Rev. 39, 164 (1932).

obtained with an efficiency of an entirely different order of magnitude from that of the methods that have hitherto been used in the separation of isotopes. The more we considered the matter the more likely it seemed that such processes could be found, and this belief seemed to be corroborated by the discovery of Washburn and Urey<sup>3</sup> that the water in an old electrolytic cell contains an appreciably larger amount of H<sup>2</sup> than does ordinary water, although they did not determine the degree of concentration.

In this laboratory there is an electrolytic cell which has been operated for four years without any change except the occasional addition of distilled water to replace the water electrolyzed. We distilled some of the liquor from this cell and found it to have a specific gravity of 1.000034, as compared with ordinary water at the same temperature. This very startling increase in density, if due to a concentration of H<sup>2</sup> isotope, would indicate the presence of H<sup>2</sup> to the extent of one part in 3000, or ten times the amount which had been estimated to be present in ordinary water.

The theory of such a fractionation is simple. If the cell runs long enough to approach a stationary state, water being continually added to maintain a constant volume, then the composition of the electrolyte must approach a constant value. If  $\alpha$  represents the percentage loss of H<sup>2</sup> divided by the percentage loss of H<sup>1</sup>, then the ratio of H<sup>2</sup> to H<sup>1</sup> in the cell must ultimately approach a value  $1/\alpha$  times as great as the initial value, and the composition of the evolved gases must approach that of the water added. Therefore our first experiment would seem to indicate that even if our electrolytic cell has nearly reached the equilibrium state, the value of  $\alpha$  cannot be greater than 0.1. All this assumes that the evolved gases contain no water vapor. The fact that water vapor is lost in appreciable amount still further reduces the possible value of  $\alpha$ .

Instead of adding water to keep the electrolyte at constant volume we may allow the total amount of electrolyte to change. If we call  $x_1$  the amount of H<sup>1</sup> and  $x_2$  the amount of H<sup>2</sup>, then in

each stage of the process

$$d \log x_2 = \alpha d \log x_1, \quad (1)$$

or, representing by  $x_1^0$  and  $x_2^0$  the initial amounts,

$$\log x_2/x_2^0 = \alpha \log x_1/x_1^0 \quad \text{or} \quad x_2/x_2^0 = (x_1/x_1^0)^\alpha. \quad (2)$$

Our next step was to carry out such an electrolysis. Some of the liquor from the large electrolytic cell was placed in a beaker with two plates of nickel as electrodes and was electrolyzed with a current of about 15 amperes until the volume had been reduced to about  $\frac{2}{3}$  of the initial volume. The electrolyte was then distilled, and the increase in density over ordinary water was found to be fifty percent greater than before. This seemed once more to indicate that practically all of the H<sup>2</sup> was left behind.

These optimistic conclusions were suddenly overthrown by a simple calculation. Professor Giauque, who had been using the large electrolytic cell, was able to make a rough calculation of the total amount of water added to the cell during its four years of operation. Taking the original concentration of H<sup>2</sup> to H<sup>1</sup> as 1 to 30,000, it became evident that not more than one-third or one-quarter as much H<sup>2</sup> had ever been added to the cell as we were finding there. This discrepancy might be explained in one of two ways. Either the concentration of H<sup>2</sup> in ordinary water is much greater than had been supposed or our increase of density was not caused by the concentration of hydrogen isotope alone, but by concentration of the heavier isotopes of oxygen, which are initially present in much larger amount.

The possibility that any large accumulation of heavy oxygen had occurred was soon eliminated. Some of the water obtained in the electrolysis which we last described, and of which the temperature of buoyancy balance was 0.31° above that of ordinary water, was distilled in such a manner that the steam passed over hot iron wool where part of it was converted into hydrogen. The gases passed on into a condenser from which the water was returned to the still while the hydrogen continued into a tube containing hot copper oxide, where it was once more converted into water and was then condensed. After this process was complete a stream of hydrogen was passed through the hot iron

<sup>3</sup> Washburn and Urey, Proc. Nat. Acad. 18, 496 (1932).

oxide, producing a second sample of water which contained all of the oxygen, while the first sample contained all of the hydrogen, of the initial water. This second sample had the density of ordinary water while the first, which contained only the hydrogen of the water under investigation, showed again a difference of  $0.31^\circ$  in buoyancy balance.

We were thus forced to the conclusion that the concentration of  $H^2$  in ordinary water is much higher than has been usually estimated, approaching more nearly the value of 1 to 4500 first predicted by Birge and Menzel<sup>4</sup> from discrepancies in the atomic weight of hydrogen.

Our electrolytic experiment can now be explained by assuming first that the ratio of  $H^2$  to  $H^1$  in the hydrogen evolved from the cell is higher than we had supposed and second that in the calculation of concentration from density, correction must be made for an appreciable difference between the densities of ordinary water and of pure  $H^1H^1O$ . While these new conclusions show a poorer efficiency in the electrolytic separation, this is partly compensated by the higher initial concentration of  $H^2$ .

We therefore engaged at once in a process designed to reduce by electrolysis 10 liters of the water from the large electrolytic cell down to 1 cc or less. In a large glass tube were placed eight parallel nickel plates, each 55 sq. cm in area, connected alternately with the positive and negative leads, which were also of nickel. A copper coil was introduced through which cooling water flowed. A current of 250 amperes was used, although this was reduced in the later stages of the electrolysis, when the volume of the electrolyte became small. In order to avoid too high a concentration of electrolyte at the end of the run, we used one liter of 5*M* alkali from the large electrolytic cell, and 9 liters of water distilled from the same liquor.

At the end of five or six days the electrolyte was reduced to one liter. Of this, ninety percent was placed in a bath at  $0^\circ C$ , while  $CO_2$  was allowed to bubble through it until all the alkali was converted to normal  $Na_2CO_3$ , indigo carmine being used as indicator. This solution was then distilled from a copper kettle which could be

heated finally to drive over all the water of crystallization. The 900 cc thus obtained, together with the 100 cc of alkaline solution reserved from the preceding electrolysis, were placed in a smaller but similar cell and electrolyzed to a volume of about 100 cc. This in turn, employing the same procedure as before, was electrolyzed in a third still smaller cell until it was reduced to 10 cc. In the fourth very small cell, which, instead of having a cooling coil, was surrounded by ice water, the volume of electrolyte was reduced to a little over half a cubic centimeter. This liquid, treated with carbon dioxide, was distilled in a vacuum into a small container. The water thus obtained was found by means of a small picnometer to have the specific gravity 1.035; in other words, 31.5 percent of all the hydrogen in this water is  $H^2$ .

In the next series of experiments changes were made in the first and the last electrolytic concentrators. In the first, the 10 liter glass cylinder was replaced by a 20 liter cylinder of monel metal with external cooling, and the current was increased to 400 amperes. In the last concentrator provision was made for saving the evolved gases. These were recombined on platinized asbestos, thus giving water containing several percent of  $H^2$ .

In this second run, concentrating from 20 liters to 0.5 cc, we obtained water of specific gravity 1.073. Accordingly, in this water 65.7 percent of the hydrogen is  $H^2$ . While our previous experiment showed conclusively that there is no large change in the ratio of oxygen isotopes in our electrolytic process, and while spectroscopic analysis has shown that the hydrogen obtained from this sample of water contains over fifty percent of  $H^2$ , two things must be done before we can, with certainty, obtain the composition from the density. First, we must subject this water to the process that we have described, which would free it from oxygen in which the isotope ratio may have changed, and second, we must prove that the density varies linearly with the composition. These two experiments have not yet been completed.

In our whole process of concentration we have attempted to adhere as nearly as possible to the conditions of our large commercial electrolytic cell until we could, by theory or experiment,

<sup>4</sup> Birge and Menzel, *Phys. Rev.* 37, 1669 (1931).

ascertain the best conditions for electrolytic separation. Thus all of our electrodes and leads were made of pure nickel. However, during the course of the experiments stray currents caused the transfer of copper from the cooling coils, and we have suspected that this copper plating may have slightly diminished the efficiency of the electrolytic separation, but we have as yet no proof of this. We have attempted to keep the temperature during electrolysis below 35°C, chiefly to avoid loss of water by evaporation, but partly also because it seemed likely that the efficiency of separation would be higher at low temperatures. Here again we have made no systematic efforts to prove the correctness of this view.

By determining the density of the water in the various stages of concentration we have attempted to determine the efficiency of the electrolytic separation. While there seemed to be some individual variations, all the results agree pretty closely with the assumption that the value of  $\alpha$  in Eq. (1) is 0.20. In other words, under equivalent conditions, five times as much  $H^1$  as  $H^2$  is evolved.

According to this figure, if the water containing 65.7 percent  $H^2$  were reduced by electrolysis to one-quarter of its volume, it would contain 99 percent of  $H^2$ . We have, however, postponed making this experiment until larger amounts of heavy water become available.

There is not much that can be said at present

regarding the theory of the electrolytic fractionation. It is evident that under the conditions of our experiments there is, between the two isotopes, a difference in the electrical polarization at the cathode amounting to four centivolts. Assuming that this represents chiefly a difference in rates, rather than in the true electrode potentials, it is hard to guess how much of this difference in rates is due to the difference in mobility of the two hydrogen ions, to the difference in rates of diffusion of the two atomic species in the nickel surface, and to a difference in rates of recombination of the atoms. These questions are now under investigation. In addition Professor Heyrovsky is planning to make direct determinations of the overvoltage of the two isotopes.

In conclusion, let us make an estimate of the amount of the heavy hydrogen isotope in ordinary water, realizing that samples from different sources may vary considerably. There are two simple ways of making this determination. By successive electrolyses, collecting and recombining the evolved gases, we may approximate to pure  $H^1H^1O$  and find the difference in density between it and ordinary water. On the other hand, we may concentrate ordinary water in an electrolytic cell of known efficiency and find the increase in density. Preliminary measurements by both methods indicate that in Berkeley city water there is one part of  $H^2$  to about 6500 parts of  $H^1$ .