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Technique for the Electrolytic Production of H^2H^2O

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A detailed description of a method of preparing heavy water in quantity is given and yields obtained over a period of months reported.

NUMEROUS requests for a detailed description of our methods for the production of water rich in heavy hydrogen isotope, first outlined elsewhere,[1] prompt the following more detailed discussion of our present practice in the light of experience attained during the past summer in the treatment of 600 gallons of used electrolyte with the production of some 80 cc of water containing upwards of 90 percent heavy hydrogen.

ELECTROLYSIS WITHOUT RECOVERY

Electrolyte from commercial electrolytic cells is distilled in order to remove the large amounts of carbonate and hydroxide present. Sodium hydroxide is added to make the distillate approximately 0.5 molar. This solution is electrolyzed in a battery of 210 cells, made from hydrometer jars, 4 cm diameter and 25 cm high, each of approximately 200 cc capacity, water-cooled by immersion in a tank containing flowing water and carrying a current of six to seven amperes. The electrodes are made of nickel plate, a strip 60 cm by 3 cm being bent twice at right angles so as to form anode and cathode in neighboring cells. The battery is subdivided into units of 30 cells each, the potential of the direct current supplied from a motor generator being adjusted so as to yield the amperage employed. After three days, when the electrolyte has diminished to 1/6 or 1/7th its original volume, it is replaced by a fresh batch of electrolyte. This process is so conducted that, while one cell is being emptied with the aid of suction, a neighboring cell is being filled with fresh electrolyte by a siphon, the whole process requiring about one hour. The concentrated electrolyte from the first electrolysis is partially neutralized by bubbling carbon dioxide through it so as to form the carbonate, with fuchsin as an indicator, and then distilled. This water is now added to another group of cells containing water of the same grade but still containing all of the sodium hydroxide originally added with the water at the start of the first electrolysis. This procedure obviates setting aside a portion of the concentrated liquor before distillation which would later be added to the distillate to give the 0.5 molar solution for the second electrolysis. In this way three successive electrolyses are carried out resulting in water of density $D_{4^\circ}^{20^\circ} = 1.001$, approximately, and which therefore contains about 2.5 percent of the heavy hydrogen isotope.

ELECTROLYSIS WITH RECOVERY

From this stage onwards the hydrogen evolved during electrolysis contains an appreciable amount of the heavy isotope which should be recovered. This has been effected in the following way. Water containing sodium hydroxide is electrolyzed in cells of 200 cc capacity carrying a current of 10 amperes each and cooled in a trough of running water. The mixed electrolytic gas passes successively, as shown in Fig. 1.

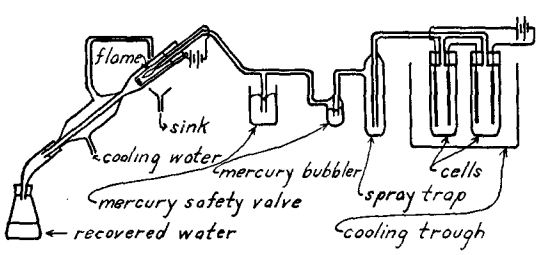

FIG. 1. Electrolytic concentration apparatus.

[1] H. S. Taylor and H. Eyring, Proc. Am. Phil. Soc. **72**, 255 (1933).

through a spray-trap, a mercury bubbler, through a T-tube immersed in mercury to form a safety valve for releasing excessive pressure, and finally flows out through a capillary nozzle of Pyrex glass where it burns as a flame. The water formed by the combustion is condensed in an inclined quartz tube surrounded at the lower end by a water jacket. A red-hot platinum filament is placed just beyond the flame in order to re-ignite the gas in case the flame should go out, which may happen every few minutes if the size of the capillary nozzle is not perfectly adjusted for the rate of gas flow from the cells. For a given rate of gas flow, if the capillary is too fine it is easily clogged up, presumably by alkali from the cells; on the other hand, if the capillary is too wide, the flame strikes back through the tubing but is prevented from reaching the cells through the mercury obstruction (about 1 cm) in the mercury bubbler. If the condenser tube in the neighborhood of the flame becomes too hot, the flame jumps to the platinum wire where it burns incompletely. This is prevented by cooling the tube slightly at this point, a fact that indicates the effect is due to an excessive pressure of water vapor which is known to hinder the explosive reaction. For two cells each carrying 10 amperes the optimum size for the capillary has been found to be about 0.3 mm. Each nozzle has a lifetime of about one day but is easily replaced by a new nozzle. Practically a quantitative recovery of the water can be obtained by this method.

Yield

In electrolyzing a dilute solution of the heavy water down to about 1/6th of the original volume, it is found that the concentration of the heavy hydrogen in the heavier 1/6th has increased by a factor of about four while the concentration in the lighter 5/6ths is about 2/5ths that of the original. The recovered water is therefore added to the water one stage back in the process. With the present arrangements seven successive stages suffice to produce water which contains about 99 percent of the hydrogen in the heavy form. Table I indicates the quality of the water now obtained at each stage of the process.

Table I.

Water obtained from electrolysis No.	Density D_4^{20}	% hydrogen which is heavy
I	0.998	—
II	0.999	0.5
III	1.001	2.5
IV	1.007	8
V	1.031	30
VI	1.098	93
VII	1.104	99

Table II shows the amounts of water put through each stage of the process during the period May 9th to September 27th, 1933.

Table II.

Electrolysis No.	Amt. electrolyzed May 9–Sept. 27, 1933
I	610 gal. (of commercial electrolyte)
II	90 gal.
III	52 l
IV	10.15 l
V	2.00 l
VI	420 cc
VII	82 cc

It is found that about 1 cc of water, 95 percent heavy, is obtained for every seven gallons of starting material. Assuming that the commercial electrolyte liquor contains one part in 3000 heavy hydrogen, it is easily calculated that approximately 10 percent of the heavy isotope of hydrogen present in the original starting material is obtained in the heavy water. Most of the loss occurs in the first three electrolyses where no attempt is made to recover the heavy hydrogen in the gas evolved during electrolysis.