INEXPENSIVE EQUIPMENT FOR THE PREPARATION AND CONCENTRATION OF PURE D₂O OR OF DEUTERIUM-RICH WATER. DESCRIPTION OF CONSTRUCTION AND OPERATION OF THE FORMER OHIO STATE UNIVERSITY HEAVY WATER PLANT[1]

HERRICK L. JOHNSTON and W. HEINLEN HALL[2]

The Ohio State University

During the spring and summer of 1934 we operated, at the Ohio State University, a "heavy water" plant with a capacity for reducing about 100 gallons of water per week. In a period of sixteen weeks about 800 grams of D_2O were produced, in pure or concentrated form, from about 1800 gallons of commercial electrolyte taken from the electrolytic hydrogen cells of the Capital City Products Co. of Columbus.[3]

Although this was one of the largest, and most economical, of the early plants for producing D_2O we have never, heretofore, described it in any detail.[4] A number of features, and observations, warrant some description, for the benefit that they may be to those who have occasion to prepare or concentrate heavy water for research, demonstration or advanced student laboratory use.

While our plant was similar, in the main, to others that have been described (1) it possessed especial simplicity and economy in construction.

General Plan of Operation

The plant was designed to operate in three main stages. The first stage reduced the initial electrolyte to about 1/32 of its initial volume and, in so doing, built up the atomic concentration of deuterium in the hydrogen of the electrolyte from its initial value of about 0.05 of 1% (2) which is about three times the deuterium concentration in normal water (3) to a value of about 0.6 of 1%. This stage was divided into five steps, in each of which the electrolyte was reduced to about half volume.

About 1000 water-coolled cells of an inexpensive type (types (a) and (b) of Figure 2) were used in this stage.

Between the first and second stages the concentration of alkali in the electrolyte was reduced, by neutralizing the bulk of the solution with CO_2. To accomplish this about 5% of the concentrated solution was set aside, to form the necessary concentration of NaOH for the next stage, and the remainder was neutralized by adding to it pieces of dry ice, in an open five gallon oil can from which the top had been cut away. The water was then distilled away from the bicarbonate solution, in a copper steam can, and added to the 5% of concentrate to form dilute electrolyte ready for the next stage.
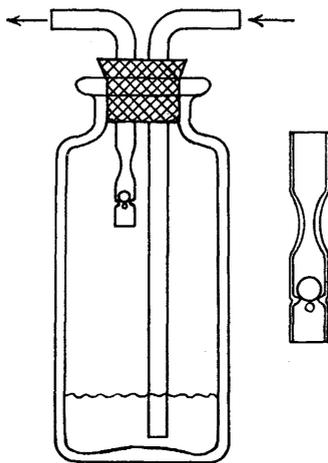

FIGURE 1

The use of solid, rather than gaseous, carbon dioxide appears to have been new with us and possesses the advantages of: (1) economy, (2) rapidity and convenience and (3) partial compensation for the heat evolved in the neutralization reaction by the heat absorbed in the sublimation. It should be noted that the CO_2 neutralization accomplishes normalization (or near normalization) of the oxygen isotope ratio (2), which is changed in the process of electrolysis (3). It may be that the effect of CO_2 from dry ice differs slightly in this respect from that customarily found for CO_2 from tanks, but this depends on the source of the original CO_2 and its method processing.

For the second stage eight tall, water jacketed cells (type f in Figure 2) were employed, in which the electrolyte could be safely reduced to about 1/5 volume in a single step. This was repeated for a second step, after which neutralization by dry ice was carried out in the manner described above. The deuterium concentration at this point in the process was between 6% and 10%.

The third stage was carried out in varying numbers of small cells (type e of Figure 2. We used a maximum of 24) which were constructed.

out of eight inch Pyrex test tubes. The number of steps and the volume
ratio reductions were determined by the desired purity, and the needs
of the moment. In the preparation of pure heavy water at least one
reduction in alkali concentration was necessary. This was usually
effected by distillation of the strong NaOH solution from a Pyrex
distilling flask, without neutralization.
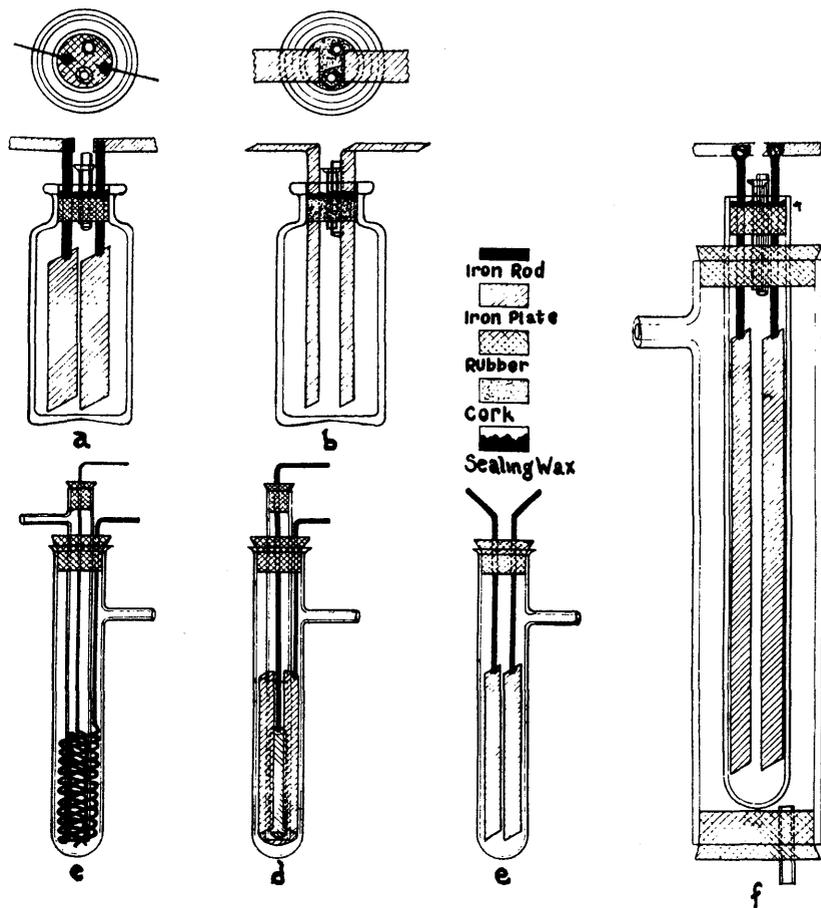
FIGURE 2

Closed cells were used in all steps of operation. In the first four
steps this was for the purpose of conducting away the large volume of
hydrogen (with oxygen) liberated in the electrolysis.[5] The cells were

[5]For small laboratory operations closed cells for these early steps can be
dispensed with if the cell troughs are placed under a hood or in a location where they
receive good ventilation. For this purpose open wide-mouthed bottles connected by
U shaped electrodes, and set in troughs of running water may be employed.

grouped in banks of 50 each connected through a gas manifold and each of the banks connected to a main steel pipe manifold which terminated in a vertical pipe that projected above the roof of the building. The steel pipe was grounded to carry off static charge produced by the flow of gas. Each of the 50 cell banks was protected against possible explosions in the main manifold or in other banks by a glass bead explosion trap (Figure 1), in series with a spray trap, at the point at which it made connection with the steel pipe manifold. These functioned properly in the few cases in which explosions occurred in 50 cell units, due to eating off of anodes (cf seq).

In the fourth step of electrolysis (Stage I) the average deuterium concentration of the hydrogen which escaped from the cells was about equal to that in the initial first step electrolyte. In the fifth step the escaping hydrogen had a deuterium enrichment about intermediate between that of the electrolyte at the beginning of steps 1 and 2 respectively. This hydrogen was recovered by recombination of the oxy-hydrogen mixture (cf infra) and returned to the first step. The electrolytic gases from all steps of the second and third stages were likewise recombined and returned to the appropriate position in the plant.

Inexpensive Forms of Closed Electrolytic Cells

Figure 2 illustrates several types of inexpensive closed cells which we built and operated. Any of these may be constructed out of materials usually on hand in a chemical storeroom.

Types (a) and (b) use 500 cc. wide mouthed glass bottles. Type (a) is made by welding short flat electrodes to 3/16″ iron rods which project through two of the four holes drilled[6] in tight fitting rubber stoppers. The other two holes carry: (a), the gas delivery tube which may be of either glass or metal and (b), a glass or metal tube for filling and emptying the cells—(the latter by siphon). The second tube should be of such a size that it can be closed with a small cork. The wetted rubber stopper, with electrodes and tubes in place is forced to a position a little below the top of the bottle neck and covered with ceiling wax. Electrical connections are made either by drilling the projecting ends of the iron rods to take small bolts with which to bolt on narrow connecting strips of sheet copper,[7] or by using battery clips. In the type (b) cells the flat electrodes project through a tight-fitting cork which is cut into three sections by two parallel cuts. The sections of cork were soaked in hot paraffin and the assembled unit covered with sealing wax. U shaped electrodes, used in common by adjacent cells, serve also for connectors. This type of cell is satisfactory for about a month of use but eventually the alkali disintegrates the cork, which then has to be replaced. We

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[6] It is best to drill these with high speed wood drills lubricated with water. The rubber stopper should be inserted in a hole drilled in a board, during the drilling operation.

[7] In drilling the rods much time is saved if a small flat surface is first ground on one side of the rod, or a thin cut taken with a milling machine, to prevent the drill from slipping. The drill holes should be parallel to the surface of the electrodes so that connectors will not require bending.

originally used (b) type cells on the first stage, but subsequently replaced them all with (a) type cells.

Both (a) and (b) cells were set in troughs of running water. They operate best at 5 to 7 amperes, which requires a littel over 4 volts per cell with 0.5 N alkali and results in an approximate 10° temperature head between electrolyte and cooling water. It is not advisable to allow the electrolyte in these cells to drop much below 200 cc. volume as, otherwise, the cells may heat up excessively. We customarily began the first step of electrolysis with 400 cc. of electrolyte and, when this volume was reduced to 200 cc, doubled up the cell contents into one-half of the original cells in preparation for the second step. The same procedure was followed after the second, third and fourth steps.

The construction of type (f) cells is clear from the diagram. The cell compartment is made from Pyrex tubing about 35 mm. in diameter. This cell offers a large cooling surface and operates well at 15 to 20 amperes. The electrolyte can safely be reduced to 1/10 volume in a single step in these cells, if desired.

Type (e) cells were used in the steps of the third and final stage. The thick iron wires that carry the electrodes are forced through small drill holes in the solid rubber stopper. The stopper with the electrodes is removed from the cell when electrolyte is added or removed and wired tightly in place when the cell is in service. This cell is set in an open wide-mouthed bottle through which cooling water circulates. The cell will carry 5 to 6 amperes without difficulty.

The above-mentioned cells permitted the electrolytic oxygen and hydrogen to mix. When, for any reason, we desired to keep them separate, we used cells of type (c) or (d) (a narrow gas outlet for the inner glass tube in (d) similar to that shown in (c) was inadvertently left off the diagram). While (c) is very eaisly constructed the use of cylindrically bent sheet metal, as in (d), is to be preferred because of much lower resistance offered to the current.

Electrodes and Separation Efficiency

Except for four hundred type (b) cells with nickel electrodes, that were subsequently replaced, electrodes for all of the cells were made of No. 20 gauge, unsurfaced Armco iron. This possesses a distinct advantage over nickel and other practical metals for efficient isotope separation. With NaOH electrolyte we obtained, with Armco iron, an electrolytic separation factor[8] of a little more than 8, whose magnitude was practically independent of current density and of the deuterium concentration in the electrolyte. This is the true separation factor applicable to the dry gas. The *practical* separation factor is somewhat less than this (about 6 or 7) due to water vapor carried out with the electrolytic gases.

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[8] α is most simply defined as the instantaneous ratio of (H/D) in the gas to (H/D) in the water. Thus, if a 10% D_2O solution (H/D = 9) is being electrolyzed and the evolving hydrogen proves to be just 2% in D (H/D = 49) the separation factor is 5.55. For low concentrations of D this resolves into the ratio of % D in the H_2 to % D in the H_2O. Thus, in the above example, 10/2 = 5.0 is nearly the correct value for α.

This factor of 8 compares with one of only 5 for nickel and makes a considerable difference in the efficiency of separation. For example, we found that when we used iron electrodes the deuterium concentration went up by a factor of about 3 for each fourfold reduction in volume. In the sixteen fold volume reduction, during which we allowed the electrolytic gases to escape, the deuterium concentration went up by a factor of 9. With nickel as electrodes the deuterium concentration goes up by a factor of only about 4. Iron electrodes, therefore, more than double the yield of D_2O as against nickel for the plan of operation which we followed.

It is obviously not practical to recombine and reclaim the electrolytic gases from the first and second steps of electrolysis, with iron electrodes, since their deuterium concentration is below that of ordinary water. Recombination in the third step is likewise impractical since the deuterium concentration is only slightly in excess of normal water. Recombination in the fourth step is about the equivalent of a 5% increase in the amount of starting material. The rather considerable amount of gas that would needs be handled to effect this economy makes recovery at this step impractical also. 7/16 of the deuterium present in the starting material is thus lost before, the recovery by recombination and repeated electrolysis becomes practical. Allowance for rejection of gas in the re-electrolysis of the water recovered in stages where recombination is practical brings this theoretical loss to a full 50%. Our 800 gram D_2O production from 1400 gallons of a starting material that held a little more than 2 Kg of D_2O initially is thus a reasonably good yield, and is superior to the yields reported by other plants (1). We experienced small accidental losses in handling. There were evaporation losses during the CO_2 neutralizations, and some electrolyte was lost, early in the operation, by explosions that resulted from corroded-off electrodes.

Recombination of Electrolytic Gases

Recombination of the stoichiometric oxy-hydrogen mixtures was brought about by combustion in a flame formed at the tip of a Pyrex capillary (4). The flame was prevented from firing back through the capillary by the high velocity of gas flow under a small pressure head developed in the cells. The choice of diameter for the capillary was determined by the rate at which the gas was generated—i. e., by the number of cells delivering gas to the burners and by the current.

We obtained best performance with tips made by fusing a four or five millimeter length of Pyrex capillary to a two or three inch length of wider tubing. We have used tips constructed in this manner for three or four weeks of nearly continuous service without need of replacement. With tips of this description, and the proper choice of capillary diameter, we have obtained satisfactory results in the wide range of gas flow that lies between the delivery from a single cell operating on 6 amperes and that of 50 cells operating at 12 amperes. For the latter the flame was over a foot long.

The oxy-hydrogen flames were directed into water-cooled Pyrex tubes that served as condensers. Tubes were chosen of such diameter as to provide at least a quarter-inch clearance around the flame. With

very large flames cylinders of copper gauze were inserted in the condensers to protect the glass.

Explosion traps to protect the cells from "backfires" in the combustion train when the gas flow would be reduced were formed from 100 cc. Pyrex round-bottom flasks tubulated at the bottom and filled with fine river sand.[9] These traps proved 100% effective in hundreds of trials with various rates of gas flow.

The burners were allowed to operate over night, without attention, except for stage 3 electrolyses. Because of the value of the water at this stage the electrolyses were given personal attention.

Foaming

Not infrequently, foaming occurred during the first half hour of electrolysis in the first stage and in stages that followed neutralization. The nature of all the impurities responsible for this were not determined but it was found that cork in the electrolyte was a particularly bad foam producer.

The impurities responsible are adsorbed in the surface and carried over with the foam. Addition of a few lumps of calcium chloride to the salvaged spray, followed by distillation, proved effective in correcting this condition. Addition of a small amount of permanganate as well as $CaCl_2$ and distillation nearly to dryness so that chlorine[10] is liberated, is helpful in extreme cases.

Corrosion of Electrodes

During nearly continuous operation of 1000 cells for a period of four months two or three dozen examples of severe corrosion were observed. The comparative infrequency of this trouble made the isolation of its causes, and hence its prevention, the more difficult. The peculiar thing is that an electrode which has been in service many weeks with little or no indication of corrosion may suddenly develop this condition and rust entirely off at the electrolyte surface within a period of six or eight hours. Other cells connected in series with the faulty cell and apparently subjected to the same operating conditions will escape corrosion altogether.

Corrosion is no more frequent with iron than with nickel electrodes. However, the advanced stages of corrosion develop more slowly with nickel on account of the more impervious character of the black oxide coating. For this reason iron offers a somewhat greater hazard in the operation of closed cells through danger of sparks between the electrolyte and an eaten off anode.

Overheated cells are more apt to develop this condition than cells which operate at lower temperatures. Electrolyte removed from a cell in which corrosion has started very frequently (but not invariably)

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[9] 60% of this sand passed through a sieve with 50 meshes to the inch. A sample of pure silica whose grains were of approximately 35 mesh size failed to stop explosions, in similar tests.

[10] All traces of chlorine or of chloride ion must be removed from the distillate before return to the cells. Otherwise corrosion results.

produces this condition in other cells to which it is added. The *distillate* from a contaminated batch of electrolyte is non-corrosive, however. Electrolyte prepared from tap water, or contaminated with tap water, increases the chance of corrosion. The presence of a trace of $CaCl_2$ which reached the distillate during distillation of a foamy batch of electrolyte produced immediate and excessive corrosion in every cell to which this distillate was added. From the latter two observations and the fact that the anode is the electrode which is attacked we conclude that chloride ion, even in traces, is the promoter of corrosion.

The only dependable protection against losses through this hazard lies in frequent inspection. For cells in which the visibility is limited current drop in the circuit containing a faulty cell and excessive heating in the cell itself are reliable criteria. The cell resistance is so increased by corrosion that even in a circuit with twenty-five cells in series corrosion in a single cell results in a 20% to 25% drop in current several hours in advance of actual rusting off.

The Deposit of Alkali Metal

In a few instances we permitted electrolysis to continue until a saturated solution of the alkali hydroxide was formed. This resulted, in one such instance, in an explosion in one of the cells a few minutes after electrolysis was stopped. The cause of the explosion was definitely traced to the presence of free alkali metal which had deposited, under a layer of the solid hydroxide, at the cathode surface. Free alkali metal deposits from aqueous solution, under these conditions, in such quantity that it can be scaled from the electrode and easily identified.

Acknowledgments

SUMMARY

The plan of operation of the former "heavy water" plant at The Ohio State University is outlined and several forms of inexpensive closed cells are described.

The advantage of iron electrodes over those of nickel, in plants for the concentration of deuterium, is pointed out and figures given as to the efficiency of deuterium production.

The construction of a durable burner tip for the combustion of the electrolytic gas in the advanced stages of electrolysis is described.

The advantages of solid carbon dioxide as an agent for neutralizing alkaline solutions, in deuterium recovery, are pointed out.

Experience in combatting foam and experiences with corrosion of iron and nickel electrodes and with the deposit of free sodium from concentrated NaOH are described.

LITERATURE CITED

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