Continuous Flow Methods of Concentrating Deuterium

Leigh C. Anderson, J. O. Halford, and John R. Bates

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Leigh C. Anderson, J. O. Halford and John R. Bates, *Department of Chemistry, University of Michigan*
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Experimental arrangements for the concentration of deuterium by electrolysis in a continuous flow system are described. These are found to be as efficient as straight electrolysis in single cells and involve considerably less manual labor. An arrangement for the recovery of off hydrogen of high deuterium content which is practically free from danger of explosion is also given.

SINCE Washburn and Urey discovered that the deuterium content[1] of an aqueous solution could be increased by electrolysis, due to the preferential liberation of protium at the cathode, several investigators have described apparatus for carrying out this concentration. The first stages which involve relatively large volumes of solution are the most cumbersome. Two types of apparatus have been developed in this laboratory which allow the concentration to be performed in a continuous and practically automatic manner. Neither type requires a low voltage source of direct current capable of delivering hundreds of amperes, a source which is not readily available in many laboratories, and which is required when one employs the apparatus described by Lewis and MacDonald[2] or that of Harkins and Doede.[3] The procedure used by Taylor, Eyring and Frost,[4] eliminates the need of such an electrical supply but introduces a considerable amount of labor in handling a large number of cells and, furthermore, the cooling tanks quickly become objectionable when the water supply is extremely hard.

The first of the two types of unit which we have developed is composed of cells illustrated in Fig. 1. The cathode B is an 18-inch length of ordinary 1-inch water pipe designated in the trade as wrought iron, but in reality a low carbon steel. (So-called pure wrought iron pipe was substituted with little or no benefit.) This is surrounded by a glass condenser jacket A for cooling. The bottom of the pipe is fitted with a rubber stopper through which pass two 7 mm glass tubes. The centered tube C acts both as a support for the anode and as the inlet tube for the alkaline electrolyte; the other tube is the outlet. The anode D is formed from two 3-foot lengths of 18 gauge nickel wire which extend through the rubber stopper and are wound around the center tube and two strips of nickel ribbon. These latter

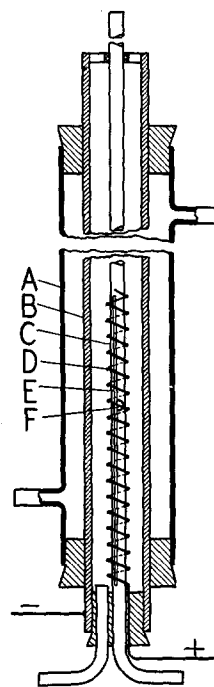[1] Washburn and Urey, Proc. Nat. Acad. Sci. **18**, 496 (1932).
[2] Lewis and MacDonald, J. Chem. Phys. **1**, 341 (1933).
[3] Harkins and Doede, J. Am. Chem. Soc. **55**, 4330 (1933).
[4] Taylor, Eyring and Frost, J. Chem. Phys. **1**, 823 (1933).

Fig. 1.

serve to equalize the potential along the whole electrode.

For convenience in handling, a bank of ten such cells is mounted in series as regards flow of electricity, alkali and cooling water. The alkali flowing in the center tube and emerging from the orifice F is partially electrolyzed in each cell before flowing out and into the next cell. Because of the height of the inlet orifice and the stirring due to the gas evolution, no channeling between inlet and outlet may be expected. The rates of inflow and outflow through the entire bank are adjusted to the rate of electrical input so that any desired concentration of alkali may be reached at the end of the bank. The inflow is regulated by means of an 8-liter Mariotte bottle, which keeps a constant head at the inlet and into which alkali is fed at a rate equal to or less than that of consumption. This removes any possibility of overflow in the cells due to small alterations in current, etc.

The factor limiting the amount of current which may be put through such a bank of cells is the back pressure which is built up in the alkali line and which may amount to a head of several inches. This is probably due to mechanical difficulties involved in the evolution of the electrolytic gas. In practice, we find that a current of about twenty amperes gives a very satisfactory performance. This current is obtained when a potential of 220 volts is applied to three banks of twenty cells each, with a two percent alkali solution being fed to, and a sixteen percent alkali solution being withdrawn from each of the banks.

The second type of unit that we have developed consists of a box four inches wide, six inches deep and twenty-five inches long made of hard rubber and with the sides slotted on the inside at intervals of one-half inch to hold nickel sheet electrodes. Cooling is accomplished internally by means of five 10 mm glass tubes running lengthwise through the box and through holes in each electrode. The electrodes are made up in two identical halves to permit easy assembly of the cooling tubes. A dilute alkali solution is fed into one end continuously and flows from one cell to the next through a narrow space left around each of the cooling tubes. A concentration gradient is built up along the box and the concentrated material is removed from the other end at any desired alkali concentration (and, of course, increased deuterium content) below that of saturation of the electrolyte. Such a unit will carry five amperes without overheating, and this current is obtained with a potential of 110 volts across the box.

The theoretical efficiency of any continuous method of electrolytic fractionation of the hydrogen isotopes is bound to be lower than that of straight electrolytic concentration in a single cell. This is due to the fact that a more dilute solution of the heavier isotope is being fed constantly to a more concentrated mixture. In the limiting case, it is obvious that when the entering liquid has a deuterium content equal to the gases evolved no further concentration occurs. However, in the "pipe" method described this latter condition is by no means approached and our actual efficiency seems to be as good or better than electrolysis in open single cells, due to less loss from spraying of the electrolyte and less evaporation because of more efficient cooling. Best results are obtained, of course, when the volume ratio of input to output in a given unit is small, but even with this ratio at seven for a bank of twenty cells, we find the concentration ratio of deuterium is about five, an extremely satisfactory factor.

Of the two types of unit the first is undoubtedly to be preferred. The chief difficulty encountered with it is the regulation of the outflow. Since, with a current of 20 amperes the outflow from a bank of twenty cells is only 700 cc of sixteen percent alkali a day, the regulation must be made of a rather small rate, about a drop every ten seconds, and this must be kept constant, as the concentration ratio is dependent almost solely upon it. The chief advantage of the box unit is that the regulation of outflow need not be accurate since this can be adjusted by removal of larger amounts at a single time when inspection shows this to be necessary. Its disadvantage lies in lack of adequate cooling and consequent limitation of the current to about five or six amperes. The pipe unit has still another consideration to recommend it. It may be used at higher concentrations of deuterium when it is necessary to recover the gases produced. This may be effected by recombining the mixed
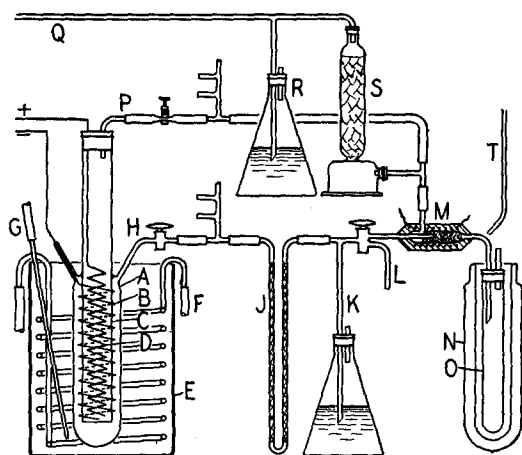
FIG. 2.

hydrogen and oxygen as described by Taylor, Eyring and Frost,[4] and by Eyring and Topley.[5] However, we have not used their procedure in this laboratory, preferring the increased safety factor introduced by separating the hydrogen and oxygen and burning the hydrogen from a quartz jet in the presence of air or oxygen. At still higher concentrations where there is insufficient gas evolution to make a flame, we have used the method illustrated in Fig. 2, using platinized asbestos as a catalyst for burning the hydrogen.

The cathode B consists of iron wire wound around the glass tube C which is sealed inside the

cell A; the anode D is either a spiral of nickel wire or a platinum gauze cylinder which is inserted inside the glass partition. When wire spirals are used, the top and bottom wires are joined together in order that the potential may be more uniform throughout the electrode. J, K and L are, respectively, a spray trap, a safety flask and an outlet for flushing out the hydrogen line at the start of operation. The oxygen passes through the tube marked P. The hydrogen and oxygen combine in the catalytic chamber M at the end of the capillary platinum tube from which the hydrogen emerges. A stream of air is directed through T to cool the vapors partially. The receiver O is kept in an ice-filled vacuum bottle N. A small excess of oxygen is introduced (through Q, R and S) to insure complete combustion of the hydrogen. Although the electrolytic cells necessary for the separation of the gases introduce more electrical resistance than those in which the gases come off together, this difficulty has not been at all troublesome and a current of eight or nine amperes gives no undue heating of the cells. Several of these cells are mounted in series electrically, the hydrogen as well as the oxygen from all cells being fed to the same combiner, whether flame or catalytic. With the smaller quantities of material that are available at the higher concentrations of deuterium, we have not adopted a flow method although this process could be introduced here also.

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[5] Eyring and Topley, J. Am. Chem. Soc. **55**, 5058 (1933).