# A Plant for the Production of Heavy Water

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(Received February 14, 1935)

A description is given of a plant for the production of deuterium oxide by the electrolytic method which operates with a higher efficiency than has been previously reported for this method. The fractionation factor, uncorrected for evaporation, averages 8.6. Steel cells, which also serve as the cathodes, are used and the entire construction is explosion-proof.

SEVERAL types of laboratory equipment for the production of deuterium oxide by the electrolytic method have been described.[1] To these published accounts we wish to add the following brief description of a plant recently constructed in this laboratory which may be of interest because we are able to report a higher efficiency than is usually realized in the electrolytic separation of hydrogen and deuterium.

This plant consists of 37 water-cooled steel cells of 3 l capacity each, operated in series at 100 amperes, and arranged in three stages, and one smaller cell of 800 cc capacity which constitutes the fourth and final stage. The gases generated in each stage are collected by iron header pipes and



FIG. 1. Cross-sectional diagram of cell.

[1] G. N. Lewis and R. T. MacDonald, J. Chem. Phys. 1, 341 (1933); H. S. Taylor and H. Eyring, Proc. Am. Phil. Soc. 72, 255 (1933); H. S. Taylor, H. Eyring and A. A. Frost, J. Chem. Phys. 1, 823 (1933); W. D. Harkins and C. Doede, J. Am. Chem. Soc. 55, 4330 (1933); L. C. Anderson, J. O. Halford and J. R. Bates, J. Chem. Phys. 2, 342 (1934.)

are conducted successively through spray traps and explosion traps into air-cooled burners in which recombination takes place. The entire construction is sufficiently rugged to withstand explosions without damage.

It was intended that this plant should operate on water already enriched to the extent of 0.5 percent deuterium oxide and with this as the starting material four stages suffice to increase the concentration to 99.9 percent, the daily production then being approximately 90 grams. However, the inadequate supply of 0.5 percent water frequently necessitates operation on water of considerably lower concentration and the average production falls far short of the figure mentioned.

## DESIGN OF THE CELLS*

The cells are constructed of Shelby seamless steel tubing, 4″ in diameter and 18″ in length. A bottom plate and a central tie-rod which secures the lid are attached by arc welding. The lid carries a gas outlet tube and a tube through which the cell is filled and drained (these tubes are not shown in the accompanying sketch). The cell itself, insulated from the cooling water by paint, serves as the cathode. The anode consists of a perforated cylinder of sheet nickel, $3\frac{1}{2}″$ in diameter and 5″ high, attached by nickel rivets to the flattened end of a $\frac{1}{2}″$ nickel rod which passes through an inverted rubber stopper in the lid of the cell. The nickel cylinder is insulated from the cell wall by small pieces of hard rubber. The small cell which constitutes the fourth stage is constructed on the same design but the material is $2\frac{1}{2}″$ iron pipe.

The current density at the cathode varies with the level of the liquid in the cell. At the anode

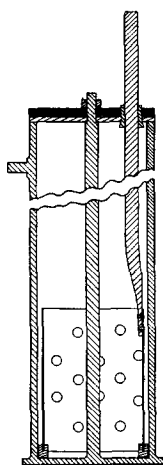* The design of the cells was worked out by Dr. D. Rittenberg and Dr. S. H. Manian.

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the current density is approximately 0.28 ampere/cm$^2$ when this electrode is completely immersed, and it increases to about twice this value at the end of a run when only half immersed.

Before use the cells were cleaned by electrolysis of a hot solution containing 30 grams each of borax and trisodium phosphate per liter. This treatment together with the care taken to ensure the purity of the solutions used subsequently in the cells appears to be effective in preventing foaming.

## CONSTRUCTION OF THE BURNERS

The gases generated in the cells of the first stage pass into iron header pipes which are connected to the cells by short sections of heavy wall rubber tubing. There are three separate header assemblies for this stage, each collecting the gas from ten cells. From these the gases pass through spray traps packed with steel wool, then through explosion traps filled with 60-mesh sand, and finally through jets at which recombination takes place. The first stage burner consists of a fan-cooled 3″ iron pipe mounted at a slight incline. A cap fitting over the upper end carries the three converging jets which project into the pipe. At the lower end a nipple conducts the steam into vertical water-cooled condensers. The jets consist of $\frac{1}{4}$″ iron plugs through which holes of 0.090″ diameter have been drilled and which are threaded into the $\frac{3}{8}$″ iron pipes projecting through the burner cap. The explosion traps are mounted rigidly on the burner cap and are connected to the spray traps by rubber tubing thus permitting the cap to be withdrawn for lighting. The entire assembly, with the exceptions mentioned, is constructed of standard plumbing fittings.

The second stage burner is similar in size and construction and the principle of multiple converging jets is retained by having two jets, each fed by three cells, with separate headers and traps. The orifice in these jets is 0.050″ in diameter.

The third and fourth stage burners are smaller in size, each having a single gas jet. The orifices are 0.028″ and 0.015″, respectively, the sizes being somewhat critical with the smaller gas flow in these burners.

## ELECTRICAL EQUIPMENT

The cells are connected in series and are operated from a 110-volt line, the current being controlled by a rheostat of 0.4 ohm resistance. An underload circuit breaker prevents the resumption of the electrolysis should an interruption in the current sufficient to extinguish the burners occur. The fourth stage cell takes approximately one-half of the current used in the other cells (100 amperes), the remaining half being passed through a shunt. This stage and the third stage are provided with short-circuiting switches allowing these stages to be switched in or out as desired. The fourth stage is operated only when attended, but the remainder of the plant is operated overnight regularly without attention.

## OPERATION OF THE PLANT

The thirty cells of the first stage are charged with 3 l each of a 3 percent sodium hydroxide solution made up of the water to be concentrated. The sodium hydroxide is a C.P. Electrolytic grade, and the water is distilled once or twice before use. When it appears desirable a distillation from alkaline permanganate is carried out. The charges are measured out and placed in the cells with the aid of a portable apparatus built for this purpose.

When the electrolysis has proceeded for approximately 72 hours, this charge, totalling 90 liters, will have been reduced to about one-sixth of its original volume. It is then removed, a part of it distilled and then transferred to the second stage. Similarly the residue from the second stage is transferred to the third, and so on. A charge of 90 l of water containing 0.5 percent deuterium oxide will yield 15 l of approximately 2.5 percent. In the second stage the concentration will have increased to about 12 percent, in the third to about 60 percent and in the fourth to better than 99 percent.

The disposal of the recombined water depends upon its concentration. Normally the water used in the first stage contains from 0.3 percent to 0.5 percent deuterium oxide and except for the first fraction the recombined water contains an appreciable amount of deuterium. It is our practice to discard recombined water containing less than 0.05 percent deuterium, and to re-

work the remainder. Recombined water from the later stages is returned to the previous stage.

### FRACTIONATION FACTORS

Samples of recombined water are collected from each stage at the end of each run. These, as well as samples from the residues, are analyzed interferometrically[2] for their deuterium content providing data from which the fractionation factors may be calculated. Data for a number of typical runs are given in Table I, together with

TABLE I.

| Run | Residue % $D_2O$ | Recom- bined % $D_2O$ | Fraction- ation factor |
|---|---|---|---|
| | First stage | | |
| 1 | 2.27 | 0.30 | 7.7 |
| 2 | 2.66 | 0.32 | 8.5 |
| 3 | 1.19 | 0.15 | 8.0 |
| 4 | 2.53 | 0.25 | 10.3 |
| 9 | 2.67 | 0.25 | 10.9 |
| 11 | 1.83 | 0.22 | 8.5 |
| 12 | 1.91 | 0.26 | 7.5 |
| | Second stage | | |
| 1 | 2.23 | 0.25 | 8.5 |
| 2 | 2.91 | 0.31 | 9.1 |
| 3 | 13.3 | 2.10 | 7.1 |
| 4 | 9.41 | 1.29 | 7.8 |
| 5 | 4.49 | 0.56 | 8.1 |
| 7 | 11.6 | 1.52 | 8.4 |
| 9 | 7.53 | 0.85 | 9.3 |
| 12 | 13.5 | 1.79 | 8.5 |
| 13 | 6.59 | 0.82 | 8.4 |
| | Third stage | | |
| 1 | 50.3 | 10.3 | 8.8 |
| 5 | 35.1 | 5.72 | 8.9 |
| 6 | 62.6 | 15.6 | 9.0 |
| 9 | 67.8 | 16.8 | 10.4 |

the fractionation factors. These are the instantaneous factors, and in a number of cases they have been checked by calculations of the overall factors, that is, the factor which must be substituted in the integrated Rayleigh distillation formula to satisfy this relation between the initial and final volumes and concentrations. In most cases, however, we have not sufficient data to calculate the overall factor since the runs are

[2] R. H. Crist, G. M. Murphy and H. C. Urey, J. Chem. Phys. 2, 112 (1934).

rarely straight runs. It happens almost always that the electrolysis is stopped one or more times during the course of a run to add recombined or other water of appropriate concentration. Thus a first stage run might be started with a charge of 0.15 percent water, to which would later be added 0.30 percent water, and perhaps later 0.50 percent water.

The average value of the fractionation factors listed in Table I is 8.6. This is appreciably higher than any previously reported.[1, 3] These values have not been corrected for evaporation. Since the temperature in the cells averages about 25°C such a correction would increase the average fractionation factor to approximately 12. Presumably this high factor could be realized by cooling the gases leaving the cells so as to collect water carried over as water vapor, but we have not yet attempted to do this.

### PURIFICATION OF HEAVY WATER

The residue from the fourth stage, after having been neutralized and distilled, is not sufficiently pure for many experimental purposes. It contains traces of organic impurities not readily removable by distillation or by refluxing with oxidizing agents, and to effect the purification we make use of an additional stage of electrolysis. In this apparatus the deuterium and oxygen generated by electrolysis in a small iron cell are mixed with an excess of pure oxygen and burned at a silica jet inserted in a Pyrex condenser. The apparatus is flushed with oxygen before electrolysis is begun and with this precaution the oxides of nitrogen, customarily present in recombined water, are excluded.

[3] R. P. Bell and J. H. Wolfenden, Nature 133, 25 (1934); B. Topley and H. Eyring, Nature 133, 292 (1934), J. Am. Chem. Soc. 55, 5058 (1933), J. Chem. Phys. 2, 217 (1934); P. Harteck, Proc. Phys. Soc. 46, 277 (1934).