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FRACTIONATION OF THE ISOTOPES OF HYDROGEN AND OF OXYGEN IN A COMMERCIAL ELECTROLYZER¹

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ABSTRACT

The electrolytic fractionation of the isotopes of hydrogen and of oxygen under the conditions prevailing in a commercial hydrogen-oxygen electrolyzer have been followed by means of measurements of density. Upon electrolysis of ordinary water, the change in its density at the beginning is caused as much by the fractionation of oxygen as of hydrogen. Curves showing the course of the fractionation of the separate isotopes are given. After an amount of water approximately equal to 10 times the volume of a commercial alkaline cell has been electrolyzed, a steady state is closely approached in which no further isotopic fractionation occurs. In this state the gases evolved have the isotopic composition existing in the water added to the cell, and the residual water left in the cell is 60 ppm heavier than ordinary water. Of this 60 ppm, 28 are contributed by the heavy isotope of hydrogen, indicating an electrolytic fractionation factor of 2.4 under the conditions described.

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I. INTRODUCTION

Since the announcement of the electrolytic method for the concentration of deuterium,² electrolysis has become the universal method of separating deuterium and of making "heavy water". Notwithstanding the large number of papers dealing with heavy water which have already appeared, much elementary work still remains to be done for a better understanding of the electrolytic method. In the original communication,³ it was stated that some concentration of the O¹⁸ isotope of oxygen also appeared possible, and in the first paper of this series⁴ it was shown that the concentration of O¹⁸ actually occurred. In the present investigation, a study has been made of the simultaneous electrolytic fractionation of the isotopes of hydrogen and of oxygen under the conditions which prevail in a commercial cell from the time the cell is filled with fresh electrolyte until equilibrium has been reached. By equilibrium is meant the steady state which is attained after the cell has been in continuous operation with the continuous addition of ordinary water for such a length of time that the hydrogen and oxygen evolved have the same

¹ This investigation was completed and the manuscript prepared by the junior authors after the death of Dr. Edward W. Washburn on February 6, 1934.

² Edward W. Washburn and H. C. Urey, Proc. Nat. Acad. Sci. 18,496(1932).

³ See footnote 2.

⁴ E. W. Washburn, E. R. Smith, and M. Frandsen, BS J. Research 11,453(1933); RP601.

isotopic composition as they have in normal water, while the water in the cell has attained an unchanging isotopic composition richer in the heavier isotopes of hydrogen and oxygen. That such an equilibrium condition must eventually occur during the operation of a commercial hydrogen-oxygen cell is obvious⁵ from the following considerations. Since the residual water in the cell is always heavier than the water formed by recombining the evolved gases, and at the beginning grows progressively denser as the electrolysis proceeds, a point will be reached where the water from the recombined gases has the same density as ordinary water. At this point ordinary water is being added to and electrolyzed from the cell at the same rate and consequently no further change occurs in the composition of the residual water. It will be seen later (fig. 2) that the evolved hydrogen attains the isotopic composition of normal hydrogen before the evolved oxygen becomes normal in composition. It is therefore of interest and importance to determine the extent of electrolysis required to produce this steady state, and the separate parts played by the hydrogen and oxygen isotopes during its attainment.

II. DESCRIPTION OF THE ELECTROLYTIC CELL

The cell used was a small electrolyzer of the filter-press type, having 56 nickel-plated cast-iron cells in series, and a capacity of 16 liters. The cell plates, which acted as anodes on one side and as cathodes on the other, were separated by asbestos cloth diaphragms, the edges of which were imbedded in rubber to form gaskets.

The electrolyte was an 18-percent solution of sodium hydroxide (5 molal), which was found in this electrolyzer to pass 12 to 15 amperes at 115 volts with a small regulating resistance in series.

Asbestos paper was fastened loosely around the outside of the cell to reduce the effect of drafts upon the temperature of the cell, its resistance, and consequently on the current and the rate of evolution of the gases. Under operating conditions the temperature of the electrolyte was about 60° C.

The cell, together with the regulating and safety devices, and the burner for recombining the gases are shown diagrammatically in figure 1. The path of the oxygen is not shown, but it follows a course similar to that indicated for the hydrogen. When operating at a normal rate, about 3 liters of hydrogen was evolved per minute. A mixture of gas and electrolyte was disgorgeed into the surge glasses where the continual rising and falling of the level of the liquid produced a pressure fluctuation in the delivery pipe which often amounted to ± 2 inches of water. The flow of gas from the electrolyzer was thus unsteady.

The gases passed through metal pipes surrounded by ice water to reflux as much as possible of the heavier water carried as vapor and liquid by the stream of gas. Thence the gases passed into a flask containing concentrated sulphuric acid, where they were deflected downward on the surface of the acid, depositing more water and a large part of the fog of finely divided sodium hydroxide particles.

⁵H. S. Taylor and H. Eyring, *Proc. Am. Phil. Soc.* 72,261(1933).

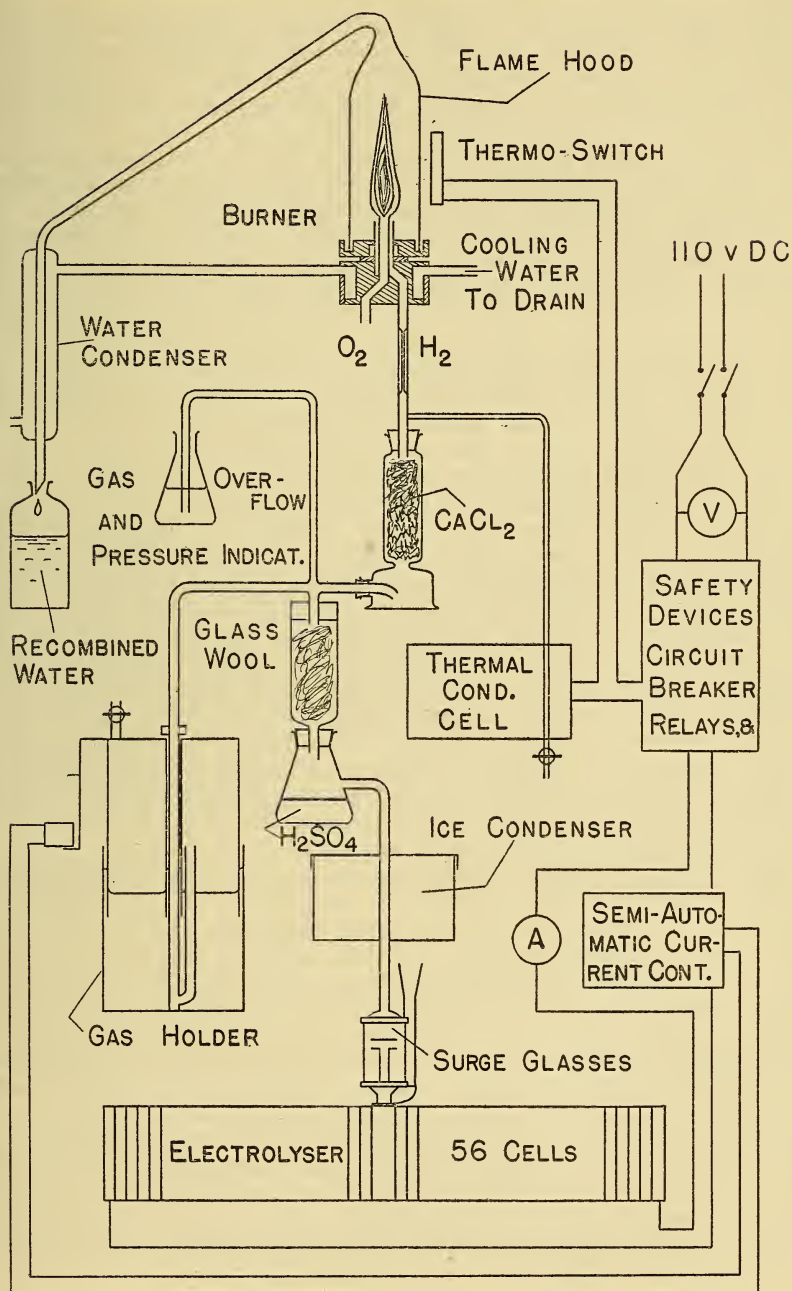


FIGURE 1.—Electrolytic cell with regulating devices.

The tower of fine glass wool which follows removed still more of the fog.⁶

The main streams of the gases then passed through towers of 8-mesh calcium chloride, to remove all but a negligible amount of heavier water vapor, through capillary tubes to control the rate of flow⁷ and thence to the burner where the oxygen was burned in a surrounding atmosphere of hydrogen.

The water vapor formed by the recombination of the gases passed from the glass flame-hood and through the water-cooled condenser from which it dripped at room temperature into liter bottles.

The burner was made of brass and the lower part was cooled by the water from the condenser, as shown, in order to prevent overheating of the rubber connections. The upper part was separated from the lower by a "transite" disk, and made thermal contact with the burner tube over only a small area. This area was so adjusted that the upper part of the burner, and the glass flame-hood, whose rim rested in a groove filled with dibutyl phthalate, would always be well above 100° C and so prevent the condensation and consequent loss at this point of any of the water formed by combustion.

In order to prevent the fluctuating flow of gases from the electrolyzer from extinguishing the flame, and to insure that the gases delivered to the burner would at all times be in constant relative proportions, water-sealed gas holders of about 20 liters capacity were attached to the line between the glass wool and calcium chloride towers. In operation, these holders were kept near their full position by adjusting the overflow bubblers which were attached to the gas line at the same point as the holders. The purpose of the overflow bubblers was to take care of momentarily excessive pressures, and the holders maintained a nearly constant flow to the burner even though the flow in the line from the electrolyzer was reversed momentarily. Indeed, the 20 liters stored in the holders was sufficient to supply the burner at normal rate for 5 minutes, or for a much longer time at reduced rate, and thus would keep the flame lighted during short interruptions of the power supply.

The hydrogen holder also served to actuate the semiautomatic current control. During prolonged periods of voltage depression caused by abnormal demands for power elsewhere, the rate of evolution of the gases was decreased and the holder, supplying the burner at a constant rate, consequently became partly emptied. When the holder bell fell to the half-full position, a contact was made which, by means of a relay, cut out a resistance in series with the electrolyzer. The resulting increase in the current could be adjusted as desired and was usually about 2 amperes. This was ordinarily sufficient to refill the holder, which on reaching its full position broke the contact, cutting in the resistance and restoring the system to its former condition of operation. In case the additional 2 amperes proved insufficient, and the holder bell fell as much as an inch farther, another contact sounded an alarm summoning an attendant to determine the cause of the reduced evolution of gas and make proper manual adjustments.

⁶ It was found that the fog could be removed almost completely by the use of electric precipitation, but this method was abandoned because the accompanying ozone caused troublesome leaks in rubber tubing used for connections.

⁷ Cocks on the burner accumulated particles of the sodium hydroxide fog and repeatedly reduced the flow nearly to extinction of the flame, particularly when the burner base was not cooled. Capillaries provide equal resistance with a much larger aperture.

A small quantity of both hydrogen and oxygen was taken from their respective lines at the outlet of the calcium chloride towers and passed through a thermal conductivity cell⁸ which served to detect any leakage of hydrogen into the oxygen, or vice versa, through the separators in the electrolyzer. The apparatus was so arranged that increasing contamination of either of the gases would interrupt the current through the electrolyzer and ring an alarm.

In addition, any one of several undesirable situations resulted in automatically opening the main circuit, for example, the extinction of the flame, the heat from which kept closed the contacts of a bimetallic thermostat. Insufficient heat caused the contacts to open, in turn opening the main circuit, which was equipped with a circuit breaker which had to be closed manually before the flow of current could be restored.

The level of the electrolyte was kept practically constant in the electrolyzer by adding 500-ml portions from time to time, and it was found that the ratio of volumes of the water collected to the water added to the electrolyzer during several 5-day runs was approximately 0.95. This indicates a total loss of only about 5 percent. Water vapor was lost to the sulphuric acid, calcium chloride, and at the mouth of the condenser. Gases were lost through the overflow bubblers, the thermal conductivity safety device and the condenser. The loss from the condenser could be followed visually by noting the behavior of a bit of fog which usually pulsed near the mid portion of the condenser tube when the loss was small. Some unburned gases always escaped, because when burning one gas in an atmosphere of the other, an excess of the surrounding gas is required if the first is to be completely burned. When the gases are supplied in equivalent volumes some of each escapes, and precautions should be taken against accidental ignition.

The electrolyzer was operated 24 hours a day, 5 days a week, and was capable of functioning unattended for periods as long as 12 hours. Normally, a momentary inspection was made at half-hour intervals. Thanks are due to A. R. Glasgow, C. N. Miller, and P. Schoonover, who performed this service during their night-shift work on petroleum research.

III. THE MEASUREMENTS

The water formed by recombining the gases was collected continuously in a series of 1-liter fractions at the rate of about 1 liter every 6 hours. The process was carried out at practically constant volume by adding ordinary water to the cell in 500-ml portions in pace with the volume consumed. At definite intervals the procedure was varied by collecting the liter fractions in three equal portions: (a) Oxygen from the cell combined with commercial electrolytic hydrogen, (b) hydrogen from the cell combined with commercial oxygen made from liquid air, (c) hydrogen and oxygen from the cell combined directly as usual. The differences between the densities of these samples and that of purified normal water were then measured at 25° C by the use of the differential pycnometer described in a previous paper.⁹

The commercial electrolytic hydrogen, obtained from the Southern Oxygen Co., whose cells have been in operation for several years, was

⁸ See P. E. Palmer and E. R. Weaver, *Tech. Pap.* BS 18, 35(1924-1925)T 249.

⁹ Edward W. Washburn and Edgar R. Smith, *BS J. Research* 12, 305(1934);RP666

shown to be of ordinary isotopic composition by combining it with atmospheric oxygen and comparing the density of the water thus formed with that of ordinary water. The density difference was less than 1 ppm.

The commercial oxygen was assumed at the start to be of ordinary isotopic composition. However, when the series of data was examined it was apparent that the density of the water formed by combining the gases directly from the cell differed from that of normal water by an amount greater than the sum of the differences between normal water and the samples obtained by burning the gases separately with commercial hydrogen and oxygen. That this uniform difference, amounting on the average to 2 or 3 ppm, was not due to water vapor in the commercial gases was shown by collecting and weighing water vapor from the cylinders during a combustion. The weight of water from this source amounted to only 0.05 g for each 100 ml of water formed by combustion, a quantity too small to have any detectable effect on the densities. The source of the discrepancy was finally found to lie in the assumption that commercial oxygen made by the fractionation of liquefied air has the same isotopic composition as atmospheric oxygen.¹⁰ The error of this assumption was demonstrated in the following way: Hydrogen from the same cylinder was burned first with oxygen from the cylinder used in this investigation and then with atmospheric oxygen drawn from outside the building, to form two 400-ml samples of water. Each of these samples was thus composed of identical hydrogen combined in one case with the commercial oxygen from the fractionation of liquefied air and in the other with oxygen from the atmosphere. After purification, the densities of the two samples were compared. The sample prepared from the commercial oxygen was found heavier by 1.4 and 2.4 ppm in successive measurements. Both samples were then repurified and the difference found to be 2.8 ppm. The average of the three values was 2.2 ± 0.5 ppm. The explanation of this difference is that during the fractionation of liquid air to eliminate nitrogen, the difference in mass and vapor pressure of the oxygen isotopes causes a slight isotopic separation so that the residual oxygen compressed in the cylinders is slightly heavier than ordinary atmospheric oxygen. Neglecting the O^{17} isotope, this increase amounts to about 0.002 percent increase in the O^{18} content of the commercial oxygen and doubtless depends somewhat on the efficiency of the fractionating column. The Southern Oxygen Co., from whom the commercial oxygen was also obtained, mix their electrolytic oxygen with the liquid air oxygen but the electrolytic oxygen, which has practically the same isotopic composition as the oxygen of the normal water supplied to the electrolyzers, never amounts to more than 5 percent of the total. A correction of 2.2 ppm was applied to the density measurements on the samples obtained by burning the hydrogen from the cell with the commercial oxygen, in order to obtain the differences in density caused by changes in the isotopic composition of the hydrogen alone. Before these measurements of the slight difference in isotopic composition of atmospheric oxygen and oxygen made from liquefied air were completed, an account of measurements was reported¹¹ which showed that when liquefied air is fractionated

¹⁰ E. R. Smith, *J. Chem. Phys.* 2,298(1934).

¹¹ R. Klar and A. Krauss, *Naturwissenschaften* 22,119(1934).

the oxygen escaping with the nitrogen at the top of a column is richer in the lighter isotopes of oxygen (and the residue of oxygen left in the still is richer in the O¹⁸ isotope) than atmospheric oxygen.

The increase in density of the water in the cell was also followed as the electrolysis progressed. This was done by stopping the electrolysis at a given point and withdrawing a sample of electrolyte for purification and measurement, after which the water was replaced in the cell and the electrolysis was continued.

When 150 liters had been collected by recombining the gases, it was found that equilibrium had been practically attained, and the hydrogen and oxygen from the cell were very close to their normal isotopic compositions. At this point the electrolysis was stopped. The increase in density of the water in the cell was then determined and its hydrogen content was normalized isotopically by successive treatments with dry ammonia gas¹² until no further decrease in density occurred. By this means an approximate measure of the isotopic composition of the water at equilibrium was obtained.

IV. FRACTIONATION OF THE ISOTOPES

The density of the water formed by recombining the gases at the beginning of the electrolysis, starting with normal water in the cell, was found to be 20.5 ppm less than normal. By burning the gases separately with normal hydrogen and with oxygen corrected to normal 13.2 ppm of this decrease was found to be contributed by the fractionation of the oxygen isotopes and 7.8 ppm by the hydrogen isotopes. At the tenth liter the respective decreases in density were 17.1, 11.0, and 6.2 ppm. The series of measurements was continued until a steady state, consisting in equilibrium water in the cell evolving isotopically normal gases, ensued. The data are given in table 1. The values given in the fourth column for the differences in density between the water formed by burning the hydrogen from the electrolyzer with oxygen corrected to normal were obtained by subtracting 2.2 ppm from the measured values, e.g., the first measured value was -5.6 ppm with the commercial oxygen which yielded water heavier than normal by 2.2 ppm and the corrected value is therefore -7.8 ppm.

TABLE 1.—Changes in density (in ppm)

Number of liters collected	Recombined gases	Cell O with normal H	Cell H with normal O	Residual H ₂ O in cell	Number of liters collected	Recombined gases	Cell O with normal H	Cell H with normal O	Residual H ₂ O in cell
1	-20.5	-13.2	-7.8	-----	73	-----	-----	-----	+43.0
10	-17.1	-11.0	-6.2	-----	75	-7.3	-5.0	-2.0	-----
20	-14.8	-10.5	-5.6	-----	105	-5.0	-3.0	-1.1	-----
30	-14.1	-8.0	-5.5	+23.9	124	-3.1	-2.0	+1.1	-----
50	-10.8	-6.3	-3.6	-----	150	-1.5	-1.1	+2.2	+57.8

The data of table 1 are shown graphically in figure 2, in which the differences in density between the samples and normal water, expressed in parts per million, are plotted as ordinates and the volumes of water electrolyzed as abscissas. The volumes plotted as abscissas, however, are expressed in terms of the total cell volume, in order to

¹² G. N. Lewis, J. Am. Chem. Soc. 55,3502(1933).

make the curves of general applicability to any commercial nickel-plated iron electrolyzer filled with alkaline electrolyte. Thus abscissa 1 means that in this case 16 liters (the total cell volume) has been electrolyzed while slightly more than 16 liters of normal water has been added to the cell to keep it full. Abscissa 10 means that a volume of water equal to 10 times the capacity of the cell has been electrolyzed, etc. Curve A shows the progressive increase in density of the unelectrolyzed water remaining in the cell, toward a limiting value of about 60 ppm. Curve B represents the portion of this

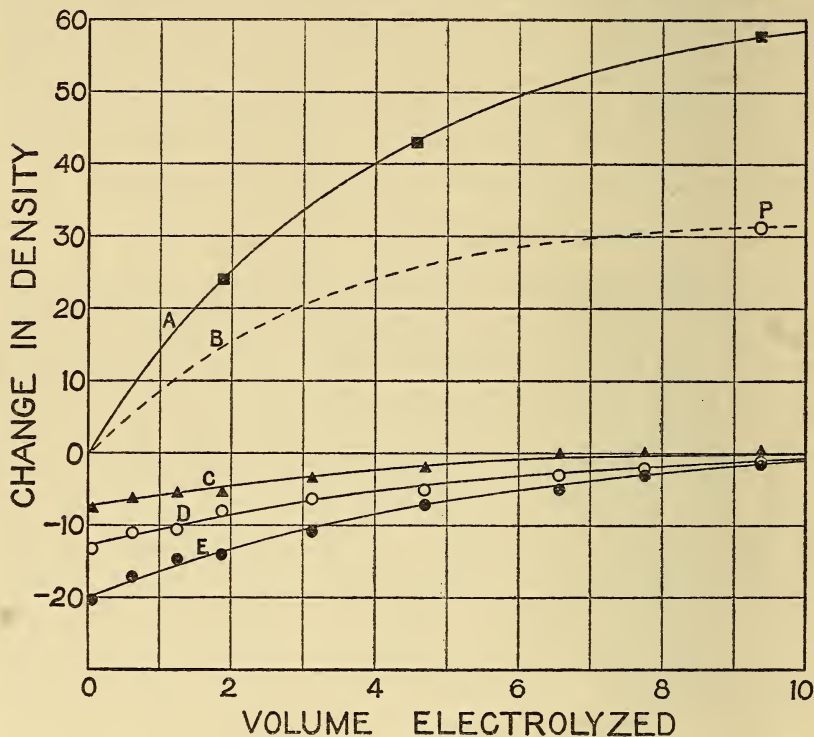


FIGURE 2.—Progressive changes in density with continued electrolysis.

The ordinates are values of the differences in density between the samples investigated and normal water, expressed in ppm. The abscissas represent the volumes of water electrolyzed expressed in terms of the volume of the cell. The curves represent the following: A, The change in the residual water in the cell due to fractionation of the isotopes of both hydrogen and oxygen; B, the change due to fractionation of the oxygen isotopes; C, water formed by burning hydrogen from the cell with normal oxygen; D, water formed by burning oxygen from the cell with normal hydrogen; E, water formed by recombining the gases from the cell.

progressive increase which is due to the fractionation of the oxygen isotopes. Point P on curve B was obtained by saturating and desaturating the equilibrium water, having $\Delta D = 57.8$ ppm, with ammonia gas until successive treatments produced no appreciable change in density. The remaining difference in density of 31 ppm in the equilibrium water is the portion resulting from the increased concentration of the heavier oxygen isotopes. The course of curve B between the origin and P was estimated. Curves C and D show the changes in density of the water formed by burning the electrolytic hydrogen from the cell with normal oxygen, and the electrolytic

oxygen from the cell burned with normal hydrogen, respectively. The density of the water formed by recombining the hydrogen and oxygen directly from the cell is shown by curve E.

V. DISCUSSION

It is apparent that a steady state is attained in a commercial alkaline hydrogen-oxygen electrolyzer after an amount of water approximately equal to 10 times the volume of the cell has been electrolyzed, after which no further isotopic fractionation occurs. However, the change in slope of curve A of figure 2 is not very marked at the outset, and indicates that it is economical for the electrolytic production of heavy water from ordinary water to add fresh water to the cell to keep the volume constant until two or three times the volume of the cell has been electrolyzed, before reducing the volume without the further addition of water. Curve A also shows that under the operating conditions described in this work, the density of the equilibrium water is about 60 ppm greater than that of normal water. Three samples of equilibrium water obtained from the Southern Oxygen Co., at different times between December 1931 and February 1933, had excess densities of 52.1, 53.5, and 53.3 ppm, an average of about 53 ppm. The Southern Oxygen Co., uses a 15 percent solution of potassium hydroxide as electrolyte and a current of 300 amperes. When it is considered that more water is lost by evaporation with the less efficient condensing manifold on commercially operated electrolyzers than on the small cell used in this investigation, and that this loss is replaced continually by ordinary water, it is to be expected that commercial equilibrium water should be slightly less concentrated. For this reason, the hydrogen and oxygen gases from commercial electrolyzers operating on their equilibrium water should ordinarily be slightly lighter than normal, respectively, assuming that the electrolyte volume is not allowed to fall below the average level. However, now that commercial equilibrium water is so widely used as the starting material for the production of heavy water, commercial electrolytic hydrogen and oxygen will more often be found lighter than normal because of the disposal of equilibrium water as a by-product. In the case of hydrogen, curve C shows that 8 ppm is the maximum decrease in terms of the density of water formed by burning the gas, and for oxygen curve D shows that 13 ppm is the maximum decrease to be found. These differences correspond to 40 percent less H^2 and 6 percent less O^{18} than in the normal gases. For precise work these variations can readily be determined by combining the gases with their normal complements to form water and measuring the variations in density.

Although the decrease in density of the water formed at the start by recombining the gases from the cell and the increase in density of the residual water in the cell are caused somewhat more by the fractionation of the isotopes of oxygen (curves E and B) than of hydrogen, the O^{18} isotope is present initially in tenfold larger proportion than the H^2 isotope, so that these changes represent really a smaller percentage fractionation of the oxygen than of the hydrogen isotopes. One of the next problems to be undertaken in this series of investigations is to determine how far the oxygen fractionation extends on continued electrolysis of progressively heavier water.

It has been pointed out¹³ that the electrolytic fractionation factor, α , defined as the ratio of the relative abundance of the hydrogen isotopes in the solution to that in the gaseous hydrogen leaving the cell, can be readily calculated from a knowledge of the abundance ratio of the isotopes in ordinary water and of the isotopic composition of equilibrium water. In natural hydrogen the abundance ratio H^2/H^1 is probably¹⁴ close to 2.0×10^{-4} . In the equilibrium water, about 32 of the 60 ppm increase in density is contributed by the fractionation of oxygen and 28 by the hydrogen. Dividing 28×10^{-6} by 0.10 (the approximate excess density due to the deuterium in 100 percent deuterium water) gives 2.8×10^{-4} for the increase in proportion of H^2 above that in normal water. To this figure must be added the 2.0×10^{-4} for the proportion of H^2 present in normal water to obtain 4.8×10^{-4} for the ratio H^2/H^1 in equilibrium water. The electrolytic fractionation factor is therefore the ratio $4.8/2.0$, or $\alpha=2.4$ for equilibrium water under the experimental conditions of this investigation. This value is of the same order of magnitude as the ratio of the mobilities of the H^1 and H^2 ions.

WASHINGTON, August 15, 1934.

¹³ H. C. Urey, *Rev. Sci. Instruments*, **4**,423(1933).

¹⁴ W. Bleakney and A. J. Gould, *Phys. Rev.* **44**,265(1933).