CONCENTRATION OF DEUTERIUM BY ELECTROLYSIS OF SULPHURIC ACID SOLUTIONS.

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Since it was found that the electrolytical fractionation of water was very efficient to concentrate deuterium, experiments have been carried out in our laboratory to prepare heavy water by this method.

The present paper is concerned with the preliminary experiments on the electrolysis of sulphuric acid solutions with lead electrodes. The commercial sulphuric acid was diluted to 10 per cent. concentration with ordinary tap water and subjected to electrolysis using lead electrodes. The results are shown in Table 1.

Table 1.

Series	Initial volume c.c.	Final volume c.c.	Parts H^2 per 1,000	α	a	b
1	6,400	100	0.8	2.2	1.50	0.62
2	50,000	1	9	2.7	1.54	0.78
3	61,000	7	7	2.4	1.58	0.62

The symbol α denotes the electrolytical separation coefficient defined by the following equation :

$$d \ln H^1 = \alpha \, d \ln H^2 .$$

The meanings of a and b will be explained later.

The electrolyzing apparatus was very simple. Tall beakers of about 200 c.c. capacity, 5 cm. diameter, and 10 cm. height, were used as cells. They were filled with the electrolyte and placed in series in running water. The lead electrodes employed consisted of 2 sheets of plates 10 cm. long and 4 cm. wide, which were joined together by a thin strip of lead plate ; one sheet formed the anode and the other the cathode in neighbouring cells. The cells were put in series in D. C. of about 4 amperes obtained either from a motor generator or from rectifiers. Upon reaching half the original volume the content of a cell was first neutralized with Na_2CO_3, distilled, and then added to the other cells with contents of the same order of concentration as the one to be added. This process was repeated until the final product was obtained. The density of the final products, after being carefully purified, was measured by means of a pycnometer or by a bouyancy balance.

In order to find the electrolytical separation coefficient α from the data thus obtained, it must be taken into consideration that fairly large amounts of the solution were lost during electrolysis owing partly to evaporation and partly to escaping sprays resulting from bubbles at electrodes. The loss due particularly to the latter factor was appreciably large in the arrangement employed by us. In order to minimize this loss, a watch glass was placed on each cell. It may be justified in stating that the amount of loss due to evaporation and escaping sprays is proportional to the total number of cells and this is again proportional to the total amount of the solution present. And in the second place, it may be assumed that the isotopic composition of the lost solution is identical with that of the solution in the cells. Therefore, the total loss of protium and deuterium during electrolysis can be expressed by the two following terms instead of an usual single term:

$$-\mathrm{d}\,N_1 = k_1 N_1\,\mathrm{d}t + K(N_1+N_2)\frac{N_1}{(N_1+N_2)}\,\mathrm{d}t\,,$$

$$-\mathrm{d}\,N_2 = k_2 N_2\,\mathrm{d}t + K(N_1+N_2)\frac{N_2}{(N_1+N_2)}\,\mathrm{d}t\,,$$

where the second term in each differential equation stands for the loss due to both evaporation and spray-formation, N_1 and N_2 the total moles of protium and deuterium respectively, and K is a constant for both evaporation and spray-formation. Hence, on integrating these two equations, we can obtain the total separation coefficient α:

$$\alpha = \frac{\ln N_{10} - \ln N_1}{\ln N_{20} - \ln N_2} = \frac{k_1+K}{k_2+K} \quad \dots\dots\dots\dots\dots\dots \text{(1)},$$

where N_0 indicates the values at the commencement of electrolysis. Here, it should be mentioned that, since we started with ordinary tap water, the ratio of total moles of deuterium to that of protium was taken as one part to 5,000.

However, as the ordinary water may be considered to consist of pure protium water, the ratio of its loss due to evaporation and spray-formation (W) to that due to pure electrolysis (E) should be equal to the ratio K/k_1:

$$W/E = K/k_1 = b \quad \dots\dots\dots\dots\dots\dots\dots\dots \text{(2)}.$$

The value b can be easily found experimentally from the total and the theoretical losses during the electrolysis. From equations (1) and (2) we can obtain the electrolytical separation coefficient α as follows:

$$\alpha = \frac{k_1}{k_2} = \frac{a}{1-b\,(a-1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3).$$

The values a, b and α obtained in this way are given in Table 1.

Our results can be compared with those of Collie⁽¹⁾ who electrolyzed 10 per cent. ordinary sulphuric acid solution using lead electrodes and obtained the electrolytical separation coefficient $\alpha = 1.2-3.8$, which is quite close to ours. Some other authors used more dilute solutions of sulphuric acid. For instance, Erlenmeyer and Gärtner⁽²⁾ started from 8 liters of ordinary 0.1 N sulphuric acid and obtained 13 c.c. of heavy water containing 5 parts H^2 per 1000. From this result it will be seen that α is 2.0, neglecting the loss due to evaporation and spray-formation. The concentration of sulphuric acid does not seem to have much influence upon the separation efficiency. More recently Topley and Eyring⁽³⁾ made careful experiments on the separation efficiencies by electrolysis and obtained α as high as 6.2—6.6 by using 0.5 N sulphuric acid and lead electrodes. The discrepancy between this and values obtained by other observers is considerable. But it must be taken into consideration that the above-mentioned investigators started with more concentrated heavy water instead of ordinary water. It may be plausible that the magnitude of α depends upon the isotopic composition of starting materials. It might be of interest to confirm this view.

The experiments on electrolytic concentration, which are now being continued by using alkaline solutions and neutral salt solutions, will be published later.

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(2) H. Erlenmeyer and H. Gärtner, *Helvetica Chim. Acta*, **17** (1934), 30.

(3) B. Topley and H. Eyring, *J. Chem. Phys.*, **2** (1934), 217.