351. *The Electrolytic Separation Factor of Deuterium at Very Low Concentrations.*

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An attempt has been made to reproduce the results of Applebey and Ogden, who obtained isotopic separation factors between 30 and 100 in electrolysing water containing about twice the deuterium content of tap-water under conditions likely to minimise secondary isotopic exchange. Their observations, if confirmed, would be of great theoretical interest, since they suggest the possibility that quantum-mechanical " tunnelling " may play a part in the electrolytic separation. The cells used in the present investigation were similar in principle to, though not identical in design with, those used by Applebey and Ogden. Completely distilled tap-water was used in making up the electrolyte; the evaporation loss during electrolysis was measured and corrected for. The separation factors obtained were not abnormally great, lying between 6·5 and 8, and were not significantly different from those obtained at higher deuterium concentrations with the same cells.

THIS work was undertaken in an attempt to repeat some striking results by Applebey and Ogden (J., 1936, 163), who obtained electrolytic separation factors between 30 and 100 at a nickel cathode by reducing to a minimum the amount of secondary isotopic exchange between cathode gas and electrolyte. The latter object was achieved by working with water of low deuterium concentration (approximately twice that of tap-water) and by designing the cell so that the circulation of electrolyte ensured very rapid removal of the evolved gas from the cathode. Applebey and Ogden's results, if authentic, are of great potential theoretical significance, because such a high separation factor could scarcely be explained except as a result of quantum-mechanical " tunnelling " of protons and deuterons through an energy barrier. We have therefore attempted to reproduce their results.

The cells used in our investigation were similar in principle to those of Applebey and Ogden. Six cells were run in series with a water voltameter which enabled us to estimate and correct for the evaporation loss during electrolysis. The electrolyte was completely distilled tap-water containing 2·5% of sodium hydroxide; this was reduced to one-fifth of its bulk by electrolysis, neutralised with carbon dioxide, and normalised with respect to the oxygen isotopes by sulphur dioxide; the density of the final product was determined by flotation temperature.

The separation factors obtained were not abnormally great, nor were they significantly higher than those obtained at higher deuterium concentrations with the same cells. They averaged about 8, Gabbard and Dole's value (*J. Amer. Chem. Soc.*, 1937, 59, 181) of 1/6,900 being taken for the abundance of deuterium in natural water. Measurements with the same cells at a higher deuterium concentration gave values of about 6; if a slightly higher value for the abundance of deuterium is assumed, this small difference between the two sets of values vanishes.

EXPERIMENTAL.

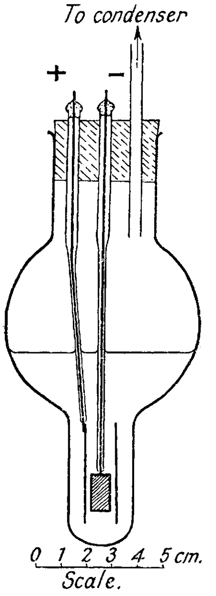
The Electrolytic Cells.—The arrangement of electrodes used was not the same as the " grid " form (I) which Applebey and Ogden used for low deuterium concentrations and with which the high separation factors were observed, but resembles the form (II) used by them at high deuterium concentrations. The latter type was chosen rather than the former because it is much more convenient for weighing and for control of the evaporation loss. Applebey and Ogden obtained separation factors with cell II with 3·7% D_2O which were *higher* than those obtained with cell I and 1·8% D_2O; since they found that in both types of cell the separation factor fell with rising deuterium concentration, there seems no reason to believe that cell I is likely to give separation factors higher than cell II.

In our cells, illustrated in the figure, the electrodes were made of nickel rods and tube, welded to nickel leads and mounted concentrically. The inner rod served as cathode, the outer tube as anode. The main difference between this arrangement and that of Applebey and Ogden (cell II) is that here the outer cylinder is prolonged upwards to give a higher column of gas-loaded electrolyte and hence more powerful circulation.

The cells were cooled to between 14° and 16° by placing them in a tank through which water circulated. Evaporation loss was further reduced by fitting the cells with condensers. The evaporation loss corresponded to a saturation temperature for the evolved gases of 11—12°. The water voltameter, which permitted the measurement of this loss, was fitted with nickel electrodes and contained 8% sodium hydroxide as electrolyte; its outlet carried drying-tubes of calcium chloride and phosphoric oxide. The difference between the loss in weight of this cell and the loss in weight of the electrolysis cells in series with it gives the amount of evaporation in the latter.

Procedure in Electrolysis, and Purification of Product.—150 C.c. of the electrolyte, which was made up from completely distilled tap-water, were pipetted into each cell; the cells were then corked and weighed. Electrolysis was carried on at 0·8 amp./cm.^{2} until the cells had lost about 120 g. in weight.

The electrolyte was first neutralised by bubbling carbon dioxide through it. After distillation, a stream of sulphur dioxide, from a siphon and dried over phosphoric oxide, was bubbled for 3 hours through the distillate cooled in a water tank. The sulphur dioxide was removed by first passing air through the liquid for 3 hours and then distilling it in a vacuum. A third and final distillation was carried out after adding a few crystals of potassium permanganate and a little sodium carbonate. All distillations were carried out in a vacuum in **H**-shaped tubes with one limb cooled in ice and the other heated in warm water. In this way it is possible to achieve complete distillation without splash.



The spacing between anode and cathode is 2 mm.

The possibility of isotopic displacement caused by evaporation during the gas bubbling was excluded by the following blank experiment: 7·9 g. of water, whose density exceeded that of natural water by 42 parts per million, were treated with 2·0 g. of sodium hydroxide (containing 2% of water). The solution was subjected to the complete procedure of purification; the density excess of the product, after allowance for the addition of the sodium hydroxide, should be 39·5 parts per million. It was found to be 39 parts per million.

Density Determination.—A few c.c. of the sample were placed in a Monax test-tube with a calibrated glass float about 2 c.c. in volume. Air was blown through for ½ hour to saturate the water, since air-saturated water is 4—5 parts per million less dense than air-free water at 13°, the temperature of the measurements. The temperature at which the float just rose from the bottom on cooling was noted. With slow cooling (<0·01°/min.) this temperature could be reproduced to ± 0·005°, corresponding to a density interval of 0·5 part per million.

The float was calibrated with magnesium sulphate solutions of known density, and a normal water standard prepared from a sample of the original electrolyte by submitting it to the same purification treatment as the solutions after electrolysis. Its density was within 1 part per million of the laboratory distilled water used in making up the standard magnesium sulphate solutions.

Calculation of Results.—(i) *The evaporation correction.* If the numbers of atoms of protium and deuterium present before and after electrolysis are denoted by H_1, D_1 and H_2, D_2 respectively, and if the proportion of water lost by evaporation to that lost by electrolysis is called k, then the true separation factor is

$$\alpha = \frac{(1 + k)\ln H_1/H_2 - k\ln(H_1 + D_1)/(H_2 + D_2)}{(1 + k)\ln D_1/D_2 - k\ln(H_1 + D_1)/(H_2 + D_2)}$$

which for small deuterium concentrations simplifies to

$$\alpha = \frac{\ln H_1/H_2}{\ln D_1/D_2 - k(\ln H_1/H_2 - \ln D_1/D_2)}$$

These expressions assume that, during the electrolysis, k is constant and that there is no isotopic discrimination in evaporation.

(ii) *The evaluation of deuterium concentration from the density.* The specific gravity of pure deuterium oxide at the flotation temperature is 1·1073 (Lewis and Macdonald, *J. Amer. Chem. Soc.*, 1933, **55**, 3057; Selwood, Taylor, Hipple and Bleakney, *ibid.*, 1935, **57**, 642). The mole-fraction of deuterium, N_2, is deduced from the expression (cf. Luten, *Physical Rev.*, 1934, **45**, 161) : density $= 1 + N_2(0{\cdot}1073 - 0{\cdot}0012N_1)$. To the value of N_2 thus obtained must be added the mole-fraction of deuterium present in natural water. Gabbard and Dole's value (*loc. cit.*) for this is 0·000145.

(iii) *Sources of error.* The principal errors are in the density determinations and may be summarised as follows :

	Effect on density (p.p.m.).
Uncertainty in float calibration	1
Uncertainty in flotation temp.	½—1
Total	1½—2

Such an error in the density might affect the separation factor by 15%. The errors in weighing would not affect the separation factor by more than ½%. A final source of error arises from the slight isotopic separation caused by the evaporation during electrolysis; this makes the observed separation factor too great by an amount unlikely to exceed 3%. The probable limits between which the separation factors lie are given in the table of results.

The following tables contain the results obtained in electrolysing natural water and water containing 0·245% deuterium respectively.

Electrolysis of natural water.

Initial electrolyte : 2·32% sodium hydroxide in completely distilled tap-water. Amount placed in each cell: 153·15 g.; H_2O before electrolysis (moles): 8·346; D_2O before electrolysis (mole): 0·00121; proportion of D before electrolysis (p.p.m.): 145; amount electrolysed (from voltameter weighings) : 115·84 g.

Cell No.	2.	3.	4.	5.	6.
Δd of solution after electrolysis (p.p.m.)	40·5	40·5	42·5	42·0	42·5
Proportion of D after electrolysis (p.p.m.)	525	525	545	540	545
H_2O after electrolysis (moles)	1·786	1·787	1·783	1·785	1·772
D_2O after electrolysis (moles $\times 10^{-6}$)	938	938	971	960	966
k (evapn. const.)	0·0200	0·0198	0·0203	0·0200	0·0220
Separation factor	$6{\cdot}7_5$	6·7	8·0	$7{\cdot}5_5$	$7{\cdot}9_5$
Probable limits of separation factor	5·8 8·3	5·8 $8{\cdot}2_5$	7·0 9·4	$6{\cdot}7_5$ 8·8	6·6 $9{\cdot}9_5$

The effect of assuming a different value for the abundance of deuterium in natural water may be judged from the fact that the separation factor for cell 2, for example, becomes $4{\cdot}7_5$ if the proportion of deuterium before electrolysis is taken as 166 p.p.m. instead of 145.

Electrolysis at a higher deuterium concentration.

Initial electrolyte : 2·07% sodium hydroxide in 0·2445% heavy water. Amount placed in each cell : *ca.* 122 g.; proportion of D before electrolysis (p.p.m.): 2445; amount electrolysed (from voltameter weighings) : 88·40 g.

Cell No.	3.	5.	6.
H_2O before electrolysis (moles)	6·673	6·669	6·674
D_2O before electrolysis (mole)	0·01637	0·01637	0·01637
Δd after electrolysis (p.p.m.)	783	794	802
Proportion of D after electrolysis (p.p.m.)	7350	7630	7705
H_2O after electrolysis (moles)	1·673	1·676	1·682
D_2O after electrolysis (mole)	0·01271	0·01290	0·01304
k (evapn. const.)	0·0191	0·0178	0·0175
Separation factor (±5%)	6·0	6·3	$6{\cdot}6_5$

Dr. Ogden kindly came to Oxford in a joint effort to discover a reason for the discrepancy between our results and those obtained by Mr. Applebey and himself. The only difference in experimental conditions which he regarded as conceivably significant was the greater opportunity for contact with the anode which was afforded to the cathode gas in our cells. On general grounds, and in view of other experiments of ours (to be published later) which show that the separation factors at nickel cathodes with rigid exclusion of oxygen and grease and no opportunity for contact of cathode gases with the anode are substantially the same as those obtained under the crudest conditions of technical electrolysis, we incline to the view that this difference in cell design cannot account for the conflict between the two sets of results. It is noteworthy that the evaporation correction which we applied would tend to produce separation factors *higher* rather than lower than those of Applebey and Ogden.

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