33. *The Electrolytic Preparation of Deuterium and the Separation Coefficient a.* *

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It has become increasingly evident during the past 18 months that the efficiency of electrolytic cells in the separation of the two isotopes of hydrogen falls far short of the value calculated from purely theoretical considerations. This calculation has been carried out by several investigators (Topley and Eyring, *J. Chem. Physics*, 1934, **2**, 217; Bowden and Kenyon, *Nature*, 1935, **135**, 105; Halpern and Gross, *J. Chem. Physics*, 1935, **3**, 453; Polanyi and Horiuti, *Nature*, 1933, **132**, 819, 931), who obtain values of α lying between 0·05 and 0·10. All these investigators are agreed that the rate-determining step in the process is the passage of the hydrogen or deuterium atom over an energy barrier, the non-classical passage through the barrier being supposed negligible. Experiment also shows that α is dependent to a certain extent on the electrode material and on the concentration of deuterium oxide in the electrolyte, whereas theoretically α should be practically independent of both these factors.

It is evident that these theories of over-voltage are not sufficient to account for the experimentally obtained values of α; if the theoretical value of 0·05—0·10 is correct, there

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* The separation coefficient a referred to in this paper is the reverse of that usually employed by workers in this field. It is given by

$$a = \frac{\text{concentration of deuterium in the gas phase}}{\text{concentration of deuterium in the liquid phase}}$$

at any instant, and is the separation coefficient employed by earlier workers.

must be some disturbing effect in the actual experimental determinations tending to give a much larger value of α than the true one. One such effect, and probably the most important, is the exchange reaction $HOD + H_2 \rightleftharpoons H_2O + HD$ (and in more concentrated solutions, $D_2O + H_2 \rightleftharpoons HOD + HD$, $D_2O + HD \rightleftharpoons HOD + D_2$). It is certain that such exchange reactions take place to some degree during electrolysis, since most metals used as electrode materials will catalyse this reaction. The catalytic effect may, indeed, be more vigorous under electrolytic conditions because the hydrogen is in an activated or nascent state. When the gas evolved contains more light hydrogen than is defined by the concentration determined from the equilibrium equation $K = [HD][H_2O]/[H_2][HOD] = 3.8$ at room temperature, the experimentally determined value of α will be greater than the ideal value of the electrolytic separation coefficient α_0, and will, in fact, approach $1/K = 0.270$. With certain metals which are good catalysts for the exchange reaction, the value of α obtained in electrolytic experiments is actually equal to 0.270, showing that equilibrium is established between the water and the gas as fast as the gas is liberated at the electrode surface. This behaviour is shown by platinum electrodes, the true electrolytic separation coefficient being completely suppressed owing to the rapidity of the catalytic exchange.

In the process of electrolysis, the concentration of hydrogen in the liquor in the neighbourhood of the cathode decreases, while that of deuterium increases, owing to the preferential electrolysis of the hydrogen. It is therefore evident that as electrolysis proceeds the local concentration of deuterium hydroxide in the neighbourhood of the cathode becomes much greater than that in the bulk of the solution; such local concentration not only in itself increases the proportion of deuterium liberated as gas, but also favours the exchange reaction by which the electrolytic separation is opposed.

These considerations have led the authors to the adoption of the following principles in the design of cells for the production of heavy water : (*a*) The metal used for the electrode material must be a poor catalyst for the exchange reactions; (*b*) the evolved hydrogen gas must be removed as quickly as possible from the electrode surface; (*c*) local concentration of deuterium hydroxide at the electrode surface must be avoided. The last two conditions can be attained by efficient stirring of the electrolyte either mechanically or by the gas evolution itself, the efficiency then depending largely on correct design of electrodes.

Two types of cell employing the latter device have been employed in production at the Billingham works of Imperial Chemical Industries, and are now described in the hope that they will be of service to other workers. The first is a small cell (Fig. 1 *a*) suitable for the later stages of concentration. It has electrodes consisting of concentric nickel cylinders, the outer cylinder fitting fairly tightly into the glass cell—the electrolysis taking place in the annular space (0·2 cm.) between the two cylinders. The whole cell is enclosed in a water-cooled jacket. During electrolysis, the liquor in the annular space, being much lighter than that in the inner hollow cylinder by reason of the gases it contains, rapidly rises and sets up a brisk circulatory motion which clears the gas away from the electrode surface and prevents any concentration gradients in the liquor itself. A series of experiments carried out in this type of cell, in which the only variant was the concentration of deuterium oxide in the electrolyte, gave the results recorded below. It is evident that α increases with increasing concentration—an effect to be expected since the exchange reaction will take place to a greater extent as the deuterium oxide concentration in the electrolyte increases. In these and all other experiments recorded in this paper, the electrolyte was sodium hydroxide of 5% initial concentration, and the current density 0·8 amp./cm.²

The temperature of the electrolyte was maintained at 13—15° by the circulation of tap water through the water-jacket of the cell. A spray trap was fitted to the cell, and was arranged so that any spray carried over by the gas was returned to the cell. In addition, the electrolytic gas passed through a reflux condenser through which ice-cold water circulated, any condensate from the gas being returned to the cell. At the conclusion of an experiment, the caustic liquor from the cell was neutralised with solid carbon dioxide, and the neutral product distilled from a copper vessel and then carefully purified. The oxygen isotope concentration of the product was " normalised " by bubbling a large volume of sulphur dioxide through it—precautions being taken to minimise any evaporation losses. The water was again distilled to free it from

dissolved sulphur dioxide, and its density determined by a float method similar to that employed by Emeléus *et al.* (J., 1934, 1207).

Mean concentration, %, of D_2O during electrolysis	3·7	29·5	58·75	86·5
Separation coefficient, a	0·19	0·18	0·23	0·29

The larger cell illustrated in Fig. 1 *b* and *c* is suited for the earlier stages of concentration. The electrodes of this cell consist of a number of parallel strips of nickel about 1 cm. high, which are alternately anode and cathode. The anode strips are all joined at their ends to a flat circular strip of thin nickel plate, about 2 cm. wide cut from a circle of 12 cm. diameter. The whole resembles a circular grating, the strips forming the grating varying in length, the outermost one on each side being the shortest and each grid electrode progressively increasing in length toward the centre. The cathode grid is built up in exactly the same way, and when the two composite electrodes are fitted together with a rubber washer between the two outer flat circular strips to

FIG. 1.

Sectional Elevation

Perspective View of One Electrode.
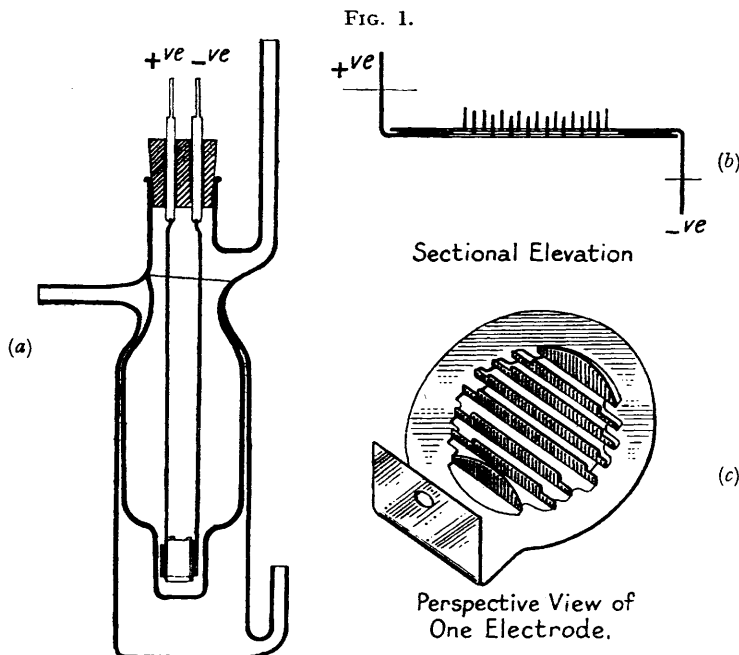
which the grids are joined, the vertical plates are alternately cathode and anode. The electrodes are contained in a glass sided cell with a metal base, the base being insulated from the electrodes by a rubber washer.

A representative series of results obtained with this cell is given in Table I.

TABLE I.

Spacing between the grids constituting electrodes .... 0·5 cm.
Material of which electrodes were constructed.................. nickel.
Concentration of deuterium in standard water .... 1 in 5500.

Initial vol. of electrolyte, ml.	Vol. after electrolysis, ml.	Concn. of D_2O initially in electrolyte.	Concn. of D_2O after electrolysis.	Separation coefficient, a.
1000	234	1/2950	1/730	0·029
1000	249	1/2800	1/708	0·010
1000	249	1/2600	1/695	0·014
1000	270	1/1295	1/512	0·120
1000	250	1/492	1/151	0·145
1000	216	1·34%	2·16%	0·236

With this cell at very low concentrations of deuterium oxide, the value of α obtained is very much lower than the predicted values obtained by various workers (0·05—0·10). These workers have, in their calculations, neglected the 'tunnel effect' and only taken

into account the different zero-point energies of the two hydrogen isotopes. Briefly, the tunnel or permeability effect follows as a direct consequence of the wave nature of matter. If a particle has an energy W, and the energy of activation required for a chemical change in that particle is E, then classical reaction kinetics stated that reaction would only take place if $W>E$ and would never take place if $W<E$. Quantum mechanics, however, states that there is a definite probability of reaction taking place even if $W<E$, the probability of reaction being a complex function of e^{E-W} and the width of the energy barrier. Ogden and Bawn (*Trans. Faraday Soc.*, 1934, **30**, 432) have calculated the electrolytic separation coefficient α, taking into account the probability of leakage through an energy barrier, and have shown that α may be as low as 0·013. A preliminary notice of these experiments has already been published by Polanyi and Horiuti (*Acta Physicochimica U.R.S.S.*, 1935, **2**, 505), who consider them to be one of the first authenticated proofs that quantum mechanical leakage is an important factor in the difference in rate of reaction of hydrogen and deuterium atoms. The authors are, however, of opinion that this conclusion can only be accepted provisionally at present, because the values of α calculated from experiments in very dilute solutions are largely affected by the particular value which is accepted for the concentration of deuterium in standard water.

Fig. 2.
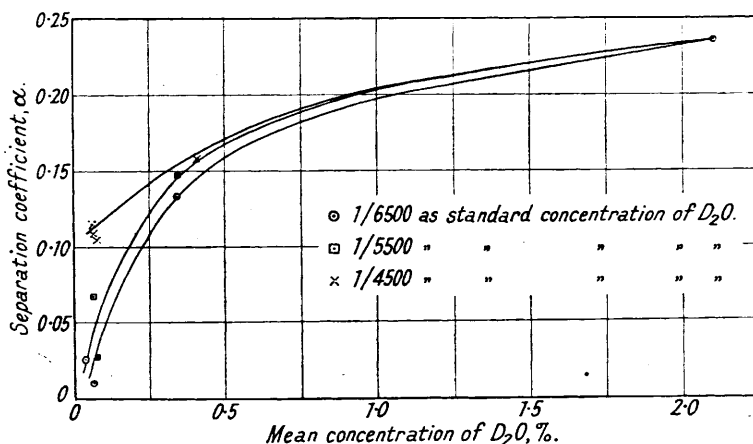
To illustrate this point, we have calculated in Table II the electrolytic separation coefficient from a single determination, assuming successively a deuterium concentration of one in 4500, 5500, 6500, and 7500. Similar calculations performed with all the determinations of Table I lead to the curves plotted in Fig. 2, which show the variation of α with the mean concentration of deuterium during electrolysis* for the same assumed values of the deuterium concentration of standard water.

Various estimates of the concentration of deuterium oxide in normal water have been made, based upon either (*a*) the mass-spectrographic method or (*b*) the preparation of pure light water or protium oxide, $H_2{}^1O^{16}$. In the latter method, water is subjected to fractional electrolysis, fractional distillation, or a combination of both methods, until the final product contains a negligible amount of deuterium. In the electrolysis of water, the hydrogen evolved from the cathode contains less deuterium than the water. This hydrogen is burnt back to water by recombination with the evolved oxygen, and the water so formed utilised in the next stage of the electrolysis. The density of the water from each stage of

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* It is easy to show that the mean concentration C during an electrolysis is

$$C_0(V_0 - V^\alpha V_0{}^{1-\alpha})/\alpha(V_0 - V)$$

where C_0 is the initial concentration of deuterium, and V_0 and V are the initial and the final volume. This formula is approximate, being strictly true only for conditions in which the concentration of light water may be taken as constant and in which changes in α during the electrolysis may be regarded as negligible.

TABLE II.

Vol. of water before electrolysis = 1000 ml. (d, 20 × 10⁻⁶ greater than that of normal water).
Vol. of water after electrolysis = 234 ml. (d, 134 × 10⁶ greater than that of normal water).

Assumed proptn. of D in standard water.	Initial concn. of D_2O in electrolyte.	Concn. of D_2O after electrolysis.	Separation coefficient, a.
1/4500	1/2520	1/697	0·107
1/5500	1/2725	1/701	0·067
1/6500	1/2950	1/716	0·026
1/7500	1/3145	1/727	— 0·009

electrolysis is measured until finally there is no change; the deuterium concentration will then be negligible. The density of the product after careful purification is measured, and if it is a p.p.m. lighter than ordinary or standard water, the deuterium content of the latter is given by $a/1079$. The figure 1079 is obtained from the density of pure deuterium oxide, given by Taylor and Selwood (*J. Amer. Chem. Soc.*, 1934, **56**, 998) as 1·1079. A more accurate figure has recently been published by Tronstad, Nordhagen, and Brun (*Nature*, 1935, **136**, 515), who give $d_{25}^{25.} = 1·1074$. This will alter the existing values of the concentration of deuterium oxide in standard water by about 0·5%—an amount which is negligible compared with the experimental error inherent in the methods employed for its determination.

This method is, however, complicated by the fact that any process which fractionally separates the two isotopes of hydrogen also separates, though to a less degree, the isotopes of oxygen. The change in the abundance ratio of the oxygen isotopes causes a corresponding decrease in density of the water sample which evidently must be allowed for.

The commonest method employed is to restore the oxygen isotope ratio back to its normal value or to some known standard value, and this is most easily accomplished by making use of the isotopic reactions discovered by Lewis (*J. Amer. Chem. Soc.*, 1933, **55**, 3502). A gas such as sulphur dioxide is bubbled through the water sample, the isotopic reaction $SO_2^{16} + 2H_2O^{18} = SO_2^{18} + 2H_2O^{16}$ then taking place. If sufficient sulphur dioxide were bubbled through the water, it was formerly believed that the water recovered its normal abundance ratio with respect to the oxygen isotopes, and any difference in density after this treatment must be due to a shift in the hydrogen abundance ratio alone. Recently, however, Urey and Grieff (*ibid.*, 1935, **57**, 521) have shown that in this reaction there is a definite equilibrium—some enrichment of O^{18} occurring in the sulphur dioxide at the expense of the water. The enrichment is only very small, the factor being 1·014 at room temperature. Therefore, ordinary water treated with a large excess of sulphur dioxide will have a concentration of O^{18} of 1 part in 639 parts of oxygen instead of the normal value of 1 in 630. This effect was easily shown by taking a sample of tap water and, after careful purification, bubbling a large excess of sulphur dioxide through one portion of the sample. After repurification and redistillation, its density was found to be 3 p.p.m. lighter than the original sample, which agrees very well with the figure of 2·3 p.p.m. calculated from Urey and Grieff's results.

Gray and his co-workers (*Nature*, 1934, **134**, 661), by a combination of fractional electrolysis and distillation, obtained light water which was 12 p.p.m. lighter than ordinary water, corresponding to a concentration of deuterium oxide in normal water of 1/9000. Reference to Table II of the present communication shows that such a value is irreconcilable with our experiments, from which the assumption of any value less than 1/7000 for the deuterium concentration leads to negative values for the separation coefficient, which are, of course, impossible. Washburn, Smith, and Frandsen (*J. Chem. Physics*, 1933, 1, 288), employing electrolytic methods, obtained water lighter than normal water by 18 p.p.m., and all this difference in density was due to loss of heavy hydrogen, which leads to a value of 1/6000 for the concentration in normal water. Recently, Johnson (*J. Amer. Chem. Soc.*, 1935, **57**, 484) prepared deuterium-free water by the electrolysis of a large volume of water —the initial 25% of the electrolytic gases evolved in each stage serving as the electrolyte in the next. The process was continued for five stages, and the allowance for the change in heavy-oxygen concentration was carried out graphically. It could be easily shown from a knowledge of the separation coefficient α of the electrolytic cell that, after the second

stage, the concentration of deuterium would be negligible, and so any further decrease in density must be due to the change in heavy-oxygen concentration—so that this change in concentration could then be allowed for in the first two stages of electrolysis. In this way, Johnson showed that the normal concentration of deuterium oxide in water is $1/5750 \pm 250$, which agrees very well with Bleakney and Gould's latest mass-spectrographic value, $1/5000 \pm 500$ (*Physical Rev.*, 1933, **44**, 265). The latest value for the concentration of deuterium oxide in normal water may be calculated from the results of Tronstad, Nordhagen, and Brun (*loc. cit.*), who prepared protium oxide containing less than 1 part in 200,000 of deuterium oxide. This water was 18·5 p.p.m. lighter than normal water, whence the concentration of deuterium oxide in ordinary water is found to be $1/5800$, in good agreement with the generally accepted value.

A consideration of the evidence collected in the foregoing paragraphs leads us to the view that the most probable concentration of deuterium in standard water is 1 in 5500. If this figure, or any slightly lower value, is confirmed, our experiments leave no escape from the conclusion that quantum-mechanical leakage has been demonstrated. On the other hand, it must be pointed out not only that a value approximating to 1 in 4500 gives α at infinite dilution a value approximating to the ideal value without tunnelling, but also that such an assumption gives a curve for the variation of α with concentration which is simpler in form and inherently more probable. Which of these alternatives must be accepted can only be decided when more precise knowledge of the constitution of standard water has been obtained.