THE RELATIVE EFFICIENCIES OF THE MULTISTAGE AND ONE STAGE PROCESS IN THE ELECTROLYTIC PREPARATION OF HEAVY WATER.

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§ 1. It has been observed by Washburn that \( \alpha' \) the measure of the efficiency of separation, in the electrolytic preparation of heavy water, carried under the same conditions as are existent in the working of a commercial cell tends to assume small values. This decrease in \( \alpha' \) can be ascribed to a number of factors. We are concerned here only with one of these, namely, the effect of the 'continual', i.e., instalmentwise or multistage addition of 'fresh-water'. The vitiating influence of this on \( \alpha' \) has been recognised as early as 1932 by Washburn. It is shown that \( \delta \) the relative magnitude of the step, i.e., the fractional amount of fresh-water added is an important determinant. It is proposed in the following to give a quantitative estimate of the decrease in \( \alpha' \) as a function of \( \delta \), etc. for the low heavy water concentration stage, taking as the basis, the formula given by Urey connecting the initial and final heavy water contents with the corresponding volumes of water in the electrolytic process.

§ 2. Urey has shown from considerations put forward by Lord Rayleigh, for the fractional distillation of two liquids, that

\[
\left( \frac{1 - N}{1 - N_0} \right)^{1/\alpha' - 1} \left( \frac{N}{N_0} \right)^{\alpha'/\alpha' - 1} = \frac{V_0}{V}
\]

where

- \( N_0 \) = initial mol fraction of heavy water in the mixture.
- \( N \) = final mol fraction of heavy water in the mixture.
- \( V_0 \) = initial volume of the mixture (before electrolysis).
- \( V \) = final volume of the mixture (after electrolysis).
- \( \alpha' \) = separation factor.

By mol fraction of heavy water is here meant the fraction,

\[
\frac{\text{No. of mols of heavy water}}{\text{No. of mols of (heavy water + ordinary water)}}
\]
For low values of $N$ and $N_0$ we can write with sufficient accuracy

$$
\left( \frac{N}{N_0} \right)^{\alpha'/\alpha'-1} = \frac{V_0}{V} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots 
$$

It is easily shown that if we mix a volume $V_1$ of mol fraction $N_1$ with volume $V_2$ of mol fraction $N_2$, the resulting mol fraction $N$ can be written with sufficient accuracy as,

$$
N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots 
$$

The error introduced on account of this approximation is easily shown to be negligible (being of the order of 0·6 per cent. when the constituents of the mixture originally contain 50 and 30 per cent. heavy water). It will be smaller still for the low concentration range considered here.

§ 3. Suppose now we start with volume $V$ containing mol fraction $N_0$ of heavy water and reduce it by electrolysis to a volume $V/m$ where $m > 1$ (vide infra). The mol fraction $N_1$ of the residue will be given by

$$
N_1 = N_0 (m)^{1/\alpha'}
$$

Add a volume $V(1 - 1/m)$ of mol fraction $N_0$ and thus bring back the volume to its initial volume $V$. The mol fraction of the resulting homogeneous mixture will be

$$
N_{02} = N_0 \left\{ \frac{m - 1}{m} + \left( \frac{1}{m} \right)^{1/\alpha'} \cdot \frac{1}{m} \right\}
$$

Substituting for $N_1$ from above

$$
N_{02} = N_0 \left\{ \frac{m - 1}{m} + (m)^{1-1/\alpha'} \cdot \frac{1}{m} \right\}
$$

In the second stage, we proceed as before; starting with volume $V$ of mol fraction $N_{02}$ we reduce it by electrolysis to a volume $V/m$ (where $m$ is the same number as before). Now, add to this a volume $V \left(1 - \frac{1}{m}\right)$ and thus bring back the volume to $V$ and so on. If we go on repeating this process $n$ times the final residue will have a mol fraction $N_n$ given by

$$
N_n = N_0 (m)^{1-1/\alpha'} \left\{ \frac{m - 1}{m} \left[ 1 + \left( \frac{1}{m} \right)^{1/\alpha'} \right] + \left( \frac{1}{m} \right)^{2/\alpha'} + \ldots + \left( \frac{1}{m} \right)^{n-2/\alpha'} + \left( \frac{1}{m} \right)^{n-1/\alpha'} \right\}
$$

§ 4. As a result of this $n$-stage process we have reduced a total volume $V + V \frac{m - 1}{m} \cdot n$ to a final volume $\frac{V}{m}$. Instead of doing this in stages, if
one had started with an initial volume \( V \left( 1 + n \cdot \frac{m - 1}{m} \right) \) and reduced it to \( \frac{V}{m} \) in a single stage, the mol fraction of heavy water in the residue of this process would have been

\[
N = N_0 \left[ \left( 1 + n \cdot \frac{m - 1}{m} \right)^m \right]^{1 - 1/a'}
\]

\[
= N_0 (m)^{1 - 1/a'} \left[ 1 + n \cdot \frac{m - 1}{m} \right]^{1 - 1/a'}
\]

Therefore,

\[
\frac{N - N_0}{N_0} = (m)^{1 - 1/a'} \left\{ \left[ 1 + n \cdot \frac{m - 1}{m} \right]^{1 - 1/a'} - \left[ \frac{m - 1}{m} \right]^{1 - \frac{3}{a'}} \right\} + \ldots + (\frac{1}{m})^{1 - 1/a'}
\]

Put \( \delta \) = fraction (by volume) electrolysed at each step, i.e., its relative magnitude, then

\[
\frac{N - N_0}{N_0} = F = \left( \frac{1}{1 - \delta} \right)^{1 - 1/a'} \left\{ \left[ 1 + n \delta \right]^{1 - 1/a'} - \left[ \delta \left( 1 + \left( \frac{1}{a'} \right) + \ldots + \left( \frac{1}{a'} \right)^{n-2} \right) \right] \right\} + \ldots + \ldots \ldots \ldots
\]

For small values of \( n \) and \( \delta \)

\[
F = \left( \frac{1}{1 - \delta} \right)^{1 - 1/a'} \left\{ 1 + \left( 1 - \frac{1}{a'} \right) n \delta - \left[ \delta (n - 1) + 1 - \frac{n - 1}{a'} \delta \right] \right\}
\]

\[
= (1 + \delta)^{1 - 1/a'} \left[ 1 - \frac{1}{a'} \delta \right].
\]

For large values of \( n \) and \( \delta \), however, no further simplification can be introduced in (6).

§ 5. It will be seen from (6) that \( F \), the relative decrease in the yield of heavy water, which is a measure of the efficiency of separation depends upon \( \delta \) the magnitude of the relative step, in such a manner that \( F \to 0 \) as \( \delta \to 0 \) showing that if water be added continuously, i.e., not stagewise, there will be no loss in efficiency. Anderson, Halford and Bates have made use of such a method, and find that no sensible loss in efficiency results in agreement with the above deduction. This result would have been hard to explain on the basis of the existing explanation, "that the continual addition of..."
fresh-water tends to reach a relatively low equilibrium value for the concentration of heavy water".

The following table gives the values of $F$ for different values of $\delta$ assuming that $a' = 3$ and $n = 10$. In the last but one column are given the percentage defects (introduced on account of the stagewise addition of water) in terms of the final values for the mol fraction of heavy water obtained in the single stage process. In the last column are given the apparent values of $a'$ that will be obtained under these circumstances, experimentally.

**Table I.**

<table>
<thead>
<tr>
<th>No.</th>
<th>$\delta$</th>
<th>$F$</th>
<th>Percentage defect</th>
<th>Apparent value of $a'$</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>0.1</td>
<td>0.07</td>
<td>4</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>0.23</td>
<td>10</td>
<td>2.4</td>
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<td>0.3</td>
<td>0.45</td>
<td>14</td>
<td>2.3</td>
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<td>4</td>
<td>0.4</td>
<td>0.98</td>
<td>23</td>
<td>2.17</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>1.68</td>
<td>32</td>
<td>2.04</td>
</tr>
</tbody>
</table>

It will be noticed that the percentage defect will increase rapidly with $n$ as well as $\delta$; it must be remembered, however, that the original assumption, viz., that the proportion of the heavy water in all the processes considered is low, sets a natural limit on the values of $n$ and $\delta$.

The equation (1) given by Urey is quite general and may therefore be applied to cases of fractional distillation, etc., the value of $a'$ being appropriate to the process considered. It is to be anticipated, therefore, that the considerations in § 5 might apply correspondingly to these cases. The generality of equation (6), however, is restricted by the approximation, introduced in (2$a$), of the equality of the molar volumes of the two components.

**Summary.**

A quantitative estimate has been given on the basis of Urey's equation, of the decrease in efficiency in the electrolytic separation of heavy water (assumed to be present in small proportions) due to the continual addition of fresh-water in terms of the variables involved. It is shown that compared
with a single stage process, there will be no less in efficiency, if fresh-water be added continuously. A relation connecting the decrease in efficiency with the relative magnitude of the step has been derived.

REFERENCES.