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Citation: [The Journal of Chemical Physics](#) **2**, 164 (1934); doi: 10.1063/1.1749446

View online: <http://dx.doi.org/10.1063/1.1749446>

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The Theory of the Electrolytic Separation of Isotopes

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(Received January 26, 1934)

(1) Gurney's treatment of overvoltage has been applied to the relative rates of discharge of two isotopes. As a first approximation it is found that the separation efficiency should be nearly independent of the electrode material and the current density. This agrees with the data at present available for the separation of the isotopes of hydrogen.

(2) A more rigid treatment predicts small variations of the efficiency with the nature of the electrode and the current density, but is not at present able to predict these variations quantitatively. (3) The application of the theory to other isotopes is indicated, and a rough estimate given of the possibility of separating Li^6 and Li^7 by electrolysis.

SINCE the original discovery of the electrolytic separation of the isotopes of hydrogen by Washburn and Urey,¹ various suggestions have been made as to the mechanism involved. A difference in the behavior of the two isotopes may reasonably be expected at one or more of the following stages in the process of electrolysis

- (a) The mobility of the hydrogen and deuterium ions.
- (b) The rate of neutralization of the two ions by electrons.
- (c) The rate of combination of hydrogen and deuterium atoms on the electrode.

In order to decide between these alternatives it is necessary to have some knowledge of the effect of various factors upon the separation, and it is only very recently that any work has been done in this direction.

Possibility (a) cannot be an important factor in the separation, since it can be carried out equally well in acid or in alkaline solution.² It is more difficult to decide between (b) and (c); however, it has recently been found by Bell

and Wolfenden³ and by Topley and Eyring⁴ that the efficiency of separation is substantially the same for a number of different cathode materials, which makes it very improbable that the observed phenomena are due to the rate of combination of atoms on the electrode surface.⁵ It is much more likely that the difference in the rates of discharge of hydrogen and deuterium is due to a difference in the rate at which their hydrated ions are neutralized by electrons. Gurney⁶ has previously shown that it is this rate of neutralization which is chiefly responsible for hydrogen overvoltage, and has developed a quantitative theory of overvoltage which agrees well with experiment, notably with the fact that the variation of current density with applied potential is independent of the nature of the cathode. The author has previously pointed out³ that Gurney's treatment can also be applied to the separation of the isotopes of hydrogen, when it predicts that the efficiency of separation will be independent of the cathode material, and gives a value of the right order of magnitude for the efficiency itself. The present paper deals with this point in more detail.

For the current density due to the discharge of a hydrated cation, Gurney derives the expression

¹ E. W. Washburn and H. C. Urey, *Proc. Nat. Acad. Sci.* **18**, 496 (1932).

² See C. H. Collie, *Nature* **132**, 568 (1933); K. F. Bonhoeffer and G. W. Brown, *Zeits. f. physik. Chemie* **B23**, 171 (1933).

³ R. P. Bell and J. H. Wolfenden, *Nature* **133**, 25 (1934).

⁴ B. Topley and H. Eyring, *J. Am. Chem. Soc.* **55**, 5058 (1933).

⁵ As suggested, e.g., by A. Sherman and H. Eyring, *J. Chem. Phys.* **1**, 345 (1933).

⁶ R. W. Gurney, *Proc. Roy. Soc. A* **134**, 137 (1932).

$$i \propto e^{(E_0/\gamma + \epsilon V - E_1)/kT} \int_{E_0}^{E_1 - \epsilon V} \exp \left\{ \frac{E}{kT} \left(1 - \frac{1}{\gamma} \right) - \frac{4\pi x' (2mE)^{\frac{1}{2}}}{h} \right\} dE, \quad (1)$$

where E_0 is the energy of neutralization of the hydrated ion in its lowest energy state by an electron,

E_1 is the work function of the metal,

V is the applied cathodic potential,

x' is the mean distance from the electrode at which the ions are discharged,

ϵ and m are the charge and mass of the electron,

γ is a correction factor a little greater than unity, introduced to account for the repulsive potential energy of the discharged ion and the water molecule immediately after discharge.

If we apply this expression to the discharge of two isotopes X and Y under comparable conditions, the only factor which will not be the same in the two cases is E_0 which will differ on account of the effect of the mass on the lowest vibration-rotation state of the hydrated ions. Gurney has shown that Eq. (1) can be brought into the form

$$\log i = \frac{E_0 - E_1 + \epsilon V}{\gamma kT} + \log \frac{\gamma T}{\gamma - 1} + \Phi, \quad (2)$$

where Φ is a complicated function having the property that its variations with V and T are negligible compared with the variations of the rest of the expression. Similar considerations show that the variations of $\log i$ with E_0 are also determined essentially by the first term of Eq. (2), so that the relative rates of discharge of the two isotopes are given by

$$\log \alpha = \log (i_X/i_Y) = [(E_0)_X - (E_0)_Y]/\gamma kT. \quad (3)$$

α may be termed the efficiency of separation of the isotopes.

This equation predicts at once that the value of α should be independent of the nature of the cathode, and is thus in agreement with the experimental results for the separation of the hydrogen isotopes. It also agrees at least qualitatively with the actual magnitude of α . Taking the mean value as $\alpha = 0.2^7$ and putting $\gamma = 2$ (the value found by Gurney to give agreement with

the observed values of $d \log i/dV$), Eq. (3) leads to $(E_0)_H - (E_0)_D = 1900$ cal. per mole. This is a reasonable figure for the difference between the zero-point energies of H and D in the ions H_3O^+ and DH_2O^+ , and is not very different from the value of 1400 cal. given by Eyring and Sherman⁵ for the links O-H and O-D. It might be possible to obtain an accurate value for this difference from the Raman spectrum of the ion H_3O^+ , but the necessary data are not yet available.⁸ It may be pointed out that any theory in which the zero point energy is regarded as contributing directly to a heat of activation will lead to the expression

$$\log \alpha = [(E_0)_X - (E_0)_Y]/kT,$$

which will only give the experimental value of $\alpha = 0.2$ by giving $(E_0)_H - (E_0)_D$ the improbably low value of 950 cal. per mole.

The above treatment assumes that γ has exactly the same value for the two isotopes, which would probably not be justifiable in a strict examination of the problem. The significance of γ appears from Fig. 1. The upper curve represents the potential energy of the ion H_3O^+ plotted against the distance of one of the hydrogen atoms from the center of gravity of the rest of the molecule, while the lower curve repre-

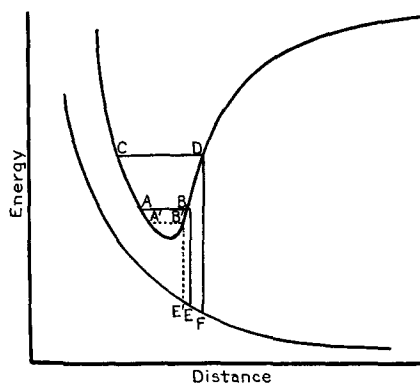


FIG. 1.

⁷ See G. N. Lewis and Macdonald, J. Chem. Phys. 1, 341 (1933); Bell and Wolfenden, reference 3, Topley and Eyring, reference 4.

⁸ The fundamental frequency in the Raman spectrum of H_2O leads to $(E_0)_H - (E_0)_D = 1600$ cal. per mole.

sents the potential energy of a discharged hydrogen atom at different distances from the center of gravity of an H_2O molecule. AB is the lowest vibrational level in the ion, and CD is the highest level to which an electron in the metal can make a transition. Gurney supposes that the curved portions EF and BD can be replaced by straight lines: if the ratio of the slopes of these straight lines is x , then $\gamma = 1 + x$. The potential

energy curves in the figure will be unaltered for the systems DH_2O^+ and $\text{D} + \text{H}_2\text{O}$, but the lowest energy state will now be somewhat lower, say at $A'B'$. The curved portions to be replaced by straight lines are now $E'F$ and $B'D$, and it is obvious from the general shape of the curves that the value of γ will be slightly greater than in the first case. Eq. (3) should therefore be replaced in general by the equation

$$\log \alpha = \frac{(E_0)_X - E_1 + \epsilon V}{\gamma_X kT} - \frac{(E_0)_Y - E_1 + \epsilon V}{\gamma_Y kT} + \log \frac{\gamma_X(\gamma_Y - 1)}{\gamma_Y(\gamma_X - 1)}, \quad (4)$$

where γ_X and γ_Y are slightly different. Without a knowledge of the exact form of the potential energy curves it is impossible to predict the magnitude of the difference between γ_H and γ_D , but it may be pointed out that since $E_0 - E_1 + \epsilon V$ has a value of the order of 20,000 cal. per mole, a very slight change in γ will produce a considerable difference in the value of α . Eq. (4) predicts that the separation factor will vary slightly with the work function E_1 (and hence with the nature of the cathode), and also with the potential V , so that it should be possible to decide by experiment how far the simple Eq. (3) is applicable. Meanwhile it is probably unwise to attach much importance to the exact value obtained for $(E_0)_H - (E_0)_D$ from Eq. (3).

Both Eq. (3) and Eq. (4) give for the variation of α with temperature

$$d \log \alpha / dT = -\alpha / T. \quad (5)$$

For the separation of hydrogen and deuterium, Eq. (5) predicts a decrease in efficiency of about 35 percent over the temperature range 0° – 100° . There are at present no accurate data on this point, but this figure is not incompatible with the results of Bell and Wolfenden.³

The above considerations will of course apply to the separation of any isotopes which can be discharged from a solvated ion. For a rough estimate of the efficiency of such a process for elements other than hydrogen, Eq. (3) will be sufficiently accurate and variations in γ may be neglected, so that the factor which essentially governs the separation is $(E_0)_X - (E_0)_Y$, the difference in the zero-point energies of the two

isotopes in the hydrated ions. This quantity may be written

$$\begin{aligned} (E_0)_X - (E_0)_Y &= \frac{1}{2} h \nu_X - \frac{1}{2} h \nu_Y \\ &= (h/4\pi)(f)^{\frac{1}{2}} \{1/M_X^{\frac{1}{2}} - 1/M_Y^{\frac{1}{2}}\} \end{aligned} \quad (6)$$

where f is the force constant of the link between the ion and the water molecule and M_X , M_Y are the reduced masses of the two isotopes. It is immediately obvious that the separation will in no case be as efficient as it is for the hydrogen isotopes, since both the force constant and the value of the expression in $\{ \dots \}$ will be smaller for all other elements. There are no data available for any reliable quantitative predictions, but the point may be illustrated by a very rough investigation of the possibility of separating the isotopes Li^6 and Li^7 by electrolysis. The heat of hydration of the H^+ ion is about 200,000 cal. per mole. The corresponding quantity (per water molecule) for the Li^+ ion is not known directly, but is probably about 15,000 cal.⁹ Assuming that the force constant is roughly proportional to the heat of hydration, Eq. (6) gives for the relative separation efficiencies

$$\frac{\log \alpha_{\text{Li}}}{\log \alpha_{\text{H}}} \sim \left(\frac{15,000}{200,000} \right)^{\frac{1}{2}} \left(\frac{1}{6^{\frac{1}{2}}} - \frac{1}{7^{\frac{1}{2}}} \right) / \left(1 - \frac{1}{2^{\frac{1}{2}}} \right)$$

which leads to $\alpha_{\text{Li}} = 0.96$. Thus in this case separation by electrolysis will probably be less efficient than other methods, and conditions will be still more unfavorable for heavier elements.

⁹ Estimated from the heat of hydration of the solid lithium halides.