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The Separation of the Hydrogen Isotopes by Electrolysis. Part I

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The equilibrium constants of the reactions $H_2O+2D=D_2O+2H$ and $H_2O+D_2O=2HDO$ are calculated and from these an expression is obtained for the electrolytic separation coefficient, valid when zero-point energy and tunnelling are negligible in the activated state. The change in this coefficient with increase in concentration of the heavy isotope is calculated. Experimental values have been determined for the separation coefficient at different metallic cathodes, ranging from 7.6 to 2.8. Local concentration disturbances round the cathode are not in general important, but may be the cause of the poor separation found with platinum black. The importance of half-quanta in the activated state is discussed. The experimental results considered in the light of the calculations indicate that tunnelling is not very important in the electrolytic separation. The vapor pressures of liquids containing isotopes are considered.

SECTION 1. INTRODUCTION

THE separation of the hydrogen isotopes by electrolysis of solutions of electrolytes in water depends essentially upon the removal of hydrogen from water molecules. The rapidity of the equilibrium reaction $2H_2O=H_3O^++OH^-$ compels us to consider the water as the fundamental source of the hydrogen evolved at the cathode.

Reactions at the anode come into question only insofar as the products of the anodic reactions diffuse to the cathode and modify the composition of the solution there. Confining attention to solutions which evolve hydrogen and oxygen in equivalent quantities, the only changes in the nature of the electrolyte during electrolysis are the increase in electrolyte concentration and the change in the relative number of H and D atoms. The effect of local changes in composition round the cathode depends upon the experimental conditions; this point is taken up in Section 3, where it is shown that under the usual conditions of experiment they may for practical purposes be ignored.

The "electrolytic separation coefficient" α is defined by

$$d \log \mathrm{H} = \alpha d \log \mathrm{D}. \tag{1}$$

When the mol fraction of electrolyte exceeds the atomic fraction of the isotope present in lesser amount, then the nature and concentration of the electrolyte will have some effect upon α. Experiment shows, however, that this effect is not a very large one.

SECTION 2. THEORY OF THE ELECTROLYTIC SEPARATION

In this section it is assumed that the solution surrounding the cathode is in thermodynamic equilibrium with the bulk of the solution (cf. Section 3) and that the mol fractions of all ionic species are small compared with the atomic fractions of both H and D.

The mechanism of the process at the cathode is not always the same in acid and alkaline solutions. For example, some of the hydrogen obtainable by electrolyzing a KOH solution with a mercury cathode is produced in a secondary reaction between the potassium amalgam and the water; similarly at a lead cathode it is usually supposed that a K-Pb alloy is formed initially, and at cathodes which show no tendency to form alloys with alkali metals, the metallic cation may nevertheless be preferentially discharged if the hydrogen overvoltage is high enough. In solutions of strong acids, direct discharge of hydrogen ions is the only possibility. The various theories of overvoltage proposed have all been designed primarily to explain the empirical relation between current density and overvoltage. The main difference between them concerns the decision as to which of the steps intervening between the original water molecules and the final hydrogen molecules is the slowest step.

We have to consider the consecutive stages:

(a) $$2H_2O = H_3O^+ + OH^-,$$

(b) $$H_3O^+ + M^- = H_2O + H - M,$$

(c) $$2H - M = H_2 + 2M.$$

Stage (b) is the neutralization of a hydrated hydrogen ion by the negatively charged metal *M*, with formation of a hydrogen atom attached in some way to the surface atom *M*. Stage (c) represents the desorption of hydrogen in the molecular form from the metal surface.

One theory of overvoltage assumes that (c) is the slow process, (a) and (b) being reversible and in equilibrium. This theory (the essentials of which were originally due to Tafel[1]) has since been modified in various directions, but for the discussion in this section, it is only important that (a) and (b) are assumed to be in equilibrium.

The well-known theories of Erdey-Gruz and Volmer[2] and of Gurney[3] both place the slow reaction at stage (b); they differ fundamentally in that the former associates the slowness with the passage of protons over a potential barrier lying midway across the Helmholtz double layer, and the latter attributes it to the slow penetration of electrons through a potential barrier of a different kind situated between the metal and the ions in the solution.

In the remainder of this paper (Part I) we discuss a number of points which are relevant to any mechanism in which the slow process involved the passage of hydrogen particles over or through the upper part of a potential barrier. We are not here thinking of a mechanism involving the slow leakage of the electrons through the potential barrier connected with the work function.

Corresponding to any special theory of the mechanism of the cathode process there is some definite activated state with which the overvoltage is correlated. Consider first the simplest case, where the activated state consists of entirely free hydrogen atoms. The reaction at the cathode cannot really involve such free atoms because the activation energy would then be prohibitively large, but the calculation forms a basis on which the consideration of mechanisms involving different activated states can be built; this calculation also applies to any activated state which fulfills two conditions: (a) that the total zero point energy in the activated state is zero, (b) that quantum mechanical leakage of the hydrogen particles through the potential barrier is negligible in comparison with the rate at which they pass over the barrier. By combining the result of this calculation with experimental values for the electrolytic separation coefficient we have a new possibility of deducing properties of the activated state.

We make the usual assumption for reaction rates,[4] that the rate of the slow process is the same when the reaction is proceeding irreversibly, in the forward direction only, as the rate in either one direction at equilibrium. This rate is the number of particles in the activated state at equilibrium multiplied by the average velocity with which they travel in the forward direction. Since for our present problem we require only the relative reaction rates of the two isotopes, we first calculate the equilibrium ratio of H to D atoms (and H^+ to D^+ ions) in free space, in equilibrium with water containing H_2O, HDO and D_2O.

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[1] Tafel, Zeits. f. physik. Chemie **34**, 200 (1900); **50**, 641 (1905).

[2] Erdey-Gruz and Volmer, Zeits. f. physik. Chemie **A150**, 209 (1930).

[3] Gurney, Proc. Roy. Soc. **A134**, 137 (1932).

[4] Tolman, *Statistical Mechanics*, p. 269 (1926).

Consider the equilibria

$$H_2O+2D=D_2O+2H, \tag{1a}$$

$$H_2O+D_2O=2HDO, \tag{1b}$$

with equilibrium constants in the gas phase K_a and K_b, respectively.

In the equations which follow, and throughout this paper, the subscripts 1, 2, 0, 3, 4 will be used to indicate the following molecular species in order: H_2O, D_2O, HDO, H and D.

We write

$$K_a=F_2F_3^2/F_1F_4^2,$$

where the partition function for H_2O in the gas phase is

$$F_1=\exp\frac{+\zeta_1}{kT}\,\frac{(2\pi m_1kT)^{\frac{3}{2}}}{h^3}\,\frac{8\pi^2(8\pi^3A_1B_1C_1)^{\frac{1}{2}}}{2h^3}$$
$$\times(kT)^{\frac{3}{2}}\prod_{i=j_1,\,k_1,\,l_1}\frac{1}{1-\exp\left(-h\nu_i/kT\right)}\times 4, \tag{2}$$

where $-\zeta_1$=energy of H_2O in its lowest state, the zero of energy being the three atoms in their lowest states; m_1=mass of H_2O molecule; A_1, B_1, C_1, =moments of inertia of H_2O molecule; the ν's with subscripts j_1, k_1, l_1, denote the vibration frequencies of the H_2O molecule; h and k are the Planck and Boltzmann constants.

$$F_3=[(2\pi m_3kT)^{\frac{3}{2}}/h^3]4. \tag{3}$$

The partition functions F_{D_2O} and F_D are similar, except that the statistical weights 4 and 4 become 9 and 6 for D_2O and D, respectively. Since, with the vibration frequencies characteristic of D_2O the quantities $\exp\left(-h\nu/kt\right)$ are practically negligible in comparison with unity, even at 100°C, we find for K_a

$$K_a=\exp\left(\frac{+\zeta_2-\zeta_1}{kT}\right)\left(\frac{m_2}{m_1}\right)^{\frac{3}{2}}\left(\frac{m_3}{m_4}\right)^3\left(\frac{A_2B_2C_2}{A_1B_1C_1}\right)^{\frac{1}{2}}, \tag{4}$$

the subscripts having the meanings already given.

For the equilibrium in the gas phase of the three kinds of water molecules we have

$$K_b=F_0^2/F_1F_2. \tag{5}$$

The partition function F_0 is the same as F_1 with the substitution of the appropriate vibration frequencies, and the mass m_0, energy $-\zeta_0$, and moments of inertia A_0, B_0, C_0, of the HDO molecule, except that the symmetry number 2 is omitted and the statistical weight is 6 instead of 4. We then have for K_b

$$K_b=\exp\frac{(+2\zeta_0-\zeta_1-\zeta_2)}{kT}\left(\frac{m_0^2}{m_1m_2}\right)^{\frac{3}{2}}$$
$$\times\frac{A_0B_0C_0}{(A_1B_1C_1A_2B_2C_2)^{\frac{1}{2}}}\times 4. \tag{6}$$

The quantities $-\zeta_1$, $-\zeta_0$ and $-\zeta_2$ enter into Eqs. (4) and (6) as differences, and since the potential function is the same for isotopic molecules,* we have only to consider the differences in the zero-point energies involved, i.e., the half-quanta for the three normal modes of vibration of each molecule. For the molecule H_2O we have taken the values obtained by Mecke[5] and his collaborators in their analysis of the infrared absorption of water vapor.

To obtain the frequencies for the isotopic molecules HDO and D_2O we have made use of the very helpful statement of the problem of the three particle system recently published by Van Vleck and Cross.[6] These authors also carried

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* We are here neglecting the change in the force constants in the water molecule caused by the mass difference between H and D. The effect can be estimated on the basis of the Heitler-London theory of binding. For a hydrogen atom the potential energy with respect to the oxygen atom is $E=(1/a_m)f(r/a_m)$ where r is the internuclear distance and a_m is the geometric mean of the quantum mechanical analogues of the Bohr orbits of the valence electrons on hydrogen and oxygen. The same function applies to the binding energy of a heavy hydrogen atom, but the new value of a_m is slightly smaller, since $a=h^2/4\pi^2\mu e^2$ where μ is the reduced mass of the electron in the H or D atom, and a is the (quantum-mechanical) orbit of the atom concerned. Since (a_mE) is the same function of r/a_m for both H and D, the potential energy is a minimum at the same value of r/a_m and $E_{\min}$ is inversely proportional to a_m, whilst $r_{\min}$ is proportional to a_m. Thus from this cause the difference $|\zeta_2-\zeta_1|$ is increased by 30 calories and the nuclear distance of OD as compared with OH is decreased by 0.00027 Angstrom. The latter decrease makes only a negligible difference to the moments of inertia. In the calculation which follows we neglect also the effect of the correction to the energy, which would amount to about 2.5 percent in the value of the separation coefficient.

[5] Mecke, Baumann and Freudenberg, Zeits. f. Physik **81**, 313, 445, 465 (1933).

[6] Van Vleck and Cross, J. Chem. Phys. **1**, 353, 357 (1933).

through a theoretical quantum-mechanical calculation of the potential function of the H_2O molecule, and with the corresponding force constants calculated the three frequencies to be $\omega_\sigma = 3520$, $\omega_\pi = 3560$, $\omega_\delta = 1660$ reciprocal cm (we are here using the subscripts employed by Mecke). The nuclear separation between H and O came out to 1.00 Angstrom, and the valence angle to 100°. Using the same molecular constants, we have repeated the calculation of the frequencies for all three molecules H_2O, HDO and D_2O. The results for HDO are $\omega_\sigma = 3560$, $\omega_\pi = 2600$, $\omega_\delta = 1450$, and for D_2O $\omega_\sigma = 2580$, $\omega_\pi = 2590$, $\omega_\delta = 1250$. As Van Vleck and Cross point out, complete quantitative agreement with experiment is not to be expected in view of the approximations necessary in their quantum-mechanical calculation. We do, however, expect that *the relative values of corresponding frequencies* in H_2O, HDO and D_2O will be fairly accurately given by the calculation, in spite of the differences of 5 and 3 percent, respectively, between the valence angle and the nuclear distance calculated by Van Vleck and Cross, and those found by Mecke, Baumann and Freudenberg. Accordingly we have taken the calculated ratios of ω_σ for H_2O : ω_σ for HDO : ω_σ for D_2O (similarly for the ω_π's and the ω_δ's) and multiplied the frequencies found by Mecke and his collaborators by the appropriate ratios. In this way we arrive at the consistent set of frequencies set out in Table I. These frequencies compare in a very reasonable way with the Raman bands in liquid heavy water observed by R. W. Wood,[7] which are included in Table I in square brackets. The Raman frequencies are naturally all somewhat lower in the liquid than in the vapor.

Mecke and his collaborators show that the moments of inertia of the molecule change slightly with the vibrational level, and in the ground state are not exactly what they would be for a rigid structure, because of the half-quanta of vibration. The difference is small, and we consider that a set of consistent moments of inertia of quite sufficient accuracy for our purpose can be obtained by taking the valence angle of 105° 6′ and the nuclear distance of 0.970 Angstrom found by Mecke for the ground state, and calculating the three moments of inertia for each of the three isotopic water molecules, using H = 1.00777, D = 2.01357, O = 16. For comparison, the values (multiplied by 10^{40}) given by Mecke for the ground state of H_2O are: $A = 0.995$, $B = 1.908$, $C = 2.980$. The axis of least moment of inertia in HDO makes an angle of 20° 38′ with the line joining the H and D nuclei.

TABLE I.

	Frequencies in cm^{-1}			Moments of inertia $\times 10^{40}$ A	B	C
H_2O	3795 [3445]	3670	1615	1.027	1.972	2.999
HDO	3838 [3500]	2680 [2623]	1411	1.219	3.142	4.361
D_2O	2782 [2517]	2670	1216	1.846	3.938	5.784

With these data Eqs. (4) and (6) give for the equilibrium constants $K_a = 126.9$ at 25° and 49.60 at 100°, $K_b = 3.26$ at 25° and 3.40 at 100°.

With regard to the reliability of these equilibrium constants, we think that since the molecules have practically the same potential function, the case is a very favorable one; the accuracy of the K's turns on the accuracy of the vibration frequencies; our opinion is that the equilibrium constants should be accurate to within ±10 percent.

A knowledge of K_a and K_b enables us to calculate the ratio $N_3°/N_4°$ of free atoms of H and D in equilibrium with water vapor of any isotopic composition. We require, however, an expression for $N_3°/N_4°$ as a function of the (analytical) composition of the liquid water.

For the equilibrium in the liquid phase we have (assuming Henry's law)

$$K_b' = N_0^2/N_1N_2 = [p_1°p_2°/(p_0°)^2]p_0^2/p_1p_2. \quad (8)$$

The $p°$'s denote vapor pressures of the pure species, and the p's partial vapor pressures. The vapor pressure of pure D_2O is known[8] over the range 20° to 110°. A direct measurement of $p_0°$ is of course impossible because of the rapidity with which the equilibrium (1b) is established through ionization. In Section 4 reasons are

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[7] R. W. Wood, Science **79**, 35 (1934).

[8] Lewis and Macdonald, J. A. C. S. **55**, 3057 (1933).

given for the assumption we now make, that the vapor pressure for the pure species HDO is the geometric mean of the vapor pressure of H_2O and D_2O. This makes the quantity in square brackets in (8) equal to unity, and therefore makes $K_b'=K_b$.

The relationships which we now write down are derived simply by combining together the expression for K_a and K_b in (1a) and (1b), the assumption of Henry's law, and the assumption that $K_b'=K_b$. The use of concentrations and pressures instead of activities is evidently allowable with such similar molecules. Writing R_e for the ratio of the (atomic) amounts of H to D in the liquid, and R_g for the corresponding ratio in the vapor:

$$\begin{aligned} R_g &= (2G_1+G_0)/(2G_2+G_0) \\ &= (2N_1p_1^\circ+N_0p_0^\circ)/(2N_2p_2^\circ+N_0p_0^\circ). \end{aligned} \quad (9)$$

G_1, G_0, and G_2 are the mol fractions of H_2O, HDO, and D_2O in the vapor phase, and the N's are the mol fractions in the liquid.

$$\begin{aligned} R_g = {} & [\beta(p_0^\circ-p_1^\circ)+p_1^\circ] \\ & /[\beta(p_0^\circ-p_2^\circ)+p_2^\circ/R_e], \end{aligned} \quad (10a)$$

where

$$\begin{aligned} \beta = {} & \left\{\frac{-K_b'}{4-K_b'}\,\frac{1+1/R_e}{2}\right\} \\ & \pm\left\{\left(\frac{K_b'}{4-K_b'}\,\frac{1+1/R_e}{2}\right)^2+\frac{K_b'}{4-K_b'}\,\frac{1}{R_e}\right\}^{\frac{1}{2}}, \end{aligned} \quad (10b)$$

positive root when $K_b'<4$, negative root when $K_b'>4$. When $K_b'=4$ (as it would be if the two kinds of hydrogen atoms were distributed at random among the oxygen atoms) then

$$\beta=1/(1+R_e). \quad (10c)$$

For the required ratio of n_3°/n_4° in the gas phase we find

$$\frac{n_3^\circ}{n_4^\circ}=K_a^{\frac{1}{2}}R_g\frac{2+(K_b')^{\frac{1}{2}}A}{2A+(K_b')^{\frac{1}{2}}}, \quad (11a)$$

in which R_g is explicitly given by Eqs. (10a, b, c) and

$$A=[(p_1^\circ(1-\beta))/(p_2^\circ(1/R_e-\beta))]^{\frac{1}{2}}, \quad (11b)$$

where β is given by (10b) or (10c).

Since the ionization potential of D exceeds that of H by 84 calories per gram-atom, the equilibrium ratio of H^+ to D^+ in free space is equal to $n_3^\circ/n_4^\circ \exp(84/RT)$.

We recall that the electrolytic separation coefficient for any process subject to two limitations, namely that the activated state consists of hydrogen atoms or ions without zero-point energy, and that quantum-mechanical leakage through the potential barrier defining the energy of activation is negligible, is given by:

$$\begin{aligned} \alpha^\circ &= d\log \mathrm{H}/d\log \mathrm{D}=(1/R_e)d\mathrm{H}/d\mathrm{D} \\ &= (1.414/R_e)n_3^\circ/n_4^\circ. \end{aligned} \quad (12)$$

The symbols H and D denote the content (in g atoms) of the isotopes in the liquid undergoing electrolysis, and the superscripts ° indicate the limitations just stated under which α° is given by this expression. The factor 1.414 enters because the relative rates at which particles of H and D pass out of the activated state are inversely as the square root of their masses. The ratio n_3°/n_4° now refers to free atoms or free ions according to which is postulated for the activated state.

Examination of Eq. (11a) shows that in general α° varies with the ratio R_e of H to D. The limiting values of α° in very dilute heavy water on the one hand, and nearly pure heavy water on the other, are

$$1.414K_a^{\frac{1}{2}}(p_1^\circ/p_2^\circ)^{\frac{1}{2}}(K_b'/2) \qquad (\text{As } R_e\to\infty),$$

$$1.414K_a^{\frac{1}{2}}(p_1^\circ/p_2^\circ)^{\frac{1}{2}}(2/K_b') \qquad (\text{As } R_e\to 0).$$

Table II exhibits the dependence of α° upon the isotopic composition of the liquid. The figures taken in order along each row show in outline how α° changes as the proportion of the heavy isotope increases from 0 to 100 percent, for the values of K_b' indicated on the left. The calculation has been made for the activated state consisting of free ions; for free atoms the figures are 14 percent less at 25° and 8.4 percent less at 100°.

It will be noticed that when $K_b'=4$ the efficiency of the separation is the same over the whole range of composition. Also for electrolysis of water in the neighborhood of 50 percent D, the efficiency is independent of the value of K_b', and has the same numerical value as it has for all compositions when $K_b'=4$.

TABLE II.

K_b'	%D =	0	10	50	90	100
				Temperature 25°		
2	$\alpha^\circ =$	13.77	16.23	19.46	25.20	27.52
3.3	$\alpha^\circ =$	17.68	18.66	19.46	20.99	21.42
4	$\alpha^\circ =$	19.46	19.46	19.46	19.46	19.46
5	$\alpha^\circ =$	21.74	20.65	19.46	17.51	17.41
				Temperature 100°		
2	$\alpha^\circ =$	8.03	9.81	11.07	14.37	15.65
3.3	$\alpha^\circ =$	10.06	10.61	11.07	12.06	12.17
4	$\alpha^\circ =$	11.07	11.07	11.07	11.07	11.07
5	$\alpha^\circ =$	12.37	11.74	11.07	10.01	9.90

The figures set out in Table II have a more general significance than appears at first sight. As they stand, they refer to any separation process in which the activated state consists essentially of free ions (or, subject to the factor exp $(84/RT)$, to free atoms also). In reality, the activated state is never simply this: the hydrogen particles in the activated state are those just at the top of some potential barrier characteristic of the particular slow process which is controlling the reaction rate, and depending for its form and magnitude upon the nature of the cathode surface, and possibly upon the applied cathodic overvoltage. We therefore consider a direct equilibrium between the particles in free space and the particles in the actual activated state, in which they are present at some other relative concentration n_3/n_4 differing from n_3°/n_4°. We write

$$n_3/n_4 = K_c n_3^\circ/n_4^\circ, \tag{13}$$

where K_c is an equilibrium constant analogous to a distribution coefficient between two phases. To calculate the actual electrolytic separation coefficient α, we have only to multiply α° by the corresponding value of K_c.

The factors determining K_c are discussed in Section 5. The energy of a given particle in the activated state at the cathode surface or in the Helmholtz double layer will not be appreciably affected by the substitution of D for H in the solution. Thus we can look upon α as being the product of two independent factors, one a property of the activated state only, the other a property of the ground state only (i.e., the interior of the solution).

It follows that for all these mechanisms the electrolytic separation coefficient will vary with the composition of the solution quantitatively in the same way.

Our calculation of K_b' gave a value 3.3 at 25°. Reference to Table II shows that this requires that α shall decrease slightly as the composition of the water varies from 0 to 100 percent D; corresponding to the estimated ±10 percent uncertainty in K_b', we conclude that α should decrease by a fractional amount lying between 10 and 30 percent of its value in very dilute heavy water. This is a theoretical conclusion which has not yet been properly tested by experiment. The available evidence shows that (in the case of electrolysis of dilute alkali hydroxide solutions with nickel cathodes at about 10°) there is not much change in α as the percentage of heavy isotope increases; the data are consistent with the theoretical prediction.

	Atomic percent D	α
Bell and Wolfenden[9]	0.2	4–6
This paper	7	5.2–5.8
Selwood[10]	97	5.5–6.5

The theory of the variation of α with the nature and concentration of electrolyte can be treated in a manner similar to the discussion in this section, but it is much more complex. It is an interesting point that measurements of the electrolyte separation coefficient can be utilized to investigate the thermodynamics properties of certain solutions, at least in principle.

SECTION 3. EXPERIMENTAL

The measurements reported in this section were done with the practical aim of finding the most efficient conditions for concentrating the heavy isotope. An accuracy of about 5 percent in the electrolytic separation coefficient was obtained.

The form of apparatus found most satisfactory is illustrated in Fig. 1. Samples of electrolyte (about 75 cc) are weighed into the electrolysis vessel, and occupy the wider part A; this is cooled (or heated) by surrounding it up to the level B with a suitable bath. The condenser C is needed only when the electrolysis is done above room temperature.

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[9] Bell and Wolfenden, Nature **133**, 25 (1934).

[10] Selwood, personal communication.

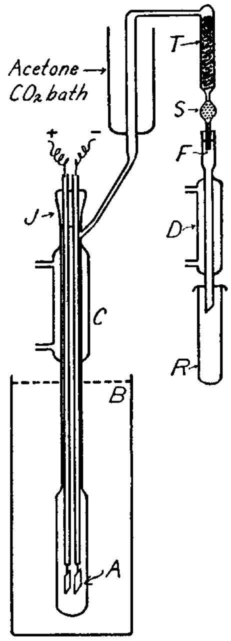

FIG. 1.

About 10 cc of water is electrolyzed and the electrolytic gas burns in a minute flame at the jet *F*. The water formed is condensed in the small condenser *D* and collected in a weighed tube *R*, which is closed with a tin-foil cover. The electrolytic separation coefficient is calculated from the relationship:

$$\alpha = (\log W_{\mathrm{H}} - \log W_{\mathrm{H}}')/(\log W_{\mathrm{D}} - \log W_{\mathrm{D}}'),$$

where W_{H}, W_{D}, and W_{H}', W_{D}' are the weights of H and D in the solution before and after a portion of the water has been electrolyzed away.

The ground joint *J* is not greased but is sealed externally with a thin ring of picein wax. The stream of electrolytic gas passes out of the electrolysis vessel at the temperature of the coldest part of the vessel (about 5° in the majority of the experiments) and loses the water vapor it carries in passing through the vertical trap surrounded by acetone and solid CO_2. The dried gas passes through a spray trap *T* packed with absorbent cotton, and then through a 10 cc bulb filled with fine sand, to the jet *F* inside the condenser *D*. This amount of sand is completely effective in extinguishing the detonation wave which fires back from the jet whenever the gas flow speed is reduced below a critical limit. This simple device has proved completely satisfactory in eliminating all risk of explosion originating at the jet. The jets are made simply by partially fusing the end of a piece of thick-walled Pyrex

TABLE III.

Cathode	Apparent current density	Electrolyte	Atomic % of D	α
Pb	1 (a)	KOH ½N	7	7.4
Pb	1 (a)	" "	8	7.2
Pb	1.3 (s)	H_2SO_4 "	8	6.2
Pb	1.3 (s)	" "	9	6.6
Pb	1.5 (b)	" "	12	6.3
Pt	1 (s)	KOH "	7	7.6
Pt	1 (s)	" "	8	6.5
Pt	1 (s)	H_2SO_4 "	8	5.7
Pt	1 (s)	" "	9	5.7
Pt	14 (b)	" "	8	5.7
Pt	14 (b)	" ¾N	12	6.4
Pt	14 (b)	" 1N	18	6.3
Pt (black)	2	" ½N	12	4.6
Pt (black)	2	" ¾N	15	4.7
Pt (black)	2	" 1N	21	4.7
Pt (activated)	4	" ½N	7	4.7
Pt (activated)	4	" ¾N	9	4.7
Pt (activated)	32	" ½N	8	3.4
Pt (activated)	32	" 1N	11	3.6
W	6 (b)	" ½N	12	5.3
Fe	1 (s)	KOH ½N	7	7.6
Fe	1 (s)	" "	8	6.9
Ni	1 (s)	" "	7	5.5
Cu	1 (s)	KOH ½N	7	6.8
Cu	1 (s)	H_2SO_4 ½N	7	5.5
Cu	1 (s)	" ¾N	8	5.8
Ag	1 (s)	KOH ½N	7	5.3
Ag	1 (s)	" "	8	5.8
Ag (c)	1 (s)	H_2SO_4 "	8	6.0
Ag (c)	1 (s)	" "	10	5.6
Hg	0.7	" "	8	2.8
Hg	0.7	" "	9	2.9
Hg	0.7	" ¾N	10	2.7
Hg	0.7	" 1N	15	2.8
Ga (supercooled)	1.5	" ½N	8	4.1
Ga (supercooled)	1.5	" "	10	4.6

(a) metal disintegrates; (b) smooth surface; (s) surface roughened with sandpaper; (c) metal blackened during use.

capillary so that the diameter of the orifice is about 1/15 mm.

The condensed water is always slightly acid with nitrogen oxides formed at the outer surface of the flame. The water produced was weighed, then made alkaline with a few mg of anhydrous sodium carbonate, and a few crystals of potassium permanganate added. The solution is boiled for a short time to free it from CO_2 and then distilled, avoiding bubble-formation as far as possible. The specific gravity was determined in a 6 cc pycnometer to an accuracy of 2 parts in a hundred thousand. The composition of the water was calculated on the basis of the figure 1.1056 for pure D_2O ($d_{25}{}^{25}$) assuming a linear relationship between composition and specific gravity.

In making up the electrolyte solutions the heavy water mixture was twice distilled from slightly alkaline permanganate before use. Ordinary C.P. potassium hydroxide and sulphuric acid were used, the acid having first been subjected to electrolysis for some time to remove metallic impurities.

In some of the experiments the water vapor was not frozen out of the gas stream; in these cases the whole of the vapor carried by the gas is of course condensed out along with the water formed in the flame, since the system operates at constant volume, being in fact normally closed by a drop of water hanging at the exit of the tube from the condenser D. A correction is therefore very easily applied to take account of this source of slight error.

The experimental results are recorded in a condensed form in Table III. The temperature of the electrolyte was between 10° and 26° in all cases, and it is sufficiently close to compare the results on the supposition that the temperature was in the neighborhood of 20°.

The second column gives the apparent current density in amperes per sq. cm when no allowance is made for the actual condition of the surface. Some idea of the relative current densities is obtained by taking into account the notes referred to by letters in brackets following the figures. The composition of the solution with respect to electrolyte is given in the third column, and with respect to the isotopic content in the fourth. These are average values during the electrolysis of the 10 cc samples. The last column gives the values of the electrolytic separation coefficient α.

The main conclusion is that there are very considerable differences between different metals, the order of efficiency taking a general view of the figures both for acid and alkaline solutions being: Pt and Pb; Fe; Cu and Ag; Ni; W; liquid Ga; Hg. Platinum black and "activated" platinum are omitted from this series for the reason discussed below.

The results for bright platinum show that the current density can be varied considerably without much affecting the efficiency. This has also been commented on in the case of nickel cathodes and alkali hydroxide solutions by Urey,[11] and by Bell and Wolfenden.[9]

The results for mercury and for bright platinum show that the electrolyte concentration and the proportion of heavy isotope can be doubled without noticeable effect on the efficiency. In general the value of α is about 15 to 20 percent lower for the same metal in the acid than in the alkaline solution; silver is only an apparent exception, since during the electrolysis in sulphuric acid the metal is blackened, presumably because of slight cathodic reduction to sulphide, so that the surface of the cathode is no longer simply silver.

The "platinum black" electrodes were prepared in the usual way by deposition from a platinic chloride solution, without addition of any lead acetate. The electrodes referred to as "activated" were also platinum electrodes covered by a grey-black deposit of platinum, but the activation of the surface was the result of electrolyzing for some time with alternating current of 60 cycles.

Electrolysis of water by 60 cycle alternating current has been studied by Shipley and Goodeve,[12] who found that a large proportion of the electrical energy could be used to effect gas evolution. Our experience was, that although this is so for a short time, the electrodes soon became so strongly activated that the yield of gas fell to practically nothing. This applies both

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[11] H. C. Urey, Science **78**, 566 (1933).

[12] Shipley and Goodeve, Trans. Am. Electrochem. Soc. **52**, 375 (1927).

to platinum and to silver electrodes; the latter, as Shipley and Goodeve found, are not seriously corroded; nevertheless silver becomes in time extremely active in causing the recombination of the electrolysis products.

The local concentration of heavy water at the cathode

During electrolysis the liquid round the cathode tends to increase in content of D relative to the main bulk of the solution, since the mobilities of the different kinds of hydrogen ion are not very different,[13] but the light isotope is preferentially discharged. This tendency is offset in several ways: by stirring of the solution by the gas evolved, by convection caused by temperature inequality, and by diffusion. With current densities such as are used in practice there is certainly vigorous stirring of the bulk of the liquid by the stream of bubbles leaving the electrodes. It may be, however, that whilst discharge of ions takes place all over the surface, the actual growth and detachment of bubbles tends to occur mainly at certain favored places, the hydrogen atoms or molecules moving over the metal surface to these places. In that case there would be a very thin layer of liquid covering parts of the cathode surface relatively remote from the places of bubble formation, which would not be effectively stirred. In such a stagnant layer mixing would take place mainly by convection and diffusion. As regards convection, there is a liberation of about one-tenth of a calorie per second per volt overvoltage for a current density of 1 ampere per sq. cm, but the greater part of this will be taken up by the metal in the first place.

As regards diffusion, an estimate of the effect to be expected can be made in the following way: we assume that covering the greater part of the cathode surface there is a thin layer of liquid which does not suffer mixing into the main bulk of the solution either by mechanical means or by thermal convection. Outside this layer there is complete mixing by the stream of bubbles.

A stationary state will then be set up in which a definite composition is maintained at the boundary of the layer, and a definite diffusion gradient is established across the layer. The conditions for such a stationary state *in a solution of an acid* are that the *whole of the current across the boundary must be carried by hydrogen ions*, and that the rate of neutralization of ions of each isotope is equal to the rate of migration of the isotope into the layer minus the rate of diffusion of the isotope out of the layer.

It is sufficient to consider the special case of a dilute solution of a strong acid, in water containing a small proportion of D.

Let C_H, C_D, and C_H', C_D' define the isotopic composition of the liquid, expressed in g atoms of H and D per cc in the bulk of the solution, and at the surface of the metal, respectively. Practically the whole of the D isotope is in the form of HDO molecules, and we assume for the purpose of obtaining a rough estimate, that the relative numbers of H and D ions at any place are in the ratio of the total H and D concentrations at that place. We neglect the transport of water arising from hydration of the ions. For the stationary state we have

$$\frac{K}{x_0}(C_D - C_D') \approx \frac{I}{F}\left(\frac{C_D'}{C_D' + \alpha C_D'} - \frac{C_D}{C_D + C_H}\right), \quad (14)$$

where K = diffusion coefficient of HDO in H_2O, in cm^2 sec.$^{-1}$; I = current density in amperes per sq. cm; F = the Faraday, α = the electrolytic separation coefficient; x_0 = thickness of stagnant layer, in cm. It is reasonable to ignore the effect of the difference between C_D' and C_D provided this difference does not amount to more than say 2 percent. We use Eq. (14) to estimate in a typical case what thickness x_0 of the unstirred layer would be required to produce a 2 percent excess of C_D' over C_D. We take:

$$C_D/(C_D + C_H) = 0.05; \quad C_D'/C_D = 1.02; \quad I = 1;$$

$$\alpha = 7; \quad K = 2.5 \times 10^{-5}.$$

This gives $x_0 \approx 4 \times 10^{-3}$ cm. It is not obvious than an unstirred layer of this thickness may not cover part of the surface, and it is therefore possible that the experimental values of α are a little lower through this cause, than the correct value, which would be found at much lower current densities.

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[13] Lewis and Doody, J. A. C. S. **55**, 3504 (1933).

According to Eq. (14) the value of x_0 remains of the same order of magnitude as α increases from about 2 to infinity.

The experimental results, indicate that the effect of local concentration round the cathode is small: thus when the current density at a smooth platinum electrode is increased 14-fold, there is no decrease in α whereas Eq. (14) indicates a decrease depending upon the value of x_0. We conclude that with smooth metal cathodes the effect of any local increase in concentration in heavy water can be neglected in determinations of α which on other grounds do not claim an accuracy greater than about 5 percent.

When the cathode surface possesses a very irregular structure, as for example when a metal is coated with platinum black, the situation is different. The tendency will be for ions to be discharged at the outer points, but insofar as any electrolysis takes place within the irregular shaped cavities, stirring, convection and diffusion will all be much less effective. This would account for the low efficiency of the separation on platinized platinum cathodes, and the explanation is supported by the fact that increase of current density in this case did lower the efficiency still further.

SECTION 4. THE VAPOR PRESSURE OF LIQUIDS CONTAINING ISOTOPIC MOLECULES

In Section 2 the assumption was made that the vapor pressure of pure HDO ($p_0°$) would be the geometric mean of the vapor pressures of H_2O ($p_1°$) and D_2O ($p_2°$). It happens that in this particular case examination of the numerical magnitudes involved shows that so far as the requirements of the argument in Section 2 are concerned, the situation is much the same if one merely assumes that $p_0°$ lies somewhere near the mean of $p_1°$ and $p_2°$, because in the range 20° to 110° $p_2°/p_1°$ is of the order 0.9.

It is, however, desirable to discuss the relative vapor pressures of liquids that differ only in having different isotopic atoms in their molecules. We formulate the discussion in terms of the particular example water, applying the conclusions reached to the question of the vapor pressure of the species HDO.

The partition function for an isolated H_2O molecule in the gas phase is

$$f_1 = \exp\frac{-\chi_1}{k\nu}\,\frac{(2\pi m_1 kT)^{\frac{3}{2}}}{h^3}V_1 \prod_{i=j_1,\,k_1,\,l_1}\frac{1}{1-\exp\left(-h\nu_i/kT\right)}\,\frac{8\pi^2(8\pi^3 A_1B_1C_1)^{\frac{1}{2}}(kT)^{\frac{3}{2}}}{2h^3}\cdot 4, \tag{15}$$

where χ_1 = the energy in its lowest state of an H_2O molecule, the zero of energy being the same molecule in its lowest state in the liquid. V_1 = the accessible volume per molecule in the gas phase.

The other symbols have the meanings defined for Eq. (2). Ideally we should solve the mechanical problem for the whole mass of water and use the normal modes of quasi-oscillation and with these the appropriate expressions $1/1-\exp(-h\nu_i/kT)$ to replace the translational part of (15). Instead of the complete treatment, which is not possible, we write for the partition function of a molecule in liquid water:

$$g_1 = \prod_{i=m_1,\,n_1,\,o_1}\frac{1}{1-\exp\left(-h\nu_i/kT\right)}\prod_{i=r_1,\,s_1,\,t_1}\frac{1}{1-\exp\left(-h\nu_i/kT\right)}\,\frac{8\pi^2(8\pi^3 A_1'B_1'C_1')^{\frac{1}{2}}}{2h^3}(kT)^{\frac{3}{2}}\cdot 4, \tag{16}$$

where the ν's with the subscripts m_1, n_1, o_1, denote the internal vibration frequencies of the H_2O molecule in liquid water, and the subscripts r_1, s_1, t_1, denote the three frequencies of quasi-oscillation of the molecule as a whole.

A_1', B_1', C_1' are the moments of inertia of the H_2O molecule in the liquid.

In g_1 the three frequencies with the subscripts r_1, s_1, t_1 are identified as the quasi-oscillatory motion of a simple molecule in the potential field of the surrounding molecules, but they can be thought of as averaged values of the quasi-frequencies in a large aggregate of liquid molecules. The condition that the vapor shall be saturated is $f_1 = g_1$. Assuming that the saturated vapor has the molar volume of a perfect gas, we can write $V_1 = kT/p_1^\circ$ and obtain at once an expression for the vapor pressure of the liquid. Similar expressions can be written for the vapor pressures p_0° and p_2° of liquid HDO and D_2O, replacing the subscripts 1 by 0 or by 2 wherever it occurs in the partition functions.

Water vapor is a very imperfect gas, so that we ought in the vapor pressure equation to take account of interactions between gas molecules as well as between molecules in the liquid. The use of a harmonic oscillator and Planck functions for intermolecular motion in the partition function of a liquid is also a very approximate procedure, but our conclusion which depends on the differences between molecules containing isotopes would not be invalidated by modifications in these details.

A liquid is a system intermediate between a gas and a solid, and a range of possible simplified mechanical models can be imagined which approach more or less closely one of two extremes. In the case of water we utilize the measurements recently made by Lewis and Macdonald[14] of the vapor pressure of pure D_2O to obtain at least a clear indication of the proper choice of idealized mechanical model from which to calculate the vapor pressure of pure HDO.

The experimental data are reproduced by the equation

$$p_2^\circ/p_1^\circ = 1.35 \exp(-259/RT) \qquad (17)$$

in the range 20° to 90°. The fact that the latent heat of evaporation is larger for the heavier molecule, in spite of the intermolecular forces being the same, is in part to be attributed to the lower zero-point energy of the quasi-oscillations of the heavier molecule. The generalization that as between chemically similar substances the one of higher molecular weight usually vaporizes at higher temperatures is a manifestation of the part played by the zero-point energy in the latent heat of vaporization.[15]

We consider first the interpretation of the factor 1.35 in Eq. (17), and for this purpose we can compare the figure 1.35 with the different numerical factors obtained by making different extreme assumptions as to the molecular mechanics of the liquid.

Case I

The molecules rotate freely in the liquid as in the gas, and have the same moments of inertia. The frequencies of the quasi-oscillation (as well as the internal frequencies) are such that $h\nu > kT$. Then from the partition functions (15) and (16) we obtain for the ratio of the vapor pressures of D_2O and H_2O

$$\begin{aligned} p_2^\circ/p_1^\circ &= (m_2/m_1)^{\frac{3}{2}} \exp((-\chi_2+\chi_1)/kT) \\ &= 1.17 \exp((-\chi_2+\chi_1)/kT). \qquad (18) \end{aligned}$$

Case II

This differs from Case I only in the assumption that for the quasi-oscillation frequencies we have the relationship $h\nu \ll kT$; whence

$$\frac{1}{1-\exp(-h\nu/kT)} \approx \frac{kT}{h\nu} = \frac{2\pi kTm^{\frac{1}{2}}}{hK^{\frac{1}{2}}}$$

where m is the mass and K the force constant of the quasi-oscillator considered. The assumption of so low a frequency is of course physically equivalent to assuming practically free translation. This leads to

$$p_2^\circ/p_1^\circ = \exp(-\chi_2+\chi_1)/kT. \qquad (19)$$

Case III

Here we assume that the rotational degrees of freedom in the gas are in the liquid replaced by oscillation for which $h\nu > kT$, and that there are no lateral quasi-oscillations of type assumed in Case I. This gives us

$$\begin{aligned} \frac{p_2^\circ}{p_1^\circ} &= \left(\frac{A_2B_2C_2}{A_1B_1C_1}\right)^{\frac{1}{2}} \exp\frac{(-\chi_2+\chi_1)}{kT} \\ &= 2.63 \exp\frac{(-\chi_2+\chi_1)}{kT}. \qquad (20) \end{aligned}$$

Case IV

Finally we have the extreme case which is the opposite of Case II: both the rotation and the translation of the gas molecules are replaced in

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[14] Lewis and Macdonald, J. A. C. S. **55**, 3057 (1933).

[15] Cf. Urey, Brickwedde and Murphy, Phys. Rev. **40**, 1 (1932).

the liquid by oscillation for which $h\nu > kT$. Then

$$\frac{p_2{}^\circ}{p_1{}^\circ}=\left(\frac{m_2}{m_1}\right)^{\frac{3}{2}}\left(\frac{A_2B_2C_2}{A_1B_1C_1}\right)^{\frac{1}{2}}\exp\frac{(-\chi_1+\chi_1)}{kT}$$
$$=1.17\times 2.63\exp(-\chi_2+\chi_1). \quad (21)$$

In the present instance of water, we attribute the excess of 259 calories in the latent heat of vaporization of D_2O as compared with H_2O to the net result of the operation in opposite directions of two effects: the zero-point energy differences of the quasi-oscillation of the H_2O and D_2O molecules as a whole, and the difference between these molecules in respect to the decrease in the internal vibrational zero-point energies associated with the fact that the Raman frequencies in the liquid water[7] are lower than in the vapor; the effect of the former outweighs the latter, so that the zero-point energies of the quasi-oscillators must be considerably greater than 259 calories. Case II is therefore ruled out.

Comparing the empirical constant 1.35 with Case I, III and IV we conclude that the actual condition of liquid water approximates more closely to Case I, i.e., there is nearly free rotation of the water molecules.

Returning now to the vapor pressure of the species HDO we remark that Cases I, III and IV all predict for HDO a numerical factor multiplying the exponential term in the expression for the vapor pressure ratio $p_0{}^\circ/p_1{}^\circ$ which is less than 4 percent different from the geometric mean of the corresponding factors for D_2O and for H_2O (unity for the latter).

Further, if we consider the fact that the quasi-oscillation frequencies depend on numbers as close as the reciprocal square roots of 18, 19 and 20, and if we examine the differences between the Raman frequencies and the infrared absorption frequencies given in Table II, we see that the latent heat of evaporation of HDO would not be far from the arithmetic mean of the other two. The arithmetic mean appears as an exponent and corresponds again to the geometric mean relationship for the vapor pressure of HDO. We conclude that for the different kinds of water, the geometric mean relationship cannot be a bad assumption.

From the data of Taylor and Jungers[16] it appears that the vapor pressure of liquid ND_3 is related to NH_3 by the expression: $p_{ND_3}/p_{NH_3} = 1.315e^{-191/RT}$. The moments of inertia[17] of NH_3 are 2.79, 2.79, 4.37 and of ND_3 5.31, 5.31, 8.74. Reasoning as above, we have for comparison with the experimental factor of 1.315, in Case I 1.275, in Case III 2.69. Thus the molecules rotate nearly but not quite as completely in the liquid as in the vapor.

Just after the completion of this paper, Lewis and Schutz[18] report that the vapor pressure of deutacetic acid CH_3COOD is not lower but higher than that of ordinary acetic acid. It seems to us that the mechanical condition of acetic acid may well approach more closely to Case IV than to Case I, since the rotation of the double and single molecules in the vapor phase may be considerably hindered in the liquid phase by association to larger aggregates, and we note that if water showed the behavior corresponding to Case IV the vapor pressure of D_2O would be 2.2 atmospheres at the boiling point of H_2O. The mass difference between heavy and light acetic acid is relatively much less than with water or ammonia, so that the half-quanta of the quasi-oscillations are less important in the liquid acetic acids. Of course the moments of inertia also differ relatively less with the acetic acids but the half-quanta unlike the moments of inertia enter into the partition functions exponentially. The problem offered by a largely associated vapor is naturally more complex than when the association can be neglected.

SECTION 5. THE ACTIVATED STATE FOR ELECTROLYSIS

In Part II of this paper we discuss the details of three mechanisms which have been proposed for the process occurring at the cathode during the electrolysis of water, in the light of the available data on the isotopic separation, and from the standpoint of the theory of hydrogen overvoltage. In this section we confine our discussion to the reason why the values of the separation coefficient on different metals are as low as experiment shows them to be.

The highest electrolytic separation coefficient so far found is only a little over one-third of the

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[16] Taylor and Jungers, J. A. C. S. **55**, 5057 (1933).

[17] W. S. Benedict, personal communication.

[18] Lewis and Schutz, J. A. C. S. **56**, 493 (1934).

maximum value of approximately 19 calculated on the assumption that penetration through the barrier is negligible. This is to be expected. The activated state whatever its nature is not at a very much higher level than the initial state. One sees this from the fact that the temperature coefficient of the rate of electrolysis at different cathode potentials corresponds to an activation energy of about 18,000 calories for zero overvoltage at a mercury cathode, and decreases as the overvoltage is raised. Thus the activated state must be one in which the hydrogen particles are still strongly bound to other atoms. For example, if the activation is required for the passage of an H or D ion from its hydrated state to a state in which it is bound to the metal, then at the summit of the barrier it is to some extent bound to both oxygen and metal. Or, if the slow process were the desorption of hydrogen molecules the activated state would be one in which the hydrogen atom is bound both to another hydrogen atom and to the metal.

In any such activated state the particle at the summit of the barrier is momentarily not changing its potential energy as it moves forward over the barrier, and for this motion along the path no half-quantum is to be considered (instead we have tunnelling, which in practice is treated as a separate problem). Motion in a plane normal to the classical path of the particle will be accompanied by increased potential energy, and may be thought of as giving rise to two half-quanta. If the particle at the summit of the barrier is partially bound to several metal atoms in the surface of the cathode, additional degrees of freedom with associated half-quanta will enter.

Thus the constant K_c introduced at the end of Section 2 depends on the relative sizes of these half-quanta in the activated state for the two isotopes. The larger the half-quanta the smaller will be the ratio n_3/n_4 in the activated state compared with n_3/n_4 in free space, which means a low value for both K_c and the electrolytic separation coefficient. In general terms one would naturally assume that in respect of these half-quanta the activated state is intermediate between the initial state of a hydrogen particle in water and the state of a free hydrogen particle with no half-quanta; so that the value of α must lie between 1.4 and 19. The experimentally found range of values seems entirely reasonable from this point of view. There will naturally be differences from one metal to another, but the order in the series of separation coefficients is not related in any obvious way to any one property of the metals.

We remark here that the importance of taking account of the existence of half-quanta in the activated state is quite general for the relative rates of reactions involving isotopes: consider a bimolecular reaction such as $H_2+I_2=2HI$ where in the activated state there are six half-quanta to consider. It is conceivable that for certain reactions of this type, just as has been pointed out by Polanyi[19] for the particular case when the initial state involves free atoms, that the heavier isotope will react more rapidly. The general condition for this to happen is simply that the sum of all the half-quanta of vibration in the activated state exceed this sum for the initial state by a sufficient amount to outweigh the velocity factor 1.414 and any tunnelling which may take place. It is to be expected that examples of all intermediate cases will be found.

As long ago as 1919 Lindemann[20] drew attention to the fact that in principle isotopes could be separated by means of chemical equilibria. Exact calculations of several gaseous equilibria involving heavy hydrogen have been given by Urey and Rittenberg[21] who show also that the differences in the (equilibrium) electrode potentials of the heavy and light isotopes are too small to produce any appreciable separation by fractional electrolysis. The advantage (for the separation) of using reaction rates rather than an equilibrium process arises entirely from the possibility of selecting a reaction for which the activated state has a lower zero-point energy than the final state (or of finding a reaction in which there is a potential barrier which allows some tunnelling). For a favorable reaction the lighter isotope is most plentiful in the first material formed, no matter in which direction the reaction proceeds. This is in marked contrast to equilibrium processes.

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[19] Polanyi, Nature **133**, 26 (1934).

[20] F. A. Lindemann, Phil. Mag. [6] **33**, 173 (1919).

[21] Urey and Rittenberg, J. Chem. Phys. **1**, 137 (1933).

In a preliminary note[22] on the experimental results, we expressed the view that if the activation is required to loosen the binding of an H^+ or D^+ ion to water, and that the potential barrier representing this activation lies symmetrically in the Helmholtz double layer, then the well-known results of Bowden[23] indicate that this barrier is 1.5 Angstroms in total width; the height of about 18,000 calories may be in effect diminished by the fall of potential across the double layer to something like 5000 calories for the high current densities employed in practice. On metals of low overvoltage the barrier is still lower. If one assumes that the symmetrical barrier is roughly parabolic in form, then the penetration of the barrier occurs near the top and can be calculated by a formula due to Wigner[24] which expresses the total amount of non-classical penetration of the barrier in terms of the curvature at the top of the barrier. For a barrier which is approximately an inverted parabola with a curvature at the top equal to that of a parabola of height 5000 calories and half-width at the base of 0.75 Angstrom it appears that the effect of the leakage would be to increase the rate of discharge of H by about 20 percent and of D by about 10 percent, which is only of secondary importance as a contribution to the separation.

In a personal communication Messrs. Ogden and Bawn of the Manchester laboratory inform us of the results they obtain by using Eckart's exact solution[25] of the Schrödinger equation. They find a very much greater leakage. This is directly traceable to the form of Eckart's potential, which has a very much greater curvature near the top than the surface we have considered. This strong separation of the isotopes is not found in practice, and it seems to us that the Eckart barrier has altogether too sharp a curvature at the top to correspond to the actual conditions. But in any case the interpretation of so small a width for the Helmholtz double layer is very difficult; if the barrier is in reality wider the curvature and hence also the contribution to isotope separation made by quantum-mechanical leakage may be even less than in our original assumption.

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[22] Topley and Eyring, J. A. C. S. **55**, 5058 (1933).

[23] Bowden, Proc. Roy. Soc. **A126**, 107 (1929).

[24] E. Wigner, Zeits. f. physik. Chemie **B19**, 203 (1932).

[25] C. Eckart, Phys. Rev. **35**, 1303 (1930).