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On the Electrolytic Separation of the Hydrogen Isotopes

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Starting from the hypothesis that the rate-determining process in the electrolysis of gases is constituted by the recombination of the gas atoms on the electrode, a formula is developed which expresses the separation coefficient as a function of well-known thermodynamic constants of H and D compounds and of the frequencies with which the

atoms carry out their thermal oscillations on the electrode. The formula gives a certain range for the value of the separation coefficient which is in good agreement with the observations. As a by-product of these calculations a relation is established between the normal electrode potentials of H and D.

I. INTRODUCTION

SINCE the discovery of the electrolytic separation of the two hydrogen isotopes a series of papers has been concerned with attempts to obtain theoretical explanations for the observed effects. A complete survey of the merits of the various theories can be found in the recently published report by Urey and Teal.¹ From it it is obvious that at present we cannot claim to possess a satisfactory theory of the phenomenon of electrolytic separation. It therefore will be attempted in the present paper to derive a theoretical expression for the separation coefficient, starting from assumptions as closely defined as possible and, as far as we know, nowhere in disagreement with experiment. In distinction from most of the theories we shall assume that the rate determining process in the electrolytic production of gases is constituted by the recombination of the gaseous atoms on the electrode.

In support of this hypothesis we can adduce the following very general experimental facts:

1. Overvoltage phenomena of a marked character seem to appear only at the electrolytic production of *gases*. We thereby, of course, discard all such cases of overvoltage in which, due to slow diffusion, an impoverishment of ions at the electrode occurs. Such cases are of no concern for the electrolytic separation of hydrogen where the ionic concentrations in the solution are invariably high. The fact that only gases show this marked retardation in the electrolytic process seems to us to indicate very strongly that it is the recombination process which de-

termines the rate of electrolysis for a given voltage.

2. The separation coefficient seems to be the same whether the electrolysis is carried out in acid or alkaline solutions. This second point seems to us to speak in disfavor of theories which attempt to ascribe the separation to a difference in the rate of *discharge* of the two kinds of hydrogen ions. In strongly acid solutions it is plausible that the discharge at the electrode is carried out by the H ions and a theory establishing a difference in the speed of discharge for the two ions could perhaps account for the observed phenomena. On the other hand, due to the smallness of the dissociation constant of water, there are no hydrogen ions present in the neighborhood of the electrode for all alkaline solutions used in the experiments. In alkaline solutions therefore, differences in the speed of discharge of the hydrogen ions would be without any importance and could not explain the observed separation.

Keeping these two facts in mind we assume that the "slow process" is determined by the recombination at the electrode while the discharge of the ions and the establishment of the equilibrium between the solution and the electrode shall be considered to be "instantaneous" processes. We do not feel certain that the diffusion between electrode and solution is always sufficiently fast, but it is probably a fair assumption to treat the process as instantaneous for not too large current densities. On the other hand, the current densities should not be taken too small because the back diffusion from the gas to the electrode would then have to be taken into account. For the following we assume these conditions to be satisfied; particularly as

¹ H. C. Urey and G. K. Teal, *Rev. Mod. Phys.* **7**, 34 (1935). Cf. particularly pp. 41-48.

far as the back diffusion of the gas is concerned, these assumptions are probably well justified.

The paper is divided into the following sections: In paragraph II we briefly review a few thermodynamic formulae and approximations which are generally used for this type of calculations. Paragraph III contains the derivation of a relation between the normal electrode potentials for H and D. This relation is derived in a rather devious manner for the sake of an extension of the method in paragraph IV which is essential for the treatment of the nonequilibrium case of electrolysis. There, on the basis of the physical factors outlined in the introduction, we derive and discuss the theoretical explanation for the separation coefficient.

II. SEVERAL THERMODYNAMIC RELATIONS

In the following calculations the solution of electrolytes (which themselves might contain hydrogen) in mixtures of heavy and light water will be treated thermodynamically as ideal solutions. Concentration symbols c , referring to the solution, the electrode and the gas phase, will as far as necessary be distinguished by an upper s , e , g . The *ratio* of the analytic concentration of light to heavy hydrogen in the solution and in the gas phase will be denoted by a^s and a^g respectively. Neglecting the hydrogen content of the electrolyte and the amount of free atoms of hydrogen in the gas phase, we have for a^s and a^g the following relations:

$$a_g = (2c_{H_2^g} + c_{HD^g}) / (c_{HD^g} + 2c_{D_2^g}), \quad (1a)$$

$$a_s = (2c_{H_2^s} + c_{HD^s}) / (c_{HD^s} + 2c_{D_2^s}). \quad (1b)$$

In the gaseous as well as in the liquid phase there exist equilibrium conditions for the different kinds of molecules containing the two hydrogens. For the following we need the relations given below

$$c_{H_2^g} / c_{H_2^s} = K_{11}, \quad (2a)$$

$$c_{H^g} c_{D^g} / c_{HD^g} = K_{12}, \quad (2b)$$

$$c_{D_2^g} / c_{D_2^s} = K_{22}, \quad (2c)$$

$$c_{H^+} c_{OH^-} / c_{H_2O^s} = L_{11}, \quad (3a)$$

$$c_{H^+} c_{OD^-} / c_{HD_2O^s} = L_{12}, \quad (3b)$$

$$c_{D^+} c_{OH^-} / c_{HD_2O^s} = L_{21}, \quad (3c)$$

$$c_{D^+} c_{OD^-} / c_{D_2O^s} = L_{22}. \quad (3d)$$

From general statistical considerations which are in fairly good agreement with experiment we assume the following relations between the various equilibrium constants to hold true:

$$K_{11} K_{22} / K_{12}^2 = L_{11} L_{22} / L_{12} \cdot L_{21} = 4. \quad (4)$$

This procedure has been adopted by most writers¹ in this field and we consider the reasons justifying these assumptions to be satisfactory. Combining the dissociation Eqs. (2) and (3) with the relations (1) and (4) we obtain the following equations:

$$c_{H^+} / c_{D^+} = (L_{11} / 2L_{12}) a^s, \quad (5a)$$

$$c_{H^g} / c_{D^g} = (K_{11} / 2K_{12}) a^g, \quad (5b)$$

$$a^g / a^s = K_F. \quad (5c)$$

The (equilibrium) value of K_F has been experimentally determined. The latest determination made by A. and L. Farkas² led to $K_F \approx 3$.

III. NORMAL ELECTRODE POTENTIALS OF H AND D

Consider an electrolytic solution of heavy and light water in *equilibrium* with the gas phase. This gas phase will also contain (unobservably small) quantities of H and D atoms. Into the solution is dipping an electrode containing H and D atoms. The nature of the electrode is indifferent to the equilibrium. We shall now formulate thermodynamic conditions for the equilibrium of the whole system.

The electric potential difference between the electrode and the solution can be expressed in two different ways

$$\Delta_H = E_{OH} + \frac{RT}{F} \log \frac{c_{H^+}}{c_{H^g} / c_{H_2O^s}}, \quad (6a)$$

$$\Delta_D = E_{OD} + \frac{RT}{F} \log \frac{c_{D^+}}{c_{D^g} / c_{D_2O^s}}. \quad (6b)$$

$c_{H_2O^s}$ and $c_{D_2O^s}$ denote the concentration of H and

² A. Farkas and L. Farkas, J. Chem. Phys. 2, 468 (1934).

D atoms on the electrode in equilibrium with H_2 or D_2 at the pressure of 1 atom. Since, for electrostatic reasons $\Delta_H = \Delta_D$ we obtain by subtracting (6b) from (6a) the relation

$$E_{0H} - E_{0D} = -\frac{RT}{F} \log \frac{c_D^e c_H^+ c_{H0}^e}{c_H^e c_D^+ c_{D0}^e}. \quad (7)$$

We now express c_H^e and c_D^e through the concentrations in the gas phase.

$$c_H^e = k_H c_{H0}^g, \quad (8a) \quad c_D^e = k_D c_{D0}^g. \quad (8b)$$

k_H and k_D denote the distribution coefficients of the atoms between electrode and gas phase. Analogously

$$c_{H0}^e = k_H c_{H0}^g = k_H K_{11}^{1/2} (c_{H2}^g)^{1/2}, \quad (9a)$$

$$c_{D0}^e = k_D c_{D0}^g = k_D K_{22}^{1/2} (c_{D2}^g)^{1/2}. \quad (9b)$$

Using (8) and (9) and inserting (5a) to (5c) into (7) we obtain

$$E_{0H} - E_{0D} = -\frac{RT}{F} \log a_s \frac{(c_{D2}^g)_0}{(c_{H2}^g)_0} \frac{1}{a^g} \frac{L_{11}}{2L_{21}}. \quad (10)$$

Since by definition $(c_{H2}^g)_0 = (c_{D2}^g)_0$ we finally arrive at the following formula for the difference of the normal electrode potentials of H and D:

$$F_{0H} - E_{0D} = -(RT/F) \log (L_{11}/2L_{21})(a^s/a_g) \\ = -(RT/F) \log (2L_{12}/L_{22})(1/K_F). \quad (11)$$

The difference between E_{0H} and E_{0D} is according to (11) very small. Though we do not have very exact determinations of $L_{11}/2L_{21}$ it has been estimated that its value lies around 3. This leads, with the value given above for K_F , to a value for $E_{0H} - E_{0D}$ which is very small.

IV. DETERMINATION OF THE SEPARATION COEFFICIENT

For the case of a current flowing the formulae of paragraph III need modification only as far as the connection between c^s and c^g is concerned while the relations between the potentials Δ and c^s , c^g remain intact according to the hypothesis explained in paragraph I. We therefore obtain here again the relations, (6a), (6b) and by subtracting,

$$0 = E_{0H} - E_{0D} + \frac{RT}{F} \log \frac{c_H^+ c_D^e c_{H0}^e}{c_D^+ c_H^e c_{D0}^e} \quad (7)$$

$$= E_{0H} - E_{0D} + \frac{RT}{F} \log \frac{L_{11}}{2L_{21}} \frac{c_D^e}{c_H^e} \frac{k_H}{k_D} \frac{L_{11}}{2L_{12}}. \quad (7a)$$

Making use of (11) and (4) we can write (7a) in the form

$$c_H^e/c_D^e = (k_H/k_D)(K_{11}/K_{22})^{1/2} K_F a^s. \quad (12)$$

The other terms in (7a) cancel each other.

To determine with the help of (12) the amount of H_2 and D_2 given off irreversibly to the gas phase we have to make an hypothesis concerning the mechanism of recombination. It seems reasonable to consider this process a bimolecular reaction. We so obtain for $[H_2]/[D_2]$ the expression

$$[H_2]/[D_2] = a^g \\ = (2\lambda_{11}c_H^{e2} + \lambda_{12}c_H^e c_D^e) / (\lambda_{12}c_H^e c_D^e + 2\lambda_{22}c_D^{e2}). \quad (13)$$

In this expression the quantities λ_{ik} are the velocity constants of the corresponding reactions. Following the assumptions made in paragraph II (cf. (4)) we correspondingly have for the ratio of the λ_{ik} the relation¹

$$\lambda_{11}\lambda_{22}/\lambda_{12}^2 = 1/4. \quad (14)$$

Thereby (13) reduces to $(\lambda_{11}/\lambda_{22})^{1/2}(c_H^e/c_D^e)$. The separation factor α is defined by the relation

$$\alpha = a^g/a^s.$$

From (12), (13), (14) we finally obtain for α the equation

$$\alpha = (k_H/k_D)(\lambda_{11}/\lambda_{22})^{1/2}(K_{11}/K_{22})^{1/2} K_F. \quad (15)$$

This theoretical expression for (15) now has to be discussed.

For the physical interpretation of (15) two kinds of factors have to be distinguished: K_F has been calculated to be about 3.0 and has been experimentally determined as well (cf. paragraph II (5c)). $(K_{11}/K_{22})^{1/2}$ though not directly empirically determined, can be easily calculated from other thermal or spectroscopical measurements. Its value at room temperature has been calculated³ from the results of Johnston and

³ We are indebted to Dr. G. M. Murphy for this calculation.

Long⁴ and of Giauque.⁵ This gives the value

$$K_{11}/K_{22}=14. \quad (16)$$

The other factors in (15) are not as fully determined as the two already discussed. For the ratio of the distribution coefficients of H and D atoms k_H/k_D we have from general statistical arguments the relation

$$\frac{k_H}{k_D} = 2^{\frac{1}{2}} e^{-\frac{3}{2} h V_H (1-1/\sqrt{2})/2kT} \frac{(1 - e^{-h V_H / \sqrt{2} kT})^3}{(1 - e^{-h V_H / kT})^3}. \quad (17)$$

(V_H = frequency of oscillation of the H atom on the electrode.) (17) is nothing but the ratio of the vapor pressure equations for the two atoms; in it, it has been assumed that the three frequencies of oscillations of the atom on the metal surface are equal to each other, and that, of course, the "heat of vaporization" for the two isotopes from the hypothetical vibrationless state shall be the same. The exponential factor in (17) is, due to the difference in zero-point energy of the oscillating atoms on the electrode.

The ratio of the velocity constants, $(\lambda_{11}/\lambda_{22})^{\frac{1}{2}}$, now can be easily calculated, assuming the activation energy Q of the process of recombination to be the same for H and D (except for the difference in zero-point energy). Writing for

Q the expression $a = N_1 h V_H = N_2 h V_D = N_2 h V_H / \sqrt{2}$ wherein N_1 and N_2 are assumed to be large compared to 1, one can easily derive for $(\lambda_{11}/\lambda_{22})^{\frac{1}{2}}$ the relation

$$(\lambda_{11}/\lambda_{22})^{\frac{1}{2}} = e^{+\frac{3}{2} h V_H (1-1/\sqrt{2})/2kT} \times \left(\frac{N_1}{N_2} \right)^{(f-1)/2} \left(\frac{1 - e^{-h V_H / kT}}{1 - e^{-h V_H / \sqrt{2} kT}} \right)^{(f-1)/2}. \quad (18)$$

In this relation the exponential factor is due to the zero-point energy while the factor $(N_1/N_2)^{(f-1)/2}$ arises from the different number of states which lead to an energy equal to, or larger than, the activation energy. In (18) f stands for the number of degrees of freedom of the particles entering into the reaction; in our case f is equal to 6.

We shall here give the derivation of (18) for a system of two degrees of freedom, a generalization is then very simple. The probability that an oscillator system of two degrees of freedom with a frequency V has an energy equal to or larger than the activation energy $Q = NhV (>> kT)$ is given by the sum of the probabilities of the following mutually exclusive conditions. (We denote in the following the energy of the first degree of freedom with ϵ_1 that of the second degree of freedom correspondingly with ϵ_2 .)

$$\left. \begin{aligned} (1) \epsilon_1 &= 0, & \epsilon_2 &\geq NhV, & p_1 &= e^{-Q/kT} (1 - e^{-hV/kT}), \\ (2) \epsilon_1 &= hV, & \epsilon_2 &\geq (N-1)hV, & p_2 &= e^{-Q/kT} (1 - e^{-hV/kT}), \\ & \vdots & & & & \\ & \vdots & & & & \end{aligned} \right\} \quad (19)$$

$$\begin{aligned} (N+1) \epsilon_1 &\geq Q_1, & \epsilon_2 &\geq 0, & p_{N+1} &= e^{-Q/kT}, \\ P &= \sum p_i. \end{aligned} \quad (20)$$

Since there are altogether $N+1 \sim N$ different cases each with the probability $e^{-Q/kT} (1 - e^{-hV/kT})$ the relation (20) takes on account of (19) the form

$$P = (Q/hV) e^{-Q/kT} (1 - e^{-hV/kT}), \quad (21)$$

from which (18) can be easily deduced. The final theoretical expression therefore for the

separation coefficient α takes the form

$$\alpha = (K_{11}/K_{22})^{\frac{1}{2}} K_F 2^{\frac{1}{2}} \left(\frac{1 - e^{-h V_H / kT}}{1 - e^{-h V_H / \sqrt{2} kT}} \right)^{\frac{1}{2}}. \quad (22)$$

The numerical value of this expression therefore depends apart from known constant on the ratio hV_H/kT .

It is of interest to compare two limiting cases, (a) $hV_H/kT < 1$. After expanding the exponentials (22) takes the form

⁴ H. L. Johnston and E. A. Long, J. Chem. Phys. 2, 389 (1934).

⁵ W. F. Giauque, J. Am. Chem. Soc. 52, 4816 (1930).

$$\alpha = (K_{11}/K_{22})^{1/2} K_F \sim 11.$$

This case corresponds physically to atoms lightly bound to the electrode (the thermal energy of the oscillators has equipartition value). (b) $(hV_H/kT) \gg 1$. This corresponds to very tightly bound atoms (large oscillatory frequency). The thermal energy of oscillation is very low. In this case (22) takes the form

$$\alpha = (K_{11}/K_{22})^{1/2} K_F 1.19,$$

with a numerical value $\alpha \sim 13$. We should therefore theoretically expect the separation coefficient to lie somewhere between the two limits.

The difference of the electrode-material according to the factors presented enters only through the difference in the oscillation frequency of the atoms bound to the metal. It seems important to emphasize that the zero-point energy of the atoms bound to the metal surface does not enter into the expression for the separation coefficient. This is due to the fact, as ascertained from (17) and (18), that the zero-point enters twice, namely, into k_H/k_D and $(\lambda_{11}/\lambda_{22})^{1/2}$ and with

opposite sign in the exponentials of the two terms.

The values theoretically obtained seem to be in good agreement with experiments. Brown and Daggett⁶ find that the fractionation factor is about 12 in the case of iron electrodes. McLaren⁷ finds that this factor depends on the surface and on the current density.

With increasing temperature the coefficient of separation should decrease because the quantities K_{11}/K_{22} and K_F have negative temperature coefficient and the ratio hV/hT decreases. All these effects tend to diminish the separation factor. We do not know of any experiments so far made which would allow a definite check on the theory in this respect, though observations reported by Urey and Teal⁸ seem to be in agreement with this prediction.

One of the authors (O. H.) has had the pleasure of privately discussing the problem treated in this paper with Professor H. C. Urey.

⁶ W. G. Brown and A. F. Daggett, *J. Chem. Phys.* **3**, 216 (1935).

⁷ J. McLaren, Private communication.

⁸ Reference 1, p. 43.

On the Dissociation Constants of Acids in Light and Heavy Water

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The ratio of dissociation constants of acids in light and heavy water is shown to become the larger the weaker the acid. This is a consequence of the differences in zero-point energy of the proton (deuteron) when attached to the anion or the neutral water molecule.

DIFFERENCES in the dissociation constant of acids when dissolved in light and heavy water have been observed rather early. These differences are of importance not only for conductivity measurements but even to a higher extent for reaction problems and catalysis phenomena in which hydrated protons and deuterons are involved. Since particularly the formation of the activated state often depends on the acceptance of the proton (deuteron) the difference in the dissociation constants for the two ions becomes of considerable importance. In the following we present a simple relation which will

allow us to predict qualitatively how this difference depends on the nature of the acid.

We discuss the dissociation of an acid in a dilute aqueous solution. The ratio K_H/K_D , where K_H and K_D stand for the dissociation constant of HA and DA , respectively, now depends mainly on the relative magnitude of the binding forces acting on the ions when attached to the anion A or to the neutral water molecule (dissociated, hydrated state). We introduce the assumption which can be proved for many cases and very probably is generally true, that the frequency of oscillation of the ions in either state