

On the Dissociation Constants of Acids in Light and Heavy Water

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

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

increases with increasing *binding energy*. It is obvious that it increases with increasing *force*, but only in very special cases, could we imagine that field of force and binding energy do not go parallel.

Now, according to thermodynamics, the ratio K_H/K_D becomes equal to

$$\frac{K_H}{K_D} = \exp - \frac{fh(V_H^w - V_H^A - V_D^w + V_D^A)}{2kT}, \quad (1)$$

f = number of degrees of freedom of oscillation.

In (1), V_H^A stands for the frequency of oscillation of the proton attached to the anion V_H^w for the frequency of oscillation of the proton when attached to the neutral water molecule, and correspondingly for the deuteron. About the relative magnitudes of V_H^w and V_H^A we can now say that, according to our hypothesis

$$V_H^w < V_H^A \quad (2)$$

except, perhaps, for the case of some extremely strong acids. This can be seen easily in the following way: Every proton has, statistically speaking, a certain number of places where it can attach itself, namely, N_w neutral water molecules and N_A anions. Since $N_w \gg N_A$ all acids should be completely dissociated if no energetic factors would enter, or, in other words, if the binding energy to the anion would not very much exceed the binding energy to the water molecule (energy of hydration). Therefore $V^w < V^A$ and since

$$V_H = \sqrt{2} V_D$$

we obtain for the ratio K_H/K_D

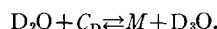
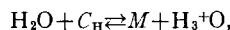
$$\frac{K_H}{K_D} = \exp - \frac{fh(1 - 1/\sqrt{2})(V_H^w - V_H^A)}{2kT} > 1. \quad (3)$$

Now the difference between V_H^A and V_H^w becomes the larger the weaker the acid, i.e., the more the binding energy of the anion exceeds

the energy of hydration. This leads to the result given in the summary that *the ratio K_H/K_D increases the weaker the acid becomes*.

As one of the weakest acids we might consider water itself. The ratio K_{H_2O}/K_{D_2O} in this case therefore should be expected to exceed the ratio of all acids which show stronger dissociation than water itself does.

If, in a chemical reaction the rate is determined by a critical complex C formed through the addition of a proton (deuteron) to some other molecule, the arguments of this paper allow a prediction as to whether the reaction in light or heavy water will be faster. For this purpose consider the critical complex C as an "acid" being able to dissociate according to the scheme



If the binding energy of the proton to M is larger than its energy of hydration, then the complex might be considered a "weak acid," and the dissociation constant of the complex will be larger for light than for heavy water, its concentration therefore, smaller, and the reaction velocity smaller in light than in heavy water. Conversely, if the binding energy of M for protons is smaller than the hydration energy the complex becomes a "strong acid." The "dissociation of the complex" is larger for heavy than for light water because the zero-point energy of H_3^+O is larger than that of C . The reaction velocity therefore is smaller in heavy than it is in light water.

It becomes apparent that no general rule exists about the relative rates of ionic reactions in heavy and light water but that everything depends on the binding energy of H^+ in the critical complex.

The author understands that Ph. Gross in Vienna and his collaborators are going to present experimental material in support of the view formulated above.