## Summary

Oxygen is shown to have three distinct effects on the work function of clean silver, as determined by means of photoelectric emission. (1) At room temperature the presence of oxygen slightly enhances the emissivity, the effect disappearing with the removal of the oxygen. (2) After heating in oxygen the silver upon heating *in vacuo* possesses abnormally large emissive properties, the effect only disappearing after long heating. (3) Heating in oxygen or exposure to ozone destroys the emissivity.

The effects observed under (1) and (2) have been associated with "physical" and "activated" adsorption respectively while (3) is due to the presence of "surface" silver oxide.

Evidence is presented to show that the lowering of the work function by "physical" and "activated" adsorption is due to positive oxygen ions, while the increase in the work for electron emission brought about by "surface" silver oxide is due to negative oxygen ions.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

# The Ionization of Some Weak Electrolytes in Heavy Water

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We have made some preliminary measurements of the conductivities and the ionization constants of deutacetic acid, chlorodeutacetic acid and deutammonia in heavy water. On account of the uncertainty in the measurements and the still greater uncertainty in their interpretation we should hesitate to publish the results at this time were it not for the extraordinary differences that we have observed between the deuto and the corresponding hydro compounds.

At the time that this work was done very little heavy water was available and it was necessary to use the same micro methods and apparatus used by Lewis and Doody.[1] In the study of all the other physico-chemical properties of compounds of deuterium we have found it possible to obtain accurate results with very small quantities of material. It is not possible, however, in the measurement of the conductivity of poorly conducting solutions. It is not only that the very small conductivity cell presents certain difficulties which have not yet been overcome, but that in working with fractions of a gram of heavy water we have never succeeded in obtaining a lower specific conductivity than $10^{-5}$. Nevertheless, we have in each case studied under the same experimental conditions the same substances in light and heavy water and the observed differences are significant. All our measurements were made at 25°.

**Deutacetic Acid,**[2] $CH_3COOD$.—By means of a capillary buret 0.00144 g. of pure glacial acetic acid was added to 0.334 cc. of ordinary conductivity water, making the solution 0.0722 *M*. The molal conductivity was found to be 6.20. Taking $\Lambda_0$ as 391 we obtain for the ionization constant at 25°, $K = 1.84 \times 10^{-5}$, which is in accord with the best values given in the literature.

The same experiment was repeated with heavy water and the same acetic acid. The heavy water used in this and other experiments contained several per cent. of light hydrogen, but the error thus introduced is negligible compared with other errors which we shall mention. The small amount of hydrogen contained in the glacial acetic acid is also negligible. Once more the solution was 0.0722 *M*. The specific conductivity proved to be $18.3 \times 10^{-5}$ while that of the heavy water was $2.2 \times 10^{-5}$. We thus find for the molal conductivity, $\Lambda = 2.53$ if no correction is made for the conductivity of the heavy water, and $\Lambda = 2.22$ if the whole conductivity of the heavy water is subtracted from that of the solution.

To the same solution another equal amount of acid was added, bringing the molality to 0.1444 *M*. Here we find $\Lambda = 1.79$ and $\Lambda = 1.63$ when no correction, and when full correction, is made for the conductivity of the solvent.

We must next consider the value of $\Lambda_0$. Lewis

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[1] Lewis and Doody, THIS JOURNAL, **55**, 3504 (1933).

[2] The results for this one electrolyte we have briefly described in an earlier communication. Lewis and Schutz, *ibid.*, **56**, 1002 (1934).

and Doody[1] obtained $\Lambda_0$ for DCl in $D_2O$ by the aid of certain assumptions which cannot be strictly accurate, since it has later been found that the viscosity of $D_2O$ is very different from that of $H_2O$.[3] However, for our present purpose it will be sufficiently accurate to assume that the ratio between $\Lambda_0$ of $CH_3COOH$ in $H_2O$ and $\Lambda_0$ of $CH_3COOD$ in $D_2O$ is the same as the ratio between $\Lambda$ of HCl in $H_2O$ and $\Lambda$ of DCl in $D_2O$, both at 0.017 *M*. This ratio was found by Lewis and Doody to be 1.390 at 25°. Hence we estimate $\Lambda_0 = 281$ for deutacetic acid in heavy water.

We then find for the ionization constant of deutacetic acid $K = 0.59 \times 10^{-5}$ at 0.0722 *M* and $K = 0.59 \times 10^{-5}$ at 0.1444 *M* when no correction for the solvent is applied. When the full correction for the conductivity of the solvent is made we find $K = 0.45 \times 10^{-5}$ and $0.49 \times 10^{-5}$ at the two concentrations. It is always hard to tell how large a correction for the conductivity of the solvent should be made in cases of this sort but however it is made we obtain the surprising result that the ionization constant for acetic acid in ordinary water is three to four times as great as that of deutacetic acid in heavy water.

**Chlorodeutacetic Acid,** $CH_2ClCOOD$.—Feeling that we might possibly be deceived in reaching the conclusions just mentioned, on account of the low conductivity of deutacetic acid and the appreciable conductivity of the heavy water, we next studied chloroacetic acid and chlorodeutacetic acid where the correction for the conductivity of the solvent is entirely negligible. The chloroacetic acid that we used was recrystallized and was free from hydrochloric acid. However, it gave values for the ionization constant $K = 1.71 \times 10^{-3}$ at 0.0376 *M* and $K = 1.74 \times 10^{-3}$ at 0.0752 *M*, larger than the value $K = 1.52 \times 10^{-3}$ given in the "International Critical Tables." We have not investigated this discrepancy further but shall use these values since we employed the same material and the same apparatus in studying the constant of chlorodeutacetic acid.

When the experiments were repeated with heavy water we found $\Lambda = 33.9$ at 0.0376 *M* and $\Lambda = 24.6$ at 0.0752 *M*. Taking $\Lambda_0 = 280$ we find $K = 0.63 \times 10^{-3}$ at both concentrations. Here again we find the ionization constant of the deuto acid much smaller than that of the hydro acid although the ratio in this case is only 2.7 and presumably will diminish further as we proceed toward stronger acids.

**Deutammonium Deutoxide,** $ND_4OD$.—A concentrated aqueous solution of ammonia was added by means of the capillary buret to light water and to heavy water. In light water we found $K = 1.82 \times 10^{-5}$ in close agreement with previous values. In heavy water we found at 0.0741 *M*, $\Lambda = 2.94$ and $\Lambda = 2.61$, without and with the solvent correction.

We have no experimental evidence regarding the mobility of $OD^-$ in heavy water. We may guess that it is something like half way between that of $D^+$ and that of other univalent ions. As a very rough estimate we have taken for $ND_4OD$ $\Lambda_0 = 214$. With this value we find $K = 1.4 \times 10^{-5}$ without correction and $K = 1.1 \times 10^{-5}$ with correction for the solvent. Thus we find that if our estimate of $\Lambda_0$ is approximately correct the ionization constant of $NH_4OH$ in $H_2O$ is about 50% greater than that of $ND_4OD$ in $D_2O$.

## Discussion

The theoretical interpretation of our results is difficult. In a gaseous molecule which may be represented by the formula $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}:\text{H}$ we may consider the potential, as a function of the distance, when the hydrogen ion is moved away from the bonding electron pair. Whatever the potential curve may be it will be almost the same for the molecule $:\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}:\text{D}$. The two curves differ slightly because of the so-called electronic isotope shift, which can be observed spectroscopically but which has not yet been calculated. Neglecting this small difference, and considering the two potential curves as identical, there remains an important difference between the two molecules in that at the lowest state of vibration the deuton, because of its greater mass, occupies a lower position on the potential curve than the proton. Moreover, this difference will be greater the more tightly the two ions are held together. On account of this familiar difference in zero point energy, between the two molecules, the energy required to remove the deuton by ionization is always greater than that required to remove the proton. If we wish to consider, not the energy of ionization, but the ionization constant, we must consider also the substantial differences in entropy.

While in the very simplest gaseous molecules it may occasionally be possible to calculate these differences in energy and entropy by the aid of

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(3) Lewis and Macdonald, THIS JOURNAL, **55**, 4730 (1933).

known spectroscopic data, such a quantitative calculation is out of the question for a complex molecule or indeed for any molecule in that very peculiar environment that exists in the aqueous solution. We may safely carry over the qualitative conclusion that the energy of ionization will always be greater for the deuton than for the proton, but the magnitude of the difference can be determined by experiment alone.

When in solution an acid ionizes according to the scheme $HX = H^+ + X^-$, not only the acid but its ions are ordinarily solvated and this solvation, together with the polar character of the environment, largely determines the degree of ionization. Nevertheless, instead of writing down all of the possible solvates it will be more convenient and probably as satisfactory to discuss ionization in terms of the simple reaction written above, and to regard as the main process in the ionization of a weak acid the separation of the proton or the deuton from the bonding electron pair of the anion.

From considerations of zero point energy we predict not only that the deuto acids will be weaker than the corresponding hydro acids but also that this difference will be greater in those cases in which the proton and deuton are more firmly held, in other words, that the ratio of the ionization constant of the hydro acid to that of deuto acid will increase as we proceed toward weaker acids. This is borne out by our observation that while this ratio is 2.7 in chloroacetic acid it is between 3 and 4 in the weaker acetic acid.

If this reasoning is correct, light water should be a stronger acid than heavy water, and in water containing equal amounts of hydrogen and deuterium there should be several times as much $H^+$ as $D^+$. One of us has pointed out[4] that the large fractionation of the hydrogen isotopes in electrolysis, which was at first universally ascribed to different rates, may in large part be ascribed to differences in equilibrium conditions. Our present work bears out this idea.

In passing from weak acids to the weak base ammonia, it was a little difficult to predict the effect of replacing hydrogen by deuterium, but every consideration indicates that the ionization constant of deutammonium deutoxide in heavy water should be less than that of ammonium hydroxide in water. If we consider the ammonia to exist chiefly as $NH_4OH$, a molecule that is held together by the hydrogen bond, we should expect greater ionization than with $ND_4OD$ which is held together by the stronger deuterium bond. If, however, we think of the ammonia as chiefly free, we should expect the reaction $ND_3 + D^+ = ND_4^+$ to go farther than the reaction $NH_3 + H^+ = NH_4^+$ when all of the concentrations are the same; but we have assumed the ionization of heavy water to be relatively small. Since $H_2O$ is a weaker acid than $NH_4^+$, we should expect the reaction $NH_3 + H_2O = NH_4^+ + OH^-$ to go farther than the reaction $ND_3 + D_2O = ND_4^+ + OD^-$. From both points of view we should expect an appreciable diminution in ionization constant when hydrogen is replaced by deuterium, and that is what we found.

## Summary

We have made preliminary measurements of the conductivity at 25° of deutacetic acid, chlorodeutacetic acid and deutammonia in heavy water. From these measurements, and rough estimates of the conductivities at infinite dilution, we have found ionization constants which are notably smaller than those found for the corresponding hydro compounds in ordinary water. The theoretical implications of these results are discussed.

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(4) Lewis, "Report of the IX International Congress of Pure and Applied Chemistry," General Conferences I, 1934.