protium and of deuterium atoms in the undecomposed water, or solution.[5] We obtain[6] $\alpha = 2.5$, which compares with electrolytic separation coefficients[7] ranging from about 5 to about 7. By a similar calculation using the data given by Bleakney and Gould[2] we get the respective values 1.3 and 1.2 for the separation factor in the iron steam reaction.

These experiments were begun in the effort to seek a possible correlation between the electrolytic separation of isotopes and a secondary reaction between discharged alkali metal and the solution. That other factors are primarily responsible is shown clearly by the recent work of Topley and Eyring.[7] However, the experimental evidence now available does not preclude the possibility that a *fraction* of the effect may be separated from that of a purely electrode process.

We are continuing experiments with other metals.

We are indebted to Prof. Edward Mack, who suggested this experiment to one of us, and to the Capital City Products Company, of Columbus, who kindly placed at our disposal two thousand gallons of commercial electrolyte from which we are preparing "heavy water."

(5) This equation is similar to that for the separation efficiency in electrolysis. It is justified by consideration of the rate equation for the reaction of a metal with either isotopic water, which is

$$-\frac{dc}{dt} = k\sigma c f(\mu)$$

where σ, the available surface of the metal, is common to both waters and $f(\mu)$, which represents some function of the ionic environment, may reasonably be supposed to be the same function for both protium and deuterium ions. $\alpha = k_P/k_D$.

(6) Δ sp. g. for pure H^1H^1O was taken to be 21 p. p. m., which corresponds with the isotopic ratio of 1 in 5000 in ordinary water (Ref. 2).

(7) Topley and Eyring, THIS JOURNAL, **55**, 5058 (1933).

DEPARTMENT OF CHEMISTRY
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CLYDE O. DAVIS
HERRICK L. JOHNSTON

RECEIVED JANUARY 22, 1934

SOME PROPERTIES OF PURE DEUTACETIC ACID

Sir:

Starting with 0.25 g. of pure $H^2{}_2O$ an equivalent amount of H^2Cl was prepared and studied (accompanying communication). This deutochloric acid was then introduced into a vessel containing silver acetate which had been thoroughly evacuated and kept dark. After twenty-four hours the system had undergone quantitatively the reaction, $H^2Cl + CH_3COOAg = AgCl + CH_3COOH^2$. After exhausting the system at −40° the deutacetic acid was distilled from the reaction chamber. It showed a very sharp melting point at 13.3°, which is 3.3° below that of ordinary acetic acid.

In all cases so far investigated the vapor pressure has been lowered by the substitution of H^2 for H^1. In this case, however, we predicted that the deutacetic acid would have the higher vapor pressure. It is becoming evident that the great differences between the isotopic forms of such substances as water and ammonia [see Lewis and Macdonald, THIS JOURNAL, **55**, 3057 (1933); Taylor and Junger, *ibid.*, **55**, 5057 (1933)] can be chiefly ascribed to the increase in strength of the H^2 bond over the H^1 bond. In such cases these bonds occur only in the liquid, but acetic acid is almost completely associated in the vapor state. Since this can be attributed to similar hydrogen bonds, it appeared likely that the association would be more complete in deutacetic acid. Preliminary measurements of the vapor density seemed to indicate that this is the case, but it must be investigated more carefully.

The increased association of the deutacetic acid in the vapor phase should lead to a higher vapor pressure and this we have established. The difference is 7.5% at 50° and 3% at 90°. Our measurements of p_2 and p_1, the vapor pressures of deutacetic acid and of ordinary acetic acid (prepared in precisely the same way and in the same apparatus) are given in the table. The values of $\log_{10} p$ are plotted against $1/T$ in the figure. Our values for ordinary acetic acid are, throughout the range, 5% higher than those of Ramsay and Young [*J. Chem. Soc.*, **49**, 805 (1886)].

TABLE

T, °C.	p_1, mm.	p_2, mm.
49.7		63.2
52.2	66.1	
64.4		120.4
65.3	117.8	
73.4		171.0
74.4	172.7	
86.0		271.5
86.9	272.9	
94.2		366.4

Finally, it was necessary to ascertain whether our deutacetic acid had remained CH_3COOH^2 or whether the deutons had become distributed between the carboxyl and the methyl groups. A part of our deutacetic acid was treated with anhydrous sodium carbonate and again with calcium carbonate until all of the acid was gone.

The water thus produced, 0.06 g., was freed from carbon dioxide and carefully distilled. If all of the deutacetic acid had remained in the form CH_3COOH^2 and if no ordinary hydrogen had been picked up in the long series of manipulations the specific gravity at 25° should be 1.106. If the H^2 had been randomly distributed between carboxyl and methyl groups the specific gravity should be 1.026. The specific gravity found was 1.096. Considering the difficulty of a density determination with so small a sample, and the many opportunities for contamination with ordinary water, this result indicates that there had been no interchange with the hydrogen of the methyl group.

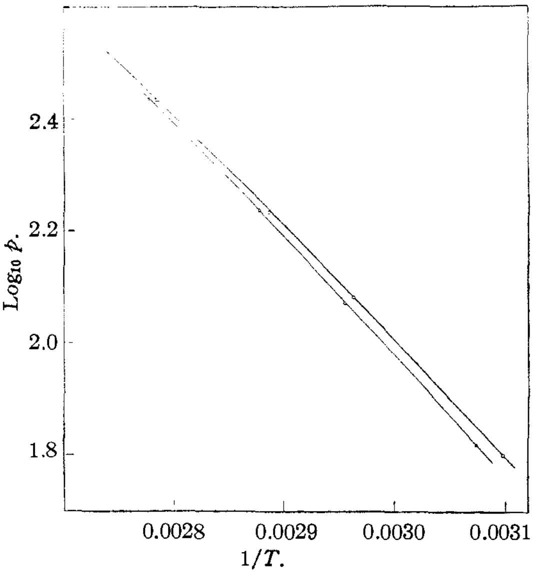

Fig. 1.—○, H^2Ac; □, H^1Ac.

DEPARTMENT OF CHEMISTRY
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GILBERT N. LEWIS
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RECEIVED JANUARY 23, 1934

THE VAPOR PRESSURE OF LIQUID AND SOLID DEUTOCHLORIC ACID

Sir:

Some time ago we attempted to measure the vapor pressure of pure deutochloric acid, H^2Cl. The values obtained were almost identical with those found for ordinary hydrochloric acid except that there was no pronounced break in the curve at the freezing point. The work was not altogether satisfactory owing to uncertainty regarding the purity of the H^2Cl and to some difficulty in maintaining and measuring the temperatures. It seemed worth while to repeat the experiments using the utmost care in these particulars.

After trying many chlorides it was found that the best H^2Cl was obtained by allowing pure $H^2{}_2O$ to react with anhydrous magnesium chloride at 600°, the system being so designed that, after removing H^2Cl, the excess water could be returned to react further with the magnesium chloride. From the vessel containing magnesium chloride the H^2Cl was finally distilled at −130° into the measuring apparatus, to remove water and any other impurities of relatively low volatility. The thermostat consisted of a Dewar tube filled with pentane which was kept at a desired temperature by external cooling and stirred by a stream of cold air. The thermocouple was calibrated by determining in the same apparatus the vapor pressure of ordinary HCl for which we have the extremely accurate and concordant data of Henning and Stock and Giauque and Wiebe [*Z. Physik*, **4**, 226 (1921); THIS JOURNAL, **50**, 101 (1928)]. Our results are given in the table. The triple point of H^2Cl was determined visually as 158.2°K.

TABLE

T,°K.	p, mm.	
152.6	54.5	Solid
154.7	67.5	Solid
157.1	84.5	Solid
157.6	88.0	Solid
159.5	104.0	Liquid
168.2	205.5	Liquid
175.0	329.0	Liquid
181.0	486.5	Liquid
188.3	757.5	Liquid
195.9	1131.5	Liquid
200.9	1474.5	Liquid

Comparing the vapor pressure of H^2Cl, p_2, with that of H^1Cl, p_1, we find that the data for the two liquids agree accurately with the equation

$$\log_{10}\frac{p_1}{p_2} = \frac{15.4}{T} - 0.075 \tag{1}$$

while those for the two solids are in rougher agreement with the equation

$$\log_{10}\frac{p_1}{p_2} = -\frac{57.7}{T} + 0.387 \tag{2}$$

It is interesting that the ratio of the two vapor pressures reaches a maximum of 1.05 at the triple point, below which they approach each other as the temperature is lowered. Assuming that the molal volumes for gas, liquid and solid are approximately the same for H^1Cl and H^2Cl