on the steam-bath, the solutions were carefully fractionated, using a 90-cm. vacuum-jacketed column. The water in each case was collected in two fractions, and the density of the second was compared with that of the original water. The results are tabulated below. Those in the first column, with ordinary water, show the reliability of the method.

Substance added	K_2CO_3	H_3PO_4	None	K_2CO_3	K_2CO_3	K_2CO_3
Mole % D (init.)	0.02	0.73	0.73	0.73	1.08	4.07
Mole % D (final)	.02	.67	.68	.38	.64	1.93
Fr. D removed	0	.08	.07	.48	.41	0.52

The presence of deuterium in the acetone which had been treated with 4.07% heavy water was demonstrated by density measurements and by returning a part of the deuterium from this "heavy" acetone to a sample of ordinary water. The "heavy" acetone was dried for twenty hours with fused potassium hydroxide, then fractionated, and its density compared with that of similarly treated ordinary acetone, showing an increase of 1.4° in the temperature of equal density. It was then warmed with ordinary water and potassium carbonate and again fractionated. The first acetone fraction, dried as before, showed a density slightly greater (0.2°) than ordinary acetone, while the last aqueous fraction contained 0.94% deuterium, corresponding to a removal of 54% of the estimated deuterium content from the acetone. The mole fraction of acetone was 0.29 as compared with 0.33 in the earlier experiments. We may estimate the equilibrium constant for the formation of monodeuteroacetone and ordinary water from acetone and HH^2O as approximately 2, with equilibrium approached in both directions.

The effectiveness of an alkaline catalyst argues for a mechanism involving the postulated enol form of acetone, a possibility which led us initially to perform these experiments. The acidic hydrogen of the enol form should exchange rapidly with the hydrogens of water, and this, coupled with a mobile equilibrium between the keto and enol forms, should result in the formation of carbon–deuterium bonds. It is doubtful whether in an organic compound not susceptible to such a reaction mechanism, the replacement of protium by deuterium by direct contact with water will be realized.

We plan to continue the study of acetone along with other compounds for which enol forms are known or postulated. At present there is no reason to doubt that the treatment of acetone with successively heavier portions of water will result in the practically complete replacement of protium by deuterium. This opens interesting possibilities in synthesis.

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J. O. HALFORD
LEIGH C. ANDERSON
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RECEIVED JANUARY 11, 1934

FRACTIONATION OF THE HYDROGEN ISOTOPES BY THE ADDITION OF SODIUM TO WATER

Sir:

Eyring[1] predicted, from zero point energy considerations, that isotopic separations will occur in the course of many reactions which do not involve electrolysis, through a difference in the reaction velocities of deuterium and of protium compounds. Such separations have been observed, and reported[2,3] for the reaction of iron with steam. We have recently made a quantitative study of the isotopic fractionation which we find to occur in the reaction of metallic sodium with water.

The reaction was carried out by adding small pieces of clean metallic sodium to a weighed quantity of water. Careful specific gravity determinations were made on the initial sample of water, on that collected by burning the evolved hydrogen and on the water distilled from the residue in the reaction flask (approximately 50% NaOH). Successive distillations with slightly alkaline permanganate yielded samples of constant density. Their specific gravities were determined by means of the buoyancy balance[4] equipped with a convenient thermostatic control which we have developed, and were reproducible to one part per million.

The quantitative results are given in the table. In the residue the hydrogen in NaOH is calculated as water.

Material		Wt., g.	ΔT, °C.	Δ sp. g. (p. p. m.)	Total Δm above ordinary water (p. p. m.)
Initial water		389.2	0.532	149	57,990
Final water	Heavy fraction	332.3	.601	168	55,820
	Light fraction	57.3	.179	50	2,860
	Totals	389.6			58,680

From these data we have derived the separation coefficient α, in the equation $d \ln n_P = \alpha d \ln n_D$ where n_P and n_D are, respectively, the number of

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(1) Eyring, *Proc. Nat. Acad. Sci.*, **19**, 78 (1933).
(2) Bleakney and Gould, *Phys. Rev.*, **44**, 265 (1933).
(3) Horiuti and Polanyi, *Nature*, **132**, 819 (1933).
(4) Lewis and Macdonald, *J. Chem. Physics*, **1**, 341 (1933).

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."

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[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

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

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).

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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.