

m. p. 130–131°. The substance is easily soluble in hot water, alcohol and acetone, less soluble in chloroform, insoluble in cold water, benzene, ether and petroleum ether.

*Anal.* After drying at 100° *in vacuo* over H<sub>2</sub>SO<sub>4</sub>, calcd. for C<sub>10</sub>H<sub>13</sub>O<sub>2</sub>N: C, 67.00; H, 7.32; N, 7.82. Found: C, 66.78; H, 7.11; N, 7.72.

*ε*-(*p*-Aminophenyl)-caproic Acid.—Ten grams of *ε*-(*p*-nitrophenyl)-caproic acid reduced in the same manner as the nitrophenylbutyric acid yielded 7.5 g. of crude *ε*-(*p*-

nitrophenyl)-caproic acid. It was recrystallized from 80 volumes of boiling water. Long narrow microscopic platelets, m. p. 108–109°. The substance is soluble in hot water, alcohol and acetone, less soluble in chloroform and benzol, insoluble in cold water, ether and petroleum ether.

*Anal.* After drying at 100° *in vacuo* over H<sub>2</sub>SO<sub>4</sub>, calcd. for C<sub>12</sub>H<sub>17</sub>O<sub>2</sub>N: C, 69.52; H, 8.27; N, 6.76. Found: C, 69.46; H, 8.36; N, 6.64.

NEW YORK, N. Y.

RECEIVED DECEMBER 30, 1933

## COMMUNICATIONS TO THE EDITOR

### ANOMALOUS FRIEDEL-CRAFTS REACTIONS WITH FURANS

Sir:

The compound formed by interaction of benzene, 2-furoic acid and aluminum chloride is *α*-naphthoic acid and not 3-phenyl-2,3-dihydro-2-furoic acid [THIS JOURNAL, 49, 565 (1927)]. The formation of *α*-naphthoic acid, probably through an endoxy compound as a consequence of 1,4-addition, may be general with related types. Other catalysts and experimental conditions, with a miscellany of compounds, are being investigated.

In the reaction between 2-furfural, isopropyl chloride and aluminum chloride in carbon disulfide [*ibid.*, 55, 4197 (1933)], the isopropyl group is introduced into a *β*-position despite the availability of an *α*-position. Bromination of the corresponding acid gives a 5-bromo-*β*-isopropyl-2-furoic acid identical with that obtained by the oxidation of the bromoaldehyde obtained from 5-bromo-2-furfural, isopropyl chloride and aluminum chloride. The same acid is obtained by hydrolysis of the ester resulting by interaction of ethyl 5-bromo-2-furoate, isopropyl chloride and aluminum chloride.

DEPARTMENT OF CHEMISTRY  
IOWA STATE COLLEGE  
AMES, IOWA

HENRY GILMAN  
M. McCORKLE  
N. O. CALLOWAY

RECEIVED DECEMBER 26, 1933

### THE MUTAROTATION OF *α*-D-GLUCOSE IN DEUTERIUM WATER

Sir:

In a previous communication [THIS JOURNAL, 55, 5056 (1933)] it has been reported that the mutarotation of *α*-*d*-glucose in 60% heavy water at 18° has a velocity coefficient of 0.00290 as

compared to 0.00546 found under identical conditions in ordinary distilled water. With the production of 100% deuterium water (D<sub>2</sub>O) in this Laboratory, it became possible to determine the velocity coefficient of the mutarotation of *α*-*d*-glucose in this medium. A 0.6030-g. sample of pure *α*-*d*-glucose was dissolved in 3.3210 g. of D<sub>2</sub>O of *d*<sub>4</sub><sup>20</sup> 1.1055 and the rotation of the solution (*d*<sub>20</sub><sup>20</sup> 1.175) was read at certain intervals of time in a 2-dm. semi-micro tube with sodium light at 20°. The first reading (*α*<sub>0</sub> 38.50°) was taken seven minutes after the addition of D<sub>2</sub>O. The results obtained are shown in Table I.

TABLE I

Time, minutes	<i>α</i>	$k_1 + k_2 = \frac{1}{t} \log \frac{\alpha_\infty - \alpha_0}{\alpha_\infty - \alpha}$
0	<i>α</i> <sub>0</sub> = 38.50	.....
15	37.05	0.00221
50	34.09	.00221
90	31.29	.00220
120	29.50	.00221
180	26.72	.00220
300	23.06	.00222
697	19.35	.00222
1440	<i>α</i> <sub>∞</sub> = 18.83	Mean 0.00221

The velocity coefficient for *α*-*d*-glucose in ordinary distilled water is given by Hudson and Dale [THIS JOURNAL, 39, 320 (1917)] as  $k_1 + k_2 = 0.00635$  at 20°, and as  $k_1 + k_2 = 0.00225$  at 10°. A comparison of these values with the mean value for  $k_1 + k_2$  in Table I shows that the velocity of the mutarotation of *α*-*d*-glucose in pure D<sub>2</sub>O at 20° is identical with that found in ordinary distilled water at 10°. In this case, therefore, the effect of the deuterium water on the velocity of the mutarotation is equivalent to a drop of 10° in the temperature. The specific rotation of the equilibrium solution in D<sub>2</sub>O is [*α*]<sub>D</sub><sup>20</sup> 18.83° ×

$3.924/2 \cdot 1.175 \cdot 0.603 = 52.14^\circ$  as compared to  $[\alpha]_D^{20} 52.06^\circ$  in distilled water [Riiber, *Ber.*, **56**, 2185 (1923)]. Evidently, the replacement of the displaceable hydrogen atom of glucose by a deuterium does not change the value of the specific rotation for the wave length of sodium light. Such a conclusion does not necessarily apply for very short wave lengths.

FRICK CHEMICAL LABORATORY  
PRINCETON UNIVERSITY  
PRINCETON, NEW JERSEY

EUGENE PACSU

RECEIVED FEBRUARY 5, 1934

#### ANALYSIS OF THE DISPERSION CURVES OF SUBSTITUTED PROPIONIC ACIDS

Sir:

It has been observed in this Laboratory that in homologous series of optically active configura-

levorotatory in alanine and in lactic acid and that they are of reverse sign in the levo iodo and dextro azido acids. Similar reversions of the partial rotations are observed in the configurationally related 2-thio and 2-sulfopropionic acids.

The direction and the values of the partial rotations were determined through the analysis of the rotatory dispersion curves in the visible and in the ultraviolet regions by a method previously described [P. A. Levene, A. Rothen and R. E. Marker, *J. Chem. Physics*, **1**, 662 (1933)]. The details of the work, the dispersion curves, and the numerical values of the partial rotation will be published in the near future.

THE ROCKEFELLER INSTITUTE  
FOR MEDICAL RESEARCH  
NEW YORK, N. Y.

P. A. LEVENE  
ALEXANDRE ROTHEN

RECEIVED FEBRUARY 2, 1934

Substance	Rotation in the visible	Groups Y COOH, CHO, CH <sub>2</sub> =CH		Groups X SH, SO <sub>2</sub> H, N <sub>3</sub> , NH <sub>2</sub> , OH, I	
		Abs. band $\lambda_y$ , Å.	Sign of $\alpha_y$	Abs. band $\lambda_x$ , Å.	Sign of $\alpha_x$
{ 2-Thiopropionic acid	Dextro	2100	-	≈2400	+
{ 2-Sulfopropionic acid	Dextro	2150	+	Schumann region	-
{ 2-Azidopropionic acid	Levo	Distant U. V.	-	≈2830	+
{ 2-Aminopropionic acid	Dextro	2100	+	Schumann region	-
{ 1-Octene-3-ol	Dextro	Distant U. V.	+	Schumann region	-
{ 2-Hydroxyheptanoic aldehyde	Levo	3000	+	Schumann region	-
{ Lactic acid	Dextro	2150	+	Schumann region	-
{ 2-Iodopropionic acid	Dextro	≈2150	-	≈2840	+

Braces indicate configurational relationship.

tionally related substances, individual members may differ in the sign of their rotations in the visible, but the partial rotations of the significant chromophoric group and of the rest of the molecule remain of the same sign. This is also often the case in configurationally related substances similar in structure, such as substances 5, 6 and 7 of the table. Comparing the partial rotations of levo iodo and of dextro azido propionic acids, it was found that the partial rotation of the carboxyl in both cases is dextrorotatory and the partial rotations of the iodine atom and of the N<sub>3</sub>- are both levo rotatory. Hence, it may be assumed that these two substances are configurationally related (and not levo iodo- and levo azidopropionic, as assumed by Freudenberg and Kuhn). Furthermore, inasmuch as dextro azidopropionic acid is correlated to levo alanine and this, in its turn, has been correlated to levo lactic acid, it may be assumed that levo lactic acid is correlated to dextro 2-azido and hence to the levo 2-iodo acid. It will be noticed from the table that the partial rotations of the carboxyl groups are

#### THE CONSTITUTION OF OESTRIN

Sir:

The work of Butenandt, *et al.*,<sup>1</sup> which demonstrated the presence of a phenanthrene system in the skeleton of the oestrin molecule, left indefinite the position of the five-membered ring which is also known to be present. The possible positions according to Butenandt for this ring were 8:14, 14:13, or 13:12, using the customary sterol nomenclature.

It does not seem to be generally realized that Butenandt's work, when taken in conjunction with the results obtained with unimolecular films of oestrin derivatives, offers a clear proof of the fact that the five-membered ring is in the same position as in the sterols, *i. e.*, 14:13. Measurements made on models show the following *minimal* areas for the cross section of the possible structures.

Formula	Position of the five-membered ring	Minimal cross-sectional area, in sq. Å.
I	8:14	39
II	14:13	33
III	13:12	38

(1) Butenandt, Weidlich and Thompson, *Ber.*, **66**, 601 (1933).

The experimental value obtained by uni-molecular film measurements<sup>3</sup> is 34 sq. Å., with a possible error certainly not greater than 2 sq. Å., so that the first and last structures are decisively eliminated. The elimination of the 8:14 structure is supported by the crystallographic structure of Bernal.<sup>3</sup>

(2) Danielli, Marrian and Haslewood, *Biochem. J.*, **27**, 311 (1933).

(3) Bernal, *Chem. Ind.*, **51**, 259 (1932).

THE PHYSIOLOGICAL LABORATORY  
PRINCETON UNIVERSITY  
PRINCETON, NEW JERSEY

J. F. DANIELLI

RECEIVED FEBRUARY 12, 1934

#### DIAMAGNETISM OF NITROSO COMPOUNDS

Sir:

Because organic nitroso compounds display certain anomalous properties, such as intense color and a marked tendency to form double molecules, G. N. Lewis<sup>1</sup> suggested that the explanation of their unusual behavior might be related to the cause of the peculiar properties of O<sub>2</sub> and NO, the former being paramagnetic and the latter showing little unsaturation, although it is an odd molecule. Pauling<sup>2</sup> proposed a structure for oxygen and nitric oxide involving the three-electron bond, which, therefore, in view of the above, led him to ascribe a similar triplet structure,  $\text{—}\ddot{\text{N}}::\ddot{\text{O}}:$ , to the nitroso group instead of the singlet configuration,  $\text{—}\ddot{\text{N}}::\ddot{\text{O}}:$ .

I have measured the magnetic susceptibilities of nitrosyl chloride (NOCl), of nitrosobenzene (C<sub>6</sub>H<sub>5</sub>NO), and of *p*-nitrosodimethylaniline ((CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NO), the first as a liquid, the second both as a solid and as a solute in benzene and toluene, the third as a solute in toluene. The Gouy<sup>3</sup> method was used. All three compounds were found to be diamagnetic, a result which cannot be accounted for by the presence of any reasonable amounts of impurities, since the paramagnetism which would be exhibited if the molecules were in the triplet state would be too large to be so masked.

Likewise the result is not explicable on the basis of the formation of double molecules. The solutions were highly colored, a property which is definitely correlated with the monomeric state. Furthermore, investigation of toluene solutions of *p*-nitrosodimethylaniline, 1 to 7% by weight,

(1) G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., Inc., New York, 1923, p. 128.

(2) Linus Pauling, *THIS JOURNAL*, **53**, 3225 (1931).

(3) E. C. Stoner, "Magnetism and Atomic Structure," p. 40.

with a Klett colorimeter showed that the depth of color was proportional to the concentration, indicating at least a high degree of dissociation into single molecules. Freezing point studies<sup>4</sup> on nitrosobenzene in benzene lead to the same result.

The conclusion is that these compounds, at least, are in singlet states,<sup>5</sup> which indicates that they do not have the similarity to oxygen previously suggested. Since at the present time there seems to be no theoretical basis for choosing between the singlet and triplet configurations for the ground state of this type of molecule, it is perhaps not worth while discussing reasons for the above experimental results. However, it is true that for each of the above compounds several singlet structures could be drawn which on the basis of energy data<sup>6</sup> are known to contribute to the stability of related molecules through resonance and which have no triplet analogs. Such resonance would certainly tend to stabilize the singlet configuration but whether this is the determining factor cannot be stated.

I should like to thank Professor Linus Pauling for suggesting this investigation.

(4) K. Auwers, *Z. physik. Chem.*, **32**, 52 (1900).

(5) Linus Pauling, *THIS JOURNAL*, **53**, 1392 (1931).

(6) Linus Pauling and J. Sherman, *J. Chem. Physics*, **1**, 606 (1933).

GATES CHEMICAL LABORATORY E. BRIGHT WILSON, JR.  
CALIFORNIA INSTITUTE OF TECHNOLOGY  
PASADENA, CALIFORNIA

RECEIVED FEBRUARY 12, 1934

#### MUTAROTATION OF $\beta$ -D-RIBOSE AND $\beta$ -L-RIBOSE

Sir:

Owing to the importance of the little known sugar, ribose, not only in its structural relation to other sugars but also in its physiological relation to animal and plant life, since it appears to be of almost universal occurrence in tissues bearing upon the regeneration of life, Phelps and Bates a number of years ago undertook the preparation of a quantity of this sugar in order to study its properties and the improvement of the existing methods of production. One of us (Isbell) has been engaged for some time in the study of the composition of sugar solutions and in the investigation of the isomeric changes which follow solution in water, and has developed a method for determining the composition of the solutions by oxidation with bromine water. Since mutarotation of ribose is not reported in the literature

[Van Ekenstein and Blanksma, *Chem. Weekblad*, **6**, 374 (1909); also Levene, "Nucleic Acids," A. C. S. Monograph No. 56, p. 131, 1931], it seemed desirable to apply the methods [*Bur. Standards J. Res.*, **8**, 615 (1932); **10**, 337 (1933)] which had been developed for the study of other sugars to the investigation of *d*- and *l*-ribose.

Measurements taken at 20 and at 1° show that both *d*-ribose and *l*-ribose exhibit a very remarkable mutarotation. The mutarotation takes place rapidly and direction of the change reverses after a few minutes, so that the initial and final rotations are not greatly different. On account of the rapidity with which the reaction takes place the mutarotation can be best observed at low temperatures.

A 2.0236-g. sample of *d*-ribose (m. p. 87°) dissolved in 45.223 g. of water at 1° gave  $[\alpha]_D^{20}$  -23.1°, 1.5 minutes after solution; -21.3°, five minutes; -19.5°, ten minutes; -18.8° (minimum), twenty minutes; -19.1°, thirty minutes; -21.2°, sixty minutes; -23.1°, one hundred and twenty minutes; -23.7°, three hundred minutes. A 1.9941-g. sample of *l*-ribose (m. p. 87°) dissolved in 45.223 g. of water at 1° gave  $[\alpha]_D^{20}$  +23.2°, two minutes; +21.5°, five minutes; +19.9°, ten minutes; +18.7° (minimum), twenty minutes; +19.4°, thirty minutes; +21.5°, sixty minutes; +23.2°, one hundred and twenty minutes; +24.3°, three hundred minutes; +24.0°, twenty-eight hours.

The complex character of the mutarotation curves shows that crystalline *d*-ribose and also *l*-ribose in water solution establish equilibrium with at least three isomers. One of the isomers is less levorotatory than the crystalline *d*-sugar and the other is more levorotatory. The mutarotation resembles that of the labile calcium chloride compound of mannose reported by Dale [*THIS JOURNAL*, **51**, 2225 (1929)] which Isbell has shown [*ibid.*, **55**, 2166 (1933)] gives  $\gamma$ -mannonic lactone when oxidized with bromine water in the presence of barium carbonate, and which probably has a 1,4 ring structure.

Oxidation of *d*- and *l*-ribose by the barium carbonate-bromine method shows that they are oxidized rapidly at first and then more slowly. The decrease in reaction rate is presumably caused by a less readily oxidized substance formed by the mutarotation reaction.

Since the rotation of *d*-ribose changes initially from a negative to a less negative value, in ac-

cordance with the usual nomenclature, the crystalline sugar will be tentatively designated as  $\beta$ -*d*-ribose and its mirror image as  $\beta$ -*l*-ribose. The similarity of  $\beta$ -*d*- and  $\beta$ -*l*-ribose to the labile calcium chloride compound of mannose suggests that these substances may have furanose structures which on solution in water change spontaneously into the corresponding pyranose forms. However, no definite classification of structures is possible until further experiments are completed.

BUREAU OF STANDARDS  
WASHINGTON, D. C.

FRANCIS P. PHELPS  
HORACE S. ISBELL  
WARD PIGMAN

RECEIVED FEBRUARY 13, 1934

#### THE ASSUMED NON-IDENTITY OF COTTON AND WOOD CELLULOSE

Sir:

On the basis of methylation experiments carried out on cotton and  $\alpha$ -celluloses prepared from five different woods, D. J. Bell [*Biochem. J.*, **26**, 590-597 (1932); **26**, 598-608 (1932); **26**, 609-614 (1932)] has questioned the identity of the chemical structure of cotton and wood cellulose. He found that a maximum methoxyl content of 36.3-39.0% was attained with the wood  $\alpha$ -celluloses as contrasted with a theoretical value of 45.6%. Bell ascribes this resistance to methylation shown by the wood  $\alpha$ -celluloses to the presence of a so-called "resistant portion." These results have been regarded by Irvine as having a marked bearing on the conclusions drawn by other authors with respect to chain length.

In an attempt to duplicate these results with rayon pulps from spruce, beech and maple wood it was not found possible to confirm the work of Bell with respect to the presence in the cellulose of a portion resistant to methylation. The following results were obtained.

Source of $\alpha$ -cellulose	No. of methylations	OMe, %
Spruce	9	44.24
Beech	5	43.08
Maple	5	43.72

The methoxyl values given above are not maximum figures since the reaction has given as yet no indication of an end-point and the methylations are therefore being continued in order to arrive, as closely as possible, at the theoretical value of 45.6% OMe.

DIVISION OF INDUSTRIAL AND  
CELLULOSE CHEMISTRY  
MCGILL UNIVERSITY  
MONTREAL, CANADA

J. BARSHA  
HAROLD HIBBERT

RECEIVED FEBRUARY 21, 1934

## NEOPENTYL DEUTERIDE

Sir:

Since an intensive study of neopentane and its derivatives is being made in this Laboratory, the importance of preparing and studying neopentyl deuteride is obvious.

A quantity of neopentylmagnesium chloride [Whitmore and Fleming, *THIS JOURNAL*, **55**, 4161 (1933)] was prepared and this material was divided into two equal portions. One portion was allowed to react with 2.5 cc. of distilled water to give neopentane. The other portion was allowed to react with 2.5 cc. of heavy water (sp. gr., 1.0735) and 6.9 g. (yield, 78%) of a mixture of neopentane and neopentyl deuteride was obtained. The reactions were carried out in the same apparatus in exactly the same manner, the only difference being the substitution of heavy water for ordinary water in the second case.

A 4.5-cc. sample of the neopentane produced in this manner was used to obtain its Raman spectrum. This material yielded a spectrum which was identical with that obtained earlier [Rank, *J. Chem. Physics*, **1**, 572 (1933)] for pure neopentane. A similar sample of neopentane and neopentyl deuteride yielded a spectrum which clearly showed the presence of the deuteride. The carbon deuterium vibration is shown by the appearance of a line at approximately  $\Delta\bar{\nu} = 2150$   $\text{cm.}^{-1}$  shift from the exciting line, which is in accord with the predictions of simple theory. The spectrum clearly shows that the introduction of the deuterium atom into the neopentane molecule partially removes the vibrational degeneracy of this molecule.

The following physical constants were then determined on the neopentane and the neopentane-neopentyl deuteride mixture, using the same apparatus and technique for both.

**Melting Point.**—The melting points were determined simultaneously and it was observed that the neopentane melted at  $-21$  to  $-20^\circ$  and the neopentane-neopentyl deuteride mixture at  $-22$  to  $-21^\circ$ . Since these two samples were prepared in precisely the same way as to reagents, conditions and treatment, it appears that the neopentyl deuteride causes a lowering of the melting point of the mixture of about  $1^\circ$ . The purest neopentane that we have had showed a freezing point of  $-19.5^\circ$  [Whitmore and Fleming, *THIS JOURNAL*, **55**, 3803 (1933)].

**Refractive Index.**—Using a Valentine refrac-

tometer of the Abbe type (manufactured by the Industro-Scientific Co., Colmar, Penna.; calibration checked by Bureau of Standards) at  $-7.4^\circ$  (room temperature,  $-7.4^\circ$ ), the refractive index of the neopentane was observed to be  $1.35375 \pm 0.00005$  and that of the neopentyl deuteride-neopentane mixture to be  $1.35360 \pm 0.00005$ .

**Boiling Point.**—The difference in the two boiling points at 740 mm. was approximately  $0.2^\circ$ , the deuteride having the lower boiling point.

Preparation of pure neopentyl deuteride is in progress, upon which accurate physical constants will be obtained. Extensive studies will be made on this unique compound.

SCHOOL OF CHEMISTRY AND  
PHYSICS  
PENNSYLVANIA STATE COLLEGE  
STATE COLLEGE, PA.

FRANK C. WHITMORE  
GEO. H. FLEMING  
D. H. RANK  
E. R. BORDNER  
K. D. LARSON

RECEIVED FEBRUARY 21, 1934

## THE ISOTOPIC FRACTIONATION OF WATER BY DISTILLATION

Sir:

In work with heavy water, particularly in exchange of experiments, distillations are frequently desirable either to separate water from substances dissolved in it, or to purify the separated water. It is perhaps worth while to call attention to the serious effect on the results which may arise from isotopic fractionation during distillation. This effect will not be found, of course, where the entire quantity of water distilled is collected, nor when a truly representative sample is obtained by discarding exactly equivalent amounts of the first and last runnings. Moreover, the work of Washburn [Washburn, Smith and Frandsen, *Bur. Stand. J. Res.*, **11**, 453-462 (1933)], and Lewis [Lewis and Cornish, *THIS JOURNAL*, **55**, 2616 (1934)], indicates that the effects to be expected on samples approaching ordinary water in composition will be very small in ordinary apparatus at atmospheric pressure. That such effects are far from negligible in dealing with more highly enriched samples is shown by the following results. (1) A sample of 125 cc. volume containing about 3% of the heavier isotope was very carefully purified and then distilled slowly at atmospheric pressure from an ordinary flask surmounted by a simple Vigreux column about 10 cm. long connected to a quartz condenser. The vertical part of the condenser before the bend was about 20 cm. long. Three fractions of the distillate

were collected and their specific gravities determined at 25°, with the following results:

Fraction of distillate	Sp. gr.	Variation from mean, %
0.00 to 0.20	1.003365	-2.6
.61 to .77	1.003444	
.77 to .96	1.003546	+2.6

The index of refraction of the samples was also determined in a Zeiss interferometer and showed a decrease from the lightest to the heaviest sample nearly, but not quite, proportional to the density increase. (2) In another experiment with 3% heavy water ten successive samples were collected and measured, and all showed a progressive decrease in index of refraction—the total decrease from the first to the ninth amounting to 5.7% of the mean value. The tenth fraction showed a further decrease of 5.8%. When a Widmer column containing a glass spiral 50 cm. long was used (with a different quartz condenser), a difference of over 15% in the apparent concentration of the heavy isotope (as shown by the refractive index) was shown by the second and next to last fractions distilled.

All of these results were obtained at atmospheric pressure. When the pressure was reduced to 10 mm. of mercury or less, a still more striking fractionation (of 2% water) was produced with the aid of an ordinary distilling flask without fractionating column. The first fifth of the distillate contained 32% less heavy isotope than the starting material, and the last fifth about 25% more.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF WISCONSIN  
MADISON, WISCONSIN

NORRIS F. HALL  
T. O. JONES

RECEIVED FEBRUARY 23, 1934

#### EXCHANGE REACTIONS OF HYDROGEN ATOMS Sir:

Approximately 2% heavy water prepared by electrolysis was allowed to dissolve various substances and later separated from them by distillation at atmospheric pressure. After purification the density of the water was found in all cases to have decreased. A slight density loss, found even when the solute contained no hydrogen, was traced to fractionation on distillation, and failure

to recover 100% of the distillate during purification. Allowing for this effect, we find as follows: (1) no interchange of hydrogen during brief contact, (potassium chloride) potassium hypophosphite, potassium acetate, sodium benzoate, hydrogen gas; (2) one-third of the hydrogen in the substance immediately exchanged, ethylene glycol; (3) extent of exchange increasing markedly with time of contact, potassium acetate, hydrogen gas. The work with hydrogen gas was carried out with the collaboration of Professor Homer Adkins, who kindly placed at our disposal his high pressure hydrogenation equipment. Ordinary electrolytic hydrogen was used in amounts approximately equimolar to the total water present. The results were as follows.

Run	1	2	3
T, °C.	230	220	230
Time of contact, hrs.	1.0	9.5	9.5
pH <sub>2</sub> , atm.	340	370	370
Ratio at start	97	85	82
H <sup>18</sup> O/H <sup>16</sup> O at end	5.1	2.5	1.9

The ratios are calculated on the assumption that the hydrogen gas used contained 0.02% deuterium. (It was obtained from a plant where the electrolyte contains approximately 0.1%.) In the first two experiments no catalyst was added to the bomb, but its walls were perhaps not entirely free from nickel from previous hydrogenations. In the third run a considerable amount of a nickel catalyst prepared according to Raney [Adkins, THIS JOURNAL, 54, 4116 (1932)] was used. These results agree with Bonhoeffer's [Bonhoeffer *et al.*, *Z. physik. Chem.*, 23B, 171 (1933); *Naturw.*, 22, 45 (1934)] on sucrose and sodium acetate, except that we find the hydrogens of the acetate group not wholly inert even when nothing is added to promote enolization. (In one run, after sixty-six hours of contact, 34% of the hydrogen in the salt had apparently exchanged.)

Our results with hydrogen do not yet indicate the position of equilibrium. The work is being continued.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF WISCONSIN  
MADISON, WISCONSIN

NORRIS F. HALL  
EVERETT BOWDEN  
T. O. JONES

RECEIVED FEBRUARY 23, 1934