Remarks.—Unpurified diphenyl from run 1 had a melting point of 69–69.5°. The temperature of 252° was the lowest at which observable decomposition took place. The lead deposit in run 1 was bright. All other runs exhibited more or less charring. In runs 2 and 6 the bulb was placed in the cold furnace and then rapidly heated. In the other runs the bulb was placed in a hot furnace. The benzene was determined by the difference in weight caused by passing a stream of air through the bulb. These values are probably high, due to the volatility of diphenyl. The undecomposed lead tetraphenyl was recovered by precipitation with acetone, and the *p*-diphenylbenzene and diphenyl separated by solution in ethyl alcohol.

DEPARTMENT OF CHEMISTRY
DE PAUL UNIVERSITY
CHICAGO, ILLINOIS

RECEIVED AUGUST 16, 1933
PUBLISHED OCTOBER 6, 1933

COMMUNICATIONS TO THE EDITOR

THE FREE METHYLENE RADICAL

Sir:

We have been decomposing diazomethane in a current of ether since some time, in attempts to isolate the methylene radical. Blank runs showed that ether alone, under the conditions of our experiments, does not decompose appreciably under 750°. Using the ether–diazomethane mixture and combining the fragments with metallic mercury [see Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932)] we obtained no trace of any organic compound of mercury with the furnace below 650°, although a considerable portion of the diazomethane decomposed, and antimony mirrors could be readily removed at furnace temperatures as low as 450°. A run at 700° gave an appreciable yield of an organo-mercury compound which was identified as dimethylmercury by adding iodine to the contents of the liquid air trap after distilling off the undecomposed diazomethane; in this way we obtained pure methylmercuric iodide, CH_3HgI, identified by its mixed melting point.

It seems reasonable to infer from these experiments that, if the CH_2 group has been formed, it does not combine with mercury to form $Hg{=}CH_2$, since the addition of iodine to this compound should give CH_2IHgI. Furthermore, it seems very probable that at temperatures of 700° and higher, the methylene group picks off a hydrogen atom from one of the surrounding ether molecules, thus producing a free methyl group.

In a further study of this problem we passed the ether–diazomethane mixture through a furnace heated only to 500°, under which conditions we had previously proved that no methyl groups are produced—and tried the effect of the fragments on metallic mirrors. We found that some metals were attacked and others not. Antimony and tellurium are two typical members of the first group, while zinc, cadmium and lead belong to the second group.

It seems possible to identify the fragments by combining them with tellurium and isolating the compound formed, or by combining them with carbon monoxide, in which case ketene, $CH_2{=}CO$, should be formed if we are dealing with a methylene radical. These experiments are now in progress.

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RECEIVED AUGUST 29, 1933 PUBLISHED OCTOBER 6, 1933

AN APPARATUS FOR THE SEPARATION OF ISOHYDROGEN (DEUTERIUM) OXIDE BY ELECTROLYSIS

Sir:

The writers have not been able to find in the literature any description of an apparatus suited for the moderate scale production of heavy water (isohydrogen or deuterium oxide) by the method discovered by Washburn, that is, the electrolysis of water. An apparatus used in this Laboratory has proved so convenient for this purpose that some of its details may be of sufficient value to be presented.

Two concentric tubes of nickel, 2.5 and 10.6 cm. in diameter (Fig. 1) are used both as the electrodes and the vessel in which the aqueous solution is contained. The portion IJ, 100 cm. in height, holds 3.5 liters of the alkaline solution, supplied by the Burdette Oxygen Company. About 1 part in 2000 of the hydrogen present in this solution initially is deuterium.

The two tubes are insulated from each other by heavy rubber washers, H, Q and K. The washer K is cemented to the metal on which it rests. The screws which hold the apparatus together are insulated on one side by the Bakelite insulators D. The solution is put in or taken out at R, and a condenser and apparatus for the prevention of the escape of mist are attached at B. Electrical connections are made at A and E. The 2.5-cm. tube P is filled with water for cooling which is admitted at M. With 100 amperes operating current the water which escapes from N has a temperature only 0.3° above that which enters at M. The apparatus is made gas tight, except for the opening into the condenser, by the packing C.

The upper length of 10-cm. tubing, 15 cm. in length, is covered with rubber (F) from the inner tube of an automobile tire, and most of the wall of the steel tube is cut away. The purpose of the rubber is to avoid danger in any accidental explosion of the gas. The lower tube IJ is supposed to be kept as full of solution as is possible under the conditions of operation. The joint at H is not essential, as the upper part of the outer tube IJ may be cut away instead. One apparatus was built in which the upper tube was made wholly of rubber, and the connection between each D and H was made by an insulating post.

The apparatus was designed to operate at 400 amperes, but this large a current has not been available.

To save expense the outer tube of our apparatus was made of steel, nickel plated on the inside, and this tube is therefore used as the electrode at which the hydrogen is liberated. The use of steel or iron for the inner tube is not recommended unless a very thick and dense nickel coating can be obtained.

Ten units such as that described are used for the preliminary separation. It is obvious that smaller units must be employed as the separation proceeds. The solution from one unit is distributed among the other nine as soon as space in them becomes available. It is planned to operate a second set of units of a different type, with acid solutions, and to use mutual neutralization as an aid to the separation of the water from the electrolyte.

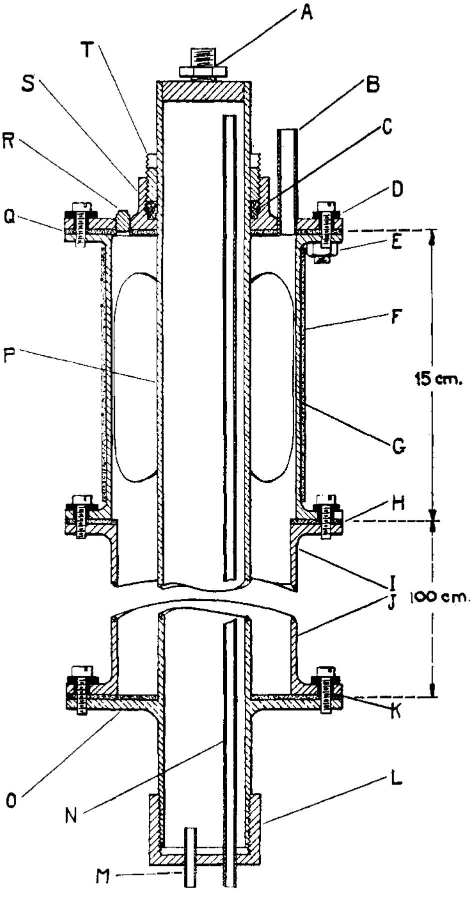

Fig. 1.—Apparatus for the separation of deuterium oxide.

In April, Dr. Washburn stated to one of us (Harkins) that he had tried the use of concentric tubes for the electrolysis, but we have no other knowledge of the apparatus employed by him.

University of Chicago
Chicago, Illinois

William D. Harkins
Clinton Doede

Received September 7, 1933 Published October 6, 1933

A POSSIBLE PHYSIOLOGICAL EFFECT OF THE HEAVY ISOTOPE OF H IN WATER

Sir:

While running experiments on the biological effect of melted ice water and recently condensed water [*Proc. Nat. Acad. Sci.*, **18**, 136, 422 (1932); **19**, 638 (1933)] I tried heavy water obtained from electrolysis in the manufacture of oxygen. The preliminary results are of interest in connection with the recent communication of G. N. Lewis [THIS JOURNAL, **55**, 3503 (1933)] reporting that tobacco seeds failed to sprout in pure H^2H^2O and that growth was considerably inhibited in water in which one-half of the hydrogen was H^2. Since the pure H^2H^2O appears to be lethal, it is probable that more interesting effects will be obtained with less concentrated water such as the sample used in the present experiments which had a specific gravity of 1.000061 (kindly determined by Drs. E. Ball and O. W. Richards).

The tests were made during May and June, 1933. In experiment No. 1 ten 250-cc. covered Pyrex beakers were used, each containing 90 cc. of water. There were four beakers of heavy water and two of each of the following: distilled water, melted ice water renewed daily, and freshly condensed water also renewed daily. Approximately equal amounts of freshly collected *Spirogyra* were rinsed in the water to be tested, drained on filter paper and placed in the beakers. The heavy water was changed after twenty-four hours to avoid dilution by water carried over with the filaments. The beakers were exposed to northern light in an unheated aquarium room (temp. 18–22°). Measurements with an illuminometer showed no differences in light intensity that might affect the results. The filaments in heavy water were characterized by their lack of movement, absence of abscission or cell disjunction [*cf.* Lloyd, *Mich. Acad.*, **6**, 275 (1927)] and greater longevity. In the distilled water controls more spreading occurred, the filaments broke into short lengths (abscission) and began to fade within twenty days. The usual effect was found in the ice and steam water, *i. e.*, almost normal condition in the former and bleaching in the latter. In experiment No. 2 consisting of two beakers of each of the four kinds of water the samples were buffered with Sørensen's phosphates to PH 7.16 and the effects secured again. In the third series the heavy water used in the preceding tests was redistilled in permanganate, buffered again and the results duplicated.

The experiments suggest a stabilizing action of water containing the heavy isotope and the hypothesis may be considered that this is an effect on the colloids in the organism whose bound water is known to be of greater density than "free" water.

*P*H determinations with brom thymol blue indicated a slightly higher *P*H for the heavy water. Further work with a glass electrode is planned to determine if this is a real effect, possibly due to the lower mobility of the heavy H isotope [*cf.* Bernal and Fowler, *J. Chem. Phys.*, 1, 515 (1933)].

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T. CUNLIFFE BARNES

RECEIVED SEPTEMBER 14, 1933 PUBLISHED OCTOBER 6, 1933

SCALE READINGS OF ISOMERIC ESTERS ON THE MAGNETO-OPTIC APPARATUS

Sir:

In a former report [THIS JOURNAL, **55**, 2614 (1933)] the scale readings of the characteristic minima of a number of organic compounds were determined and were found to increase with the increasing weight of positive radicals and to decrease with the increasing weight of the negative radicals. We desired to determine whether these observations held true in the case of isomeric esters or whether it might be that compounds having the same total mass would also have identical scale readings. In order to test this point, the scale readings of various types of esters which are isomeric with the normal alkyl acetates (published in the above mentioned report and reproduced here) were determined experimentally. The readings referred to carbon bisulfide are given in the table herewith.

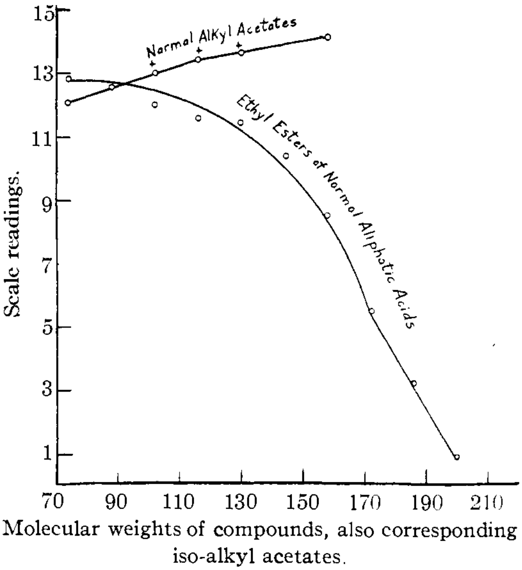

Fig. 1.—Scale readings of isomeric esters on the magneto-optic apparatus.

The usual precautions regarding impurities and contaminations were observed. All readings were made in both water and ether.

A study of the table will show that in the case of corresponding iso and normal acetates, where there is no change in the weights of the positive and negative radicals, the scale readings are identical. But for isomers such as methyl acetate and ethyl formate, where there is a change in the weight of both positive and negative radicals, different scale readings for the two compounds are obtained.

Ester	Scale Reading	Mol. Wt.	Ester	Scale Reading
Methyl acetate	12.00	74	Ethyl formate	12.74
Ethyl acetate	12.50	88	Ethyl acetate	12.50
Propyl acetate	12.97	102	Ethyl propionate	11.93
Butyl acetate	13.39	116	Ethyl butyrate	11.54
Amyl acetate	13.60	130	Ethyl valerate	11.42
		144	Ethyl caproate	10.32
Heptyl acetate	14.11	158	Ethyl heptylate	8.50
		172	Ethyl caprylate	5.50
		186	Ethyl pelargonate	3.26
		200	Ethyl caprate	0.89
Isopropyl acetate	12.97	102		
Isobutyl acetate	13.39	116		
Isoamyl acetate	13.60	130		

EMORY UNIVERSITY
EMORY UNIVERSITY, GEORGIA
J. L. MCGHEE
MARGARET LAWRENZ

RECEIVED SEPTEMBER 16, 1933 PUBLISHED OCTOBER 6, 1933

THE SOLUBILITY OF SALTS IN H^2H^2O

Sir:

Preliminary experiments in this Laboratory have indicated that the solubility of salts in water containing a high concentration of H^2H^2O is markedly less than in ordinary distilled water at the same temperature. These solubility measurements were conducted in the usual way by preparing a saturated salt solution, removing and weighing a portion of the saturated solution, and finally weighing the residual salt after evaporation and suitable drying. By reason of the small volume of heavy water available, however, these operations were performed on a small scale using a special technique. The validity of the procedure was tested by first determining the solubility of a typical salt in ordinary water, and it was found that such solubility measurements could be made with an error of less than one per cent.

In the case of sodium chloride where 1.000 g. of ordinary water dissolves 0.359 g. at 25°, it was found that 1.000 g. of water containing 92% H^2H^2O dissolves only 0.305 g. of this salt, a difference of −15.0%. On a molar basis this corresponds to 0.111 mole of sodium chloride dissolved by a mole of ordinary water as contrasted to approximately 0.103 mole dissolved by one mole of heavy water, a difference of −7.2%. Similarly with barium chloride where 1.000 g. of ordinary water dissolves 0.357 g. of the anhydrous salt at 20°, it was found that 1.000 g. of water containing 92% H^2H^2O dissolves only 0.289 g. of the dehydrated salt at this temperature, a difference of −19.0%. This corresponds to 0.0309 mole of barium chloride dissolved by a mole of ordinary water in contrast to approximately 0.0275 mole dissolved by one mole of the heavy water, a difference of −11.0%. In the course of the last experiment well crystallized barium chloride hydrated with H^2H^2O was obtained with the view to examination for possible differences in crystal form as compared with the ordinary hydrate.

This decreased solubility of salts in H^2H^2O as contrasted with ordinary water is probably a general effect governed by the fundamental differences between the two liquids. Further investigation should show other interesting differences between the two liquids as solvents.

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HUGH S. TAYLOR
EARLE R. CALEY
HENRY EYRING

RECEIVED SEPTEMBER 19, 1933 PUBLISHED OCTOBER 6, 1933

SOME PROPERTIES OF HEAVY WATER

Sir:

We have measured a few characteristic properties of water containing various proportions of the heavy hydrogen isotope up to 92%, and have used these values for the purpose of extrapolation to 100%. The heavy water used in the experiments described in this communication was prepared by prolonged electrolysis of an alkaline solution with nickel electrodes. In estimating the proportion of H^2 from the density measurements, the value d_{20}^{4} 1.1056 given by Lewis and Macdonald [THIS JOURNAL, **55**, 3057 (1933)] was used. All our experimental data are given so that even should the figure 1.1056 later prove to be wrong, our results will not be without value. The molar quantities are calculated assuming the molecular weight to be 20.032.

We have also attempted to determine the concentration of oxygen isotope O^{18} by decomposing the heavy water and combining the hydrogen and oxygen with ordinary oxygen and hydrogen, respectively. This was done in the apparatus shown. The heavy water was passed back and forth over hot iron between the traps A and B, liquid air being used to collect the fractions. As the hydrogen was released it was passed over hot copper oxide and the resulting water was caught in trap C (Fraction X). Ordinary dry, oxygen-

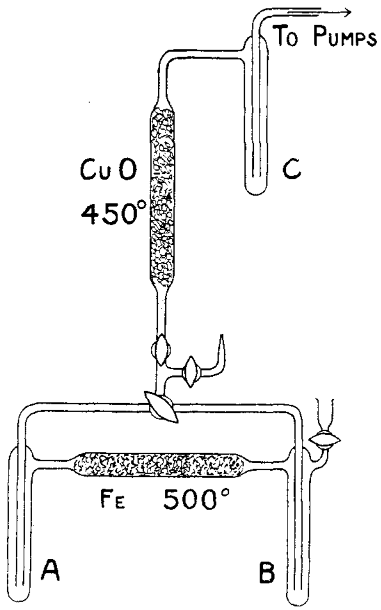

Fig. 1.—Apparatus for analysis of heavy water.

TABULATED DATA ON HEAVY WATER

	Ordinary water	31%	63.5%	92%	100% (calcd.)
Density d_{20}^{4}	0.9982	1.0314	1.0664	1.0970	1.1056 (Lewis)
Refractive index n_{20}^{D}	1.33293	1.33138	1.32992	1.32849	1.3281
Refractive index n_{20}^{C}	1.33094	1.32959	1.32824	1.32683	1.3265
Molar refr. (D line)	3.711	.....	.....	.....	3.677
Viscosity η_{20} (mp.)	10.87	11.4	12.7	13.7	14.2
Surface tension 20° (dynes/cm.)	72.75	71.5	69.8	68.1	67.8
Magnetic susceptibility $\chi \times 10^6$/g.	−0.72	.....	.....	−0.65	.....
Molar susceptibility $\times 10^6$	−13	.....	.....	−13	.....

free hydrogen was passed over the iron–iron oxide mixture and the water formed was frozen out in A (Fraction Y). Excess hydrogen was burned at the jet shown.

Fraction X was found to be identical in properties with the initial heavy water. Fraction Y could not be distinguished from ordinary water. There is, therefore, no appreciable concentration of O^{18} in the electrolytic process.

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P. W. SELWOOD
ARTHUR A. FROST

RECEIVED SEPTEMBER 22, 1933 PUBLISHED OCTOBER 6, 1933

NEW BOOKS

Ternäre Systeme. Elementare Einführung in die Theorie der Dreistofflegierungen. (**Ternary Systems.** An Elementary Introduction to the Theory of Three-Component Alloys.) By DR. G. MASING, Scientific Consultant, Siemens-Konzern, and Lecturer at the Technical High School of Berlin. Akademische Verlagsgesellschaft m. b. H., Markgrafenstrasse 6, Leipzig C 1, Germany, 1933. viii + 164 pp. 166 figs. 15 × 5 × 23.5 cm. Price, M. 8.30; cardboard cover, M. 9.60.

"The purpose of this work," writes the author, "is . . . to give the fundamentals of the science of ternary systems in complete representation," somewhat freely translated. This has been done to a fuller extent than in any other text, as far as the reviewer knows. Even the standard Roozeboom, in the latest section on three-component bodies, issued as long ago as 1913, omits discussion of the occurrence of solid solutions, which a practical metallurgist could hardly leave out of consideration. Masing's text is particularly complete with respect to the treatment of systems in which solid solution occurs, and is written with thoroughness and clarity. The first eight chapters contain discussion of a purely general nature, on isotherms, crystallization processes and representations of isoplethal sections ("zur Konzentrationsebene sehnrechte Schnitte"). This purely general treatment is intentional, and advantageous to the author's plan of making the treatment complete; an occasional reference to actual systems which show