COMMUNICATIONS TO THE EDITOR

GRIGNARD REAGENTS FROM DIALKYL SULFATES

Sir:

In a study of some of the reactions of di-*n*-butyl sulfate it was found that this compound reacts with *n*-butylmagnesium bromide according to the equation: $(n\text{-}C_4H_9)_2SO_4 + n\text{-}C_4H_9MgBr \longrightarrow n\text{-}C_4H_9MgOSO_2OC_4H_9 + n\text{-}C_4H_9Br$. This indicated that dialkyl sulfates might form Grignard reagents directly and this has been found to be the case. Diethyl sulfate reacts readily with magnesium in dry ether to give a slightly soluble Grignard reagent as follows: $(C_2H_5)_2SO_4 + Mg \longrightarrow C_2H_5Mg(C_2H_5)SO_4$. This with benzaldehyde gave a good yield of phenylethylcarbinol. Di-*n*-butyl sulfate similarly formed a compound which hydrolyzed readily to give *n*-butane. So far as we are at present aware this type of Grignard reagent has not been studied heretofore.

The investigation upon the preparation and properties of di-*n*-butyl sulfate will be published shortly. Work upon the Grignard reagents from dialkyl sulfates is still in progress.

CHEMISTRY DEPARTMENT
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

C. M. SUTER
HOWARD L. GERHART

RECEIVED JUNE 5, 1933 PUBLISHED AUGUST 5, 1933

CONVERSION OF ORTHO TO PARA HYDROGEN OVER PROMOTED IRON SYNTHETIC AMMONIA CATALYSTS AT −190°

Sir:

The catalytic conversion of ortho to para hydrogen at about −190° has now been reported for a number of catalysts. It is generally recognized that the mechanism of the low temperature conversion, whatever be its nature, is quite different from that involved in the high temperature conversion (from 0 to 500°). The experiments on a promoted iron catalyst to be summarized briefly in the present letter afford several additional contrasts between the characteristics of the high and the low temperature conversion.

The adsorption of hydrogen by a promoted iron synthetic ammonia catalyst was found to inhibit markedly the activity of the latter toward the ortho-para conversion at −190°. Thus at a space velocity of 12,000 practically 100% conversion of a 25:75 to a 47:53 para-ortho mixture could be obtained if the freshly reduced sample was degassed at 450° and cooled to −190° in helium; whereas if the sample was cooled in hydrogen from 450°, it was found capable of effecting only a 12% conversion at −190°. Furthermore, exposing a sample of helium-cooled catalyst to hydrogen at 100° and 760 mm. pressure for 5, 15, 30, 60, 120 and 200 minutes resulted in the catalyst being able to effect 43, 20, 16, 15, 10 and 15% conversion, respectively, at −190°; similar exposure of a sample to hydrogen at 200° for 15, 30 and 60 minutes left the catalyst able to effect a 32% conversion in each case. These data combined with measurements that have been made on the rate and amount of hydrogen adsorbed by the catalyst at 100 and 200° appear to indicate definitely that the activated adsorption of hydrogen at the higher temperatures is primarily a surface adsorption and not a solution within the iron sample. If this inhibitive effect of high temperature hydrogen adsorption on the low temperature conversion activity of metal catalysts proves to be a general one, it should be a useful tool for differentiating between the adsorption of gases by catalyst surfaces and solution within metal catalysts.

Permitting the promoted catalyst to take up oxygen between room temperature and 450° almost eliminates its high temperature activity toward the para-ortho conversion but only slightly impairs the activity toward the conversion at −190°. Since the iron oxide that would be formed first by the reaction of oxygen and iron is magnetite (Fe_3O_4), the retention of activity at −190° by the partially oxidized catalyst is perhaps not surprising for as Bonhoeffer, Farkas and Rummel [*Z. physik. Chem.*, **B21,** 225 (1933)] and Taylor and Diamond [THIS JOURNAL, **55,** 2613 (1933)] have suggested, the low temperature conversion may be associated with magnetic characteristics of the catalyst surface.

U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.
R. W. HARKNESS
P. H. EMMETT

RECEIVED JUNE 19, 1933 PUBLISHED AUGUST 5, 1933

THE LOW TEMPERATURE ABSORPTION SPECTRUM OF PEPSIN

Sir:

Preliminary measurements indicate that pepsin has an absorption band in the ultraviolet in the region 2600–2900 Å. If the pepsin is cooled, say to −100°, then it is found that this wide band is "resolved" into a number of sharp, narrow bands. At the present time it appears probable that certain of these bands may be correlated with activity.

It has also been found that proteins such as serum albumin and egg albumin show narrow band formation at low temperatures. It seems that there is a difference in the temperature required to produce the narrow bands in the case of the albumins and that of pepsin; apparently a lower temperature is necessary for pepsin.

The apparatus used in the low temperature work is very simple and is shown in the accompanying diagram. It consists essentially of two concentric tubes and the cooling is produced by the circulation of precooled nitrogen. The design is after a suggestion of Dr. F. Simon.

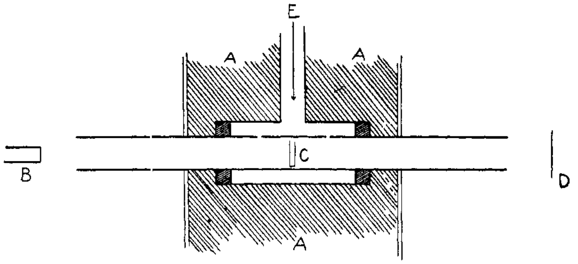

Fig. 1.—A, Lagging (cotton waste); B, hydrogen discharge tube; C, pepsin; D, spectrograph; E, pre-cooled nitrogen.

Further details will be published shortly.

FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY
AND THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH
PRINCETON, N. J.
G. I. LAVIN
J. H. NORTHROP
H. S. TAYLOR

RECEIVED JUNE 21, 1933 PUBLISHED AUGUST 5, 1933

THE REACTION BETWEEN ATOMIC HYDROGEN AND CARBON TETRACHLORIDE

Sir:

Previous studies on the reactions of atomic hydrogen with organic compounds have not yielded information about the mechanisms of these changes, due to the complexity of the products and to the large number of consecutive reactions taking place. In a recent series of experiments, it has been found that the reaction between atomic hydrogen and carbon tetrachloride vapor leads to the formation of relatively simple products in addition to the high polymers usually found.

The apparatus is of the conventional type: carbon tetrachloride vapor is admitted to a stream of atomic hydrogen drawn from a Wood discharge tube, the pressure in the reaction zone being maintained at about 0.7 mm. The volatile products of the reaction, together with the unchanged carbon tetrachloride, are frozen out in a liquid air trap.

That extensive reaction takes place is shown by the heat evolved in the reaction zone, the presence of considerable hydrogen chloride in the liquid air trap, the deposition of a solid product on the walls of the reaction chamber, and, if the pressure is sufficiently low, a moderately intense greenish-blue luminescence, appearing at the region of mixing. The solid product is soluble in carbon tetrachloride, but decomposes without melting slightly below red heat. It contains about 55% chlorine and does not decolorize bromine water. The liquid air condensate is mostly carbon tetrachloride and hydrogen chloride. Tests for chloroform and for phosgene were negative. A brown oily residue remained after distillation of the carbon tetrachloride.

The most striking result, however, is the presence in the condensate of a small amount of a volatile substance, which explodes on coming in contact with the air. If, at the conclusion of a run, the contents of the trap are rapidly melted in air, the boiling off of the hydrogen chloride is attended by small repeated explosions. In some of the runs the condensate was covered with water immediately upon removal of the liquid air. Upon warming, the hydrogen chloride passed into the water layer and the explosive substance remained in solution in the carbon tetrachloride. This was evidenced by the fact that the first few drops of distillate from the latter layer exploded on forming in the condenser. These explosions were accompanied by the deposition of a considerable amount of soot.

It seems most plausible to assume that the initial reaction is $CCl_4 + H = CCl_3 + HCl$. The solid product is evidently formed by the association of the CCl_3 fragments and subsequent dechlorination by atomic hydrogen, the removal of chlorine being followed by polymerization. The dechlorination must take place, at least in part, after the material has condensed on the walls. The explosive substance has not been identified. Professor Kohler has pointed out that it might be either mono- or dichloroacetylene. The work will be continued with the objects of establishing the identity of this substance and of deducing the mechanism of its formation.

HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
HUGH F. SMYSER
HUGH M. SMALLWOOD

RECEIVED JUNE 29, 1933 PUBLISHED AUGUST 5, 1933

THE FORMATION OF METHYL RADICALS IN THE DECOMPOSITION OF AZOMETHANE

Sir:

The formation of the observed products in the homogeneous thermal decompositions of the two unsymmetrical azo compounds, methylisopropyl diimide and dimethyltriazene, is best explained by the assumption that the azo compounds liberate radicals on decomposition and that these radicals later combine at random. In some recently completed work which concerned itself with the possibility that short reaction chains accompany the unimolecular decomposition of azomethane, it was assumed that methyl radicals were formed in that decomposition. In order to avoid ambiguity in the conclusions drawn from the experiments, it was thought advisable to obtain more direct evidence that methyl radicals are actually liberated when azomethane decomposes.

Azomethane was decomposed in an apparatus similar to that described by Rice, Johnston and Evering [THIS JOURNAL, **54**, 3529 (1932)] in which water vapor served as a carrier gas, and the decomposition products were allowed to pass over cold lead mirrors. It was found that the products readily removed the mirrors when the temperature of the furnace was above 475° and that removals could be observed when the mirrors were as far as 10 cm. from the furnace.

These facts indicate very strongly that methyl radicals are formed when azomethane decomposes thermally. Ramsperger found that from 275 to 330° the products of the decomposition were independent of temperature. It is not absolutely certain that the products at 475° would be the same as those at 330°, but it is probable that they would be so if no explosion of the gas occurred. No explosions were observed to have taken place in the experiments here reported.

CHEMICAL LABORATORIES OF HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
JOHN A. LEERMAKERS
NATIONAL RESEARCH FELLOW IN CHEMISTRY

RECEIVED JUNE 30, 1933 PUBLISHED AUGUST 5, 1933

SOME FURTHER REMARKS ON THE USE OF THE MAGNETO-OPTIC METHOD

Sir:

Allison and Murphy [THIS JOURNAL, **52**, 3769 (1930)] presented their very important work on the magneto-optic apparatus. Since that time several other papers have come from their laboratory giving further data on the use of this apparatus. Their results have been so astounding that many chemists, physicists and other scientists have been a little hesitant in accepting this work and have also failed to see its wide application and use in the field of science, especially in the field of chemistry and biochemistry. Due to this feeling of skepticism, and to our interest in the method, we decided to apply it in the study of the localization of some metals in the organs and tissues of animals.

We believe, therefore, that the experience which we have had in the application of this method to the analysis of solutions of uranium nitrate will be of general interest.

Following the procedure of Bishop and Dollins [THIS JOURNAL, **54**, 4585 (1932)] we determined the concentration at which the characteristic minimum of the most abundant isotope of uranium appeared on progressive concentrations and that at which it disappeared on progressive dilutions. In a total of 126 analyses, many of which were checked by two different observers, readings could be repeated within 3 mm., corresponding to 0.02 division of the magneto-optic scale, and the results as obtained lead us to believe that the method is accurate by very careful manipulation to within ±10%. However, one must observe all the precautions outlined in the literature descriptive of the method and a trained observer is essential. For such an observer this is indeed a comparatively easy method of analysis.

We were interested in the application of this method to uranium because we wished to study the distribution in the blood, urine and various organs of a foreign material injected into the blood of animals. This we were able to do with satisfaction and we believe that we have given the method a fair and thorough test, as all the 126 samples of which analyses were made were unknowns to the observer. We are also of the opinion that it can be used advantageously by chemists and biological chemists, as well as by physicists, especially if dealing with very small quantities. The details of this work will be published in full in the *American Journal of Physiology.*

LABORATORY OF BIOCHEMISTRY, DEPARTMENT OF CHEMISTRY HERMAN D. JONES
LABORATORY OF PHYSICS ROY GOSLIN
ALABAMA POLYTECHNIC INSTITUTE
AUBURN, ALABAMA

RECEIVED JULY 5, 1933 PUBLISHED AUGUST 5, 1933

THE VESICANT ACTION OF HALOGENATED SULFIDES

Sir:

Dawson, in an article entitled, "Reactions of Certain Halogen Substituted Aryl, Alkyl and Di-alkyl Sulfides with Benzylamine. I" [THIS JOURNAL, **55,** 2070 (1933)], discusses the mechanism of vesicant action of halogenated sulfides and states, "The data obtained from these reactions may be regarded as further substantiating the condensation theory of vesicant action, but they entirely eliminate thiazane formation as an important factor and appear to demand a new limitation, that of a reactive halogen on the beta carbon atom."

In 1928 I published an article [*ibid.*, **50,** 2446 (1928)] dealing with the synthesis of β-chloroethyl and γ-chloropropyl *methyl* sulfides. The vesicant action of these compounds was studied and the following conclusion was drawn: "It is quite apparent that *only when the halogen is in the β position with respect to the sulfur atom will the resulting compound possess vesicant properties.*" This conclusion was confirmed in a study I made of the vesicant action of the analogous β-chloroethyl and γ-chloropropyl *phenyl* sulfides [Kirner and Richter, *ibid.*, **51,** 3413 (1929)] and also, later, by Gilman and Hewlett [*ibid.*, **52,** 2141 (1930)] in a study of the vesicant action of β-chloroethyl and γ-chloropropyl *furfuryl* sulfides.

In connection with the synthesis of β- (and γ)-chloropropyl *ethyl* sulfides, Dawson used a modification of the method I described for the above-mentioned methyl sulfides and gave a reference to my work, but he apparently overlooked the conclusions which were drawn in this paper regarding the vesicant action of these compounds.

I would like to point out that the "new limitation, that of a reactive halogen on the beta carbon atom," just suggested by Dawson, was first presented in my paper of five years ago.

COAL RESEARCH LABORATORY
CARNEGIE INSTITUTE OF TECHNOLOGY
PITTSBURGH, PENNSYLVANIA
W. R. KIRNER

RECEIVED JULY 12, 1933 PUBLISHED AUGUST 5, 1933

A SIMPLE TYPE OF ISOTOPIC REACTION

Sir:

It was shown by Lewis and Cornish [THIS JOURNAL, **55**, 2616 (1933)] that when water is distilled through a fractionating column, a large separation of the isotopes of hydrogen and oxygen can be effected, especially if the distillation is carried out under reduced pressure. In order to concentrate considerable amounts of these isotopes, Professor Merle Randall has now designed and constructed, in this Laboratory, a large still which has been in operation for about two months. The density of the water at the bottom of the still has been steadily increasing and it is important to know how much of the increase in density is due to H^2 and how much to O^{18}. The method used by Lewis and Macdonald [*J. Chem. Phys.*, **1**, 341 (1933)] for separating the hydrogen and oxygen of a given sample of water, which consisted in passing the steam over hot iron, is cumbrous. I have therefore sought some simpler process depending upon the interchange of isotopes in an aqueous solution, such as may be exemplified by the reaction

$$H^1H^2O + NH^1H^1H^1 = H^1H^1O + NH^1H^1H^2$$

Ammonia in water may be regarded as forming ammonium hydroxide, and again dehydrating, this process proceeding back and forth with very great velocity. Now the fourth hydrogen of the ammonium group is exactly like the others and when the dehydration occurs, each of the four hydrogens has an equal chance of being lost. Therefore there must be a rapid interchange of such hydrogen isotope as is present so as to give almost immediately a nearly random distribution of the isotope between NH_3 and H_2O. When ammonia gas is passed into water at 0°, one mole of water absorbs nearly one mole of ammonia and since ammonia has three hydrogen atoms, while water has two, more than half of the H^2 in the system will escape when the ammonia is pumped off.

A sample from the still which showed an excess density (over ordinary water) of 0.000182 was saturated with ammonia at 0° and then the ammonia was pumped off at room temperature. This process was performed six times, at the end of which all but about one per cent. of the accumulated H^2 should have disappeared if saturation and exhaustion had been complete in each step. However, no pains were taken in these respects so that probably several per cent. remain of the original accumulation of H^2. After purifying the remaining water its excess density proved to be 0.000085, or in other words, at least 0.000097 of the original excess density was due to H^2.

Another part of the same sample was treated with sulfur dioxide, which removes the excess of oxygen isotope by a corresponding reaction

$$H_2O^{18} + SO^{16}O^{16} = H_2O^{16} + SO^{16}O^{18}$$

In this case the sulfur dioxide was allowed merely to bubble through the water for several days. The excess density of the residue was 0.000109, showing that of the original density excess at least 0.000073 was due to O^{18}. We thus account for 0.000170 of the original 0.000182. This crude experiment shows that with a little refinement we shall have an exact method for analyzing water containing isotopes of both oxygen and hydrogen. In work of precision the isotopic composition of the ammonia must be ascertained, especially if it is prepared from electrolytic hydrogen, and precautions must be taken against any large loss of water by evaporation.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
GILBERT N. LEWIS

RECEIVED JULY 22, 1933 PUBLISHED AUGUST 5, 1933

THE BIOCHEMISTRY OF WATER CONTAINING HYDROGEN ISOTOPE

Sir:

Even before I had succeeded in concentrating the isotope of hydrogen, I predicted that H^2H^2O would not support life and would be lethal to higher organisms. As soon as heavy water became available experiments to test this idea were begun, but it was necessary to choose an experiment which would require the minimum of biological technique and also very small quantities of water.

The minute seeds of tobacco (*nicotiana tabacum var. purpurea*), which Professor C. B. Lipman has kindly furnished me, were found to germinate almost infallibly under favorable conditions. I then placed twelve of these seeds in pairs in

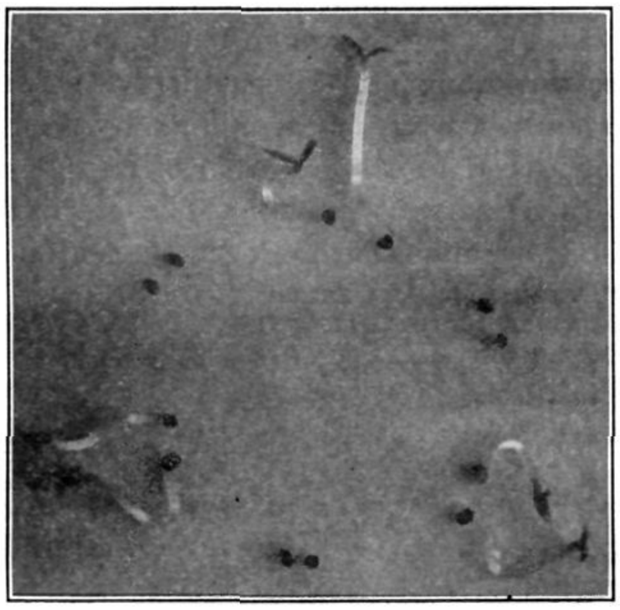

Fig. 1.

six similar glass tubes and added to each of three tubes 0.02 cc. of ordinary distilled water and to each of the other three tubes 0.02 cc. of pure H^2H^2O. The six tubes were then hermetically sealed and placed in a thermostat at 25°. The three pairs of seeds in ordinary water began to sprout in two days and at the end of two weeks formed the well-developed seedlings shown in Fig. 1. The three pairs of seeds in H^2H^2O showed, at least macroscopically, no development. These three pairs alternate with the seedlings in Fig. 1. These undeveloped seeds have now been restored to ordinary water and it will be interesting to see whether their development has been only inhibited or whether they have been killed.

Six entirely similar tubes, each containing two seeds, were filled alternately with ordinary distilled water and with water in which one-half of the hydrogen is H^2, thus corresponding, on the average, to the formula H^1H^2O. At the end of four days all six of the seeds in ordinary water gave well-developed seedlings, while those in the heavier water all showed about the same degree of sprouting as occurs in ordinary water in two days. Whether the seeds will continue to develop in water containing 50% of H^2 remains to be seen. The present development is shown in Fig. 2. I am greatly indebted to Mr. J. A. Gullberg for making the photographs.

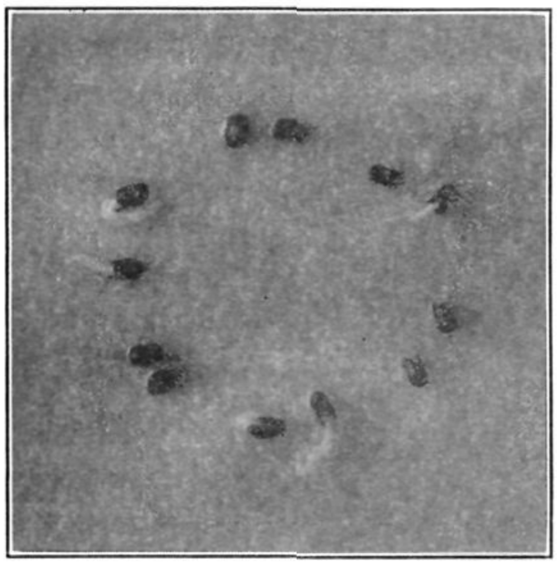

Fig. 2.

I have long desired to determine the proportions of isotopes in living matter, in order to see whether the extraordinary selective power of living organisms, which is exemplified by their behavior toward optical isomers, might lead to a segregation of isotopes in some of the substances which are necessary to growth. The marked biochemical differences between the two isotopes of hydrogen lends a further incentive to this search.

DEPARTMENT OF CHEMISTRY
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BERKELEY, CALIFORNIA
GILBERT N. LEWIS

RECEIVED JULY 22, 1933 PUBLISHED AUGUST 5, 1933

THE MOBILITY OF IONS IN H^2H^2O

Sir:

We have compared the conductivity of hydrogen and potassium chlorides in ordinary water and in nearly pure H^2H^2O. Since only about 0.3

cc. of the latter was available, a cell containing 0.25 cc. was constructed with electrodes of bare platinum wire and gave excellent results. To equal quantities of the two kinds of water one cubic millimeter of ordinary constant-boiling hydrochloric acid was added by means of a buret made from the capillary of a broken Beckmann thermometer and accurate to 0.000001 cc. The addition of this small amount of ordinary hydrochloric acid solution is equivalent to adding H^1 to the extent of 0.4 per cent. of the total hydrogen present. The measured resistance of the cell with these solutions (approximately 0.017 *M*) in ordinary and in heavy water at various temperatures is shown in Curves B_1 and B_2 of Fig. 2.

The solution in heavy water was neutralized with dry sodium carbonate and distilled. Its density showed it to be 97% H^2H^2O. Equivalent solutions (approximately 0.086 *M*) of potassium chloride in this and in ordinary water were then made up, the salt being weighed out with a microbalance. The resistance of these two solutions is shown by the Curves A_2 and A_1 of Fig. 2.

Taking the data from the curves, at even temperatures, and making a slight extrapolation to pure H^2H^2O, assuming that the resistance changes linearly with the isotopic content of the solvent, we obtain the values given in Table I, where x(KCl) is the ratio of the equivalent conductance of potassium chloride in ordinary water to that in pure H^2H^2O and x(HCl) is the ratio of the equivalent conductance of H^1Cl

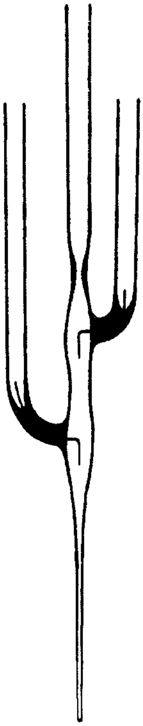

Fig. 1.

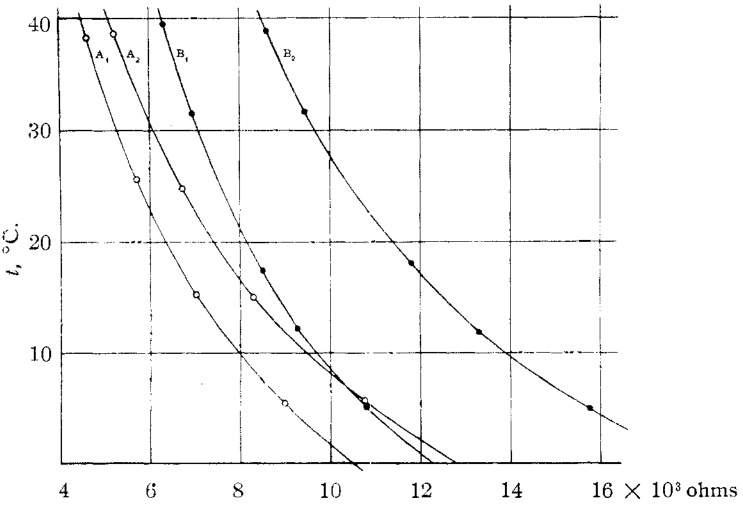

Fig. 2.

in ordinary water to that of H^2Cl in pure H^2H^2O. We believe these figures to be accurate to 0.5%.

TABLE I

t, °C.	5	15	25	35	18
x(KCl)	1.212	1.180	1.162	1.152	1.173
x(HCl)	1.476	1.426	1.390	1.362	1.414

It seems safe to assume that the ratio of equivalent conductance to equivalent conductance at infinite dilution is the same for each electrolyte in the two solvents, and further, that the ratio of the mobilities of K^+ and Cl^- is the same in both solvents. We then obtain the mobilities at 18° of H^{2+}, K^+ and Cl^- in pure H^2H^2O as 213.7, 54.5 and 55.3 if we take the corresponding mobilities of H^{1+}, K^+ and Cl^- from the "International Critical Tables" as 315.2, 64.2 and 65.2.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
GILBERT N. LEWIS
THOMAS C. DOODY

RECEIVED JULY 24, 1933 PUBLISHED AUGUST 5, 1933

VESICANT ACTION OF CHLOROALKYL SULFIDES

Sir:

I realize that the first published statement on the relationship between beta substitution of chloroalkyl sulfides and vesicant action was made by Kirner [THIS JOURNAL, **50**, 2446 (1928)] and deeply regret that the statement in my recent article [*ibid.*, **55**, 2070 (1933)] was not so phrased as to indicate clearly the limitation I had in mind, which was the application of this principle to the condensation theory of vesicant action.

It has been current knowledge at Edgewood Arsenal for many years that the vesicant action of mustard gas and its homologs is limited to those substituted on the beta carbon atom. This information was unpublished and detracts in no way from Kirner's recognition of the fact. However, it was this knowledge, coupled with certain difficulties in accepting completely the hydrochloric acid theory of vesicant action, that led Lawson and Reid [*ibid.*, **47**, 2821 (1925)] to bring up again the condensation theory and to suggest the possibility of thiazane formation as an important factor. The results published in my recent paper demonstrate that thiazane formation is not essential to vesicant action and indicate that if the condensation theory is to be retained it must assume an additional limitation, a reactive halogen on the beta carbon atom.

EDGEWOOD ARSENAL, MD.
THOMAS P. DAWSON

RECEIVED JULY 25, 1933 PUBLISHED AUGUST 5, 1933