COMMUNICATIONS TO THE EDITOR

PHOTOSYNTHESIS IN VITRO

Sir:

Baly[1] originally required a pre-activated catalyst of colloidal nature for the reduction of carbon dioxide to formaldehyde and carbohydrates *in vitro*. Neither Emerson[2] nor Zscheile[3] confirms his results. Later, supporting his catalyst on an aluminated kieselguhr, Baly[4] found pre-activation unnecessary. Bell[5] does not confirm this. Baly[6] has insisted throughout that the catalyst must be alkali-free. Dhar, Rao and Ram,[7] and Rao and Dhar[8] obtain formaldehyde with nickel carbonate and colloidal ferric hydroxide as catalysts in alkaline solution (2% $NaHCO_3$).

In synthesizing formaldehyde there are two essentials: an active catalyst, and light of the proper wave length. Rao and Dhar (Ref. 8, p. 1424) used glass containers, stating that the ultraviolet under such conditions must be of limited effect. Kruyt and van der Spek[9] state that $Fe(OH)_3$ can be negatively charged in a limited range of alkaline concentrations. More alkali precipitates the sol, independently of the concentration of the catalyst. Pure $Fe(OH)_3$ sols appear unstable in 2% $NaHCO_3$. Rao and Dhar's $NiCO_3$ was apparently not colloidal.

The writer prepared catalysts as follows: (a) $Fe(OH_3)$—Krecke's method; (b) $NiCO_3$—(1) triturated $NiCO_3$ (Kahlbaum) washed free from chloride and sulfate with boiling water, (2) by precipitation from the nitrate with $NaHCO_3$, removing the nitrate by dialysis.

The following experiments were performed: (a) 500 cc. of 2% $NaHCO_3$ (Merck's c. p.) with $NiCO_3$ (quantities ranging from 0.2–10 g.); (b) 500 cc. of 2% $NaHCO_3$ with $Fe(OH)_3$ (approximately 0.5 g. added from a stable aqueous sol); (c) 500 cc. of 2% $NaHCO_3$ with $NiCO_3$, 1 g. and 25 cc. of 0.1% dimedone solution.

All were exposed for sixty hours to sunlight. The flasks were periodically shaken, as the catalyst settled out. Tests were made on all for formaldehyde (Schiff's reagent, described by Rao and Dhar) and for carbohydrates (Molisch's reagent). The sediment in experiment (c) was examined for the typical crystals that formaldehyde forms with dimedone. All results were negative.

[1] Baly, *Science*, **68**, 364–365 (1926).
[2] Emerson, *J. Gen. Physiol.*, **13**, 163 (1929).
[3] Zscheile, THIS JOURNAL, **54**, 973 (1932).
[4] Baly, *Nature*, **126**, 666 (1930).
[5] Bell, *Trans. Faraday Soc.*, **27**, 771 (1931).
[6] Baly, "Photochemical Processes," Faraday Soc. April, p. 545 (1931).
[7] Dhar, Rao and Ram, *ibid.*, p. 554.
[8] Rao and Dhar, *J. Phys. Chem.*, **35**, 1418–1432 (1931).
[9] Kruyt and van der Spek, *Kolloid-Z.*, **25**, 1–20 (1919).

Later, in a letter, Professor Dhar emphasized the necessity of incident light of wave lengths 2900–3000 Å. and preferred Schryver's test to Schiff's. The writer then irradiated an uncovered beaker containing 300 cc. of 2% $NaHCO_3$ and colloidal $Fe(OH)_3$ with a mercury arc lamp. Schryver's and Molisch's tests were negative.

The status of this problem is extraordinarily involved, though it can hardly be doubted that some workers have succeeded in obtaining formaldehyde *in vitro*. Baly[4] claims that small amounts of thorium oxide markedly affect yields. Accurate quantitative data are required, particularly with varying amounts of impurities which promote or inhibit the reaction. The writer cannot claim, either with sunlight or with the arc lamp, to have duplicated exactly the illumination used by Rao and Dhar. The Indian sunlight may be sufficiently intense in the ultraviolet region that glass containers do not filter out all these rays. With the arc lamp, secondary reactions may occur, *e. g.*, polymerization of formaldehyde to sugars, though the writer found none.

One concludes that no procedure has yet been published whereby conditions for obtaining formaldehyde and carbohydrates *in vitro* can be duplicated in other laboratories.

DIVISION OF PLANT NUTRITION   G. MACKINNEY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

GASEOUS PHOTO DECOMPOSITION OF CHLORINE DIOXIDE

Sir:

Qualitative investigations of the photo formation of Cl_2O_6 from ClO_2 have already been made.[1,2] Bodenstein and Schumacher[3] discuss this reaction and arrive at one molecule of Cl_2O_6 per two quanta absorbed, their equations leading to a maximum decrease in volume of one mole per einstein. The absorption spectrum of ClO_2[4] indicates a region of predissociation below 3750 Å. The schemes given by Schumacher for decomposition in this region and the Band region lead to the same decrease in volume per einstein as before.

Preliminary quantitative experiments on the gaseous photo ClO_2 decomposition point to a chain reaction. ClO_2 was prepared by the method used by Bodenstein[2] and no attempt was made to remove Cl_2. The gas was contained in a Suprax cell 10 cm. long, fitted with plane ends 5 cm. in diameter. The cell was filled by streaming a small percentage of the

[1] Booth and Bowen, *J. Chem. Soc.*, 510 (1925).

[2] Bodenstein, Harteck and Padelt, *Z. anorg. Chem.*, 147, 233 (1925).

[3] Bodenstein and Schumacher, *Z. physik. Chem.*, 5B, 233 (1929).

[4] Schumacher, *Z. physik. Chem.*, Bodenstein Band, 704 (1931).

gas through in the presence of oxygen, at a total pressure of one atmosphere and at 15°. The reaction was followed by the pressure changes on a sulfuric acid manometer.

The light absorbed was measured with a thermopile–galvanometer system which was calibrated using a filament lamp from the Bureau of Standards and checked by experiments on Cl_2–O_3 mixtures. On insolation with light of 3650 Å. there was a sharp decrease in pressure which was eventually followed by an almost equally sharp increase in pressure. The decrease in pressure in the first part of the experiment appears to be due to the formation of Cl_2O_6 and its deposition on the walls. It is suggested that the increase in pressure which follows is due to the sensitized decomposition of Cl_2O_6 by Cl atoms.[5] Using higher concentrations of ClO_2, larger amounts of Cl_2O_6 accumulate and after-effects of insolation indicate that it may start to decompose at an appreciable rate before all the ClO_2 has decomposed, and furthermore it does not all decompose to $Cl_2 + O_2$. One would expect the state of the surface to be an important factor.

The final rise in pressure shows a close resemblance to that obtained with Cl_2–O_3.[6] A similar rise is recorded in one experiment[7] with Cl_2O and since the formation of ClO_2 has been shown to occur in this reaction it is possible that it can also be explained by the final decomposition of Cl_2O_6, which only occurs when Cl atoms are no longer used up by ClO_2, Cl_2O and O_3 in the different experiments. Quantitative experiments with 3650 Å. showed an over-all decrease in volume varying between 5 and 23 moles per einstein in the first part of different experiments on the photo decomposition of gaseous ClO_2, while the end gave increases in volume up to 10 moles per einstein absorbed, indicating that we are probably dealing with a chain reaction.

    [5] Allmand and Spinks, *Chem. News*, **142**, 333 (1931).
    [6] Allmand and Spinks, *J. Chem. Soc.*, 1652 (1931).
    [7] Finkelnburg, Schumacher and Stieger, *Z. physik. Chem.*, **15B**, 153 (1931).

DEPARTMENT OF CHEMISTRY   J. W. T. SPINKS
UNIVERSITY OF SASKATCHEWAN
SASKATOON, SASKATCHEWAN

ALKYLATIONS OF NITRILES IN LIQUID AMMONIA

Sir:

The reaction of phenylacetonitrile which has been communicated by J. A. Nieuwland and L. H. Baldinger [THIS JOURNAL, **54**, 828 (1932)] has also been observed by the writer and E. C. Knowles [Knowles, M. S. Dissertation, R. P. I., 1929]. Similar alkylations of nitriles in liquid ammonia have also been reported [Cloke, Anderson, Lachmann and Smith, THIS JOURNAL, **53**, 2791 (1931); Knowles and Cloke, "Substituted Phenyl-

acetonitriles and Derivatives," in press]. These facts are mentioned since we are still at work on similar alkylations, which, however, are probably distinct from those under way at Notre Dame.

DEPARTMENT OF CHEMISTRY   JOHN B. CLOKE
RENSSELAER POLYTECHNIC INSTITUTE
TROY, N. Y.

ISOLATION OF SPARTEINE FROM LUPINUS BARBIGER (WATSON)

Sir:

Sparteine has been found in one species of lupine, *L. luteus*, where it is accompanied by a second alkaloid, lupinine. Although a number of other species of lupines has been examined these two alkaloids have not again been found. The isolation of sparteine from *L. barbiger*, recently effected in this Laboratory is, therefore, of interest.

Leaves and stems of this plant, collected at Hilltop, ten miles north of Fairview, Utah, were obtained through the courtesy of A. B. Clawson and were identified by W. W. Eggleston. The alkaloids were extracted[1] and submitted to the action of solvents to separate them. The fraction soluble in petroleum ether contained sparteine and a second base from which it could not be separated by fractional distillation in a vacuum. The mixture yielded a picrate, platinum chloride and methiodide which had the constants of sparteine. Separation was effected through the mercuric chloride double compound, from which pure sparteine could be recovered by treatment with ammonia, shaking out with chloroform, removing the solvent and distilling under reduced pressure. The greater part came over at 185° and 7 mm. and showed n_D^{27} 1.5256 and $[\alpha]_D^{30}$ −6.07°. Willstätter and Marx[2] gave −5.96° at 20°. Moureu and Valeur[3] give n_D^{19} 1.5293. The indices of refraction for a specimen of authentic sparteine were determined in this Laboratory as 1.5263 (24°), 1.5253 (26°), 1.5248 (28°), 1.5242 (29°). The specimen from *L. barbiger* was positive to the Jorissen[4] H_2S–S and the modified Grant[5] tests for sparteine. The picrate melted at 205–206° and did not depress the m. p. of sparteine picrate. The platinum chloride melted with decomposition at 248° and did not depress the melting point of sparteine platinum chloride.

The hydrobromide melted at 197° and was levorotatory $[\alpha]_D^{29}$ −18.33°. Found: H_2O, 4.40, 4.54; Br, 38.51, 38.50. $C_{15}H_{26}N_2 \cdot 2HBr \cdot H_2O$ requires

[1] The procedure was in general that already described, THIS JOURNAL, 47, 2584 (1925).

[2] Willstätter and Marx, *Ber.*, 37, 2351 (1904).

[3] *Bull. soc. chim. Paris*, [3] 29, 1135 (1903).

[4] *Anal. Chim. Analyt.*, 16, 412 (1911).

[5] *Am. J. Pharm.*, 97, 38 (1925).

H_2O, 4.35; Br, 38.63. The alkaloid regenerated from a portion of the salt showed n_D^{27} 1.5259 and yielded a picrate, m. p. 206°.

The methyl iodide was readily prepared by mixing the original fraction with excess of methyl iodide and allowing to stand in the cold. After a half-hour the whole solidified to a mass of white crystals. Sparteine usually shows no such behavior. A mixture of sparteine and methyl iodide remains liquid for weeks, unless warmed, but eventually deposits crystals. In our preparation the second alkaloid appears to catalyze the reaction.

The methyl iodide so prepared was recrystallized several times from alcohol. Dried in a desiccator the purest crop melted at 239–240°. Found: N, 7.51; I, 33.72, 33.63. $C_{15}H_{26}N_2CH_3I$ requires N, 7.45; I, 33.75. Moureu and Valeur[3] give the melting point "about 240°." Further crops of crystals obtained in the above preparation gave 6.91 and 7.19% N, indicating admixture with the second alkaloid.

These data establish the presence of sparteine in *L. barbiger*. Two or three other alkaloids are present but are not sufficiently characterized at present for identification. No evidence indicating the presence of lupinine has as yet been obtained.

PATHOLOGICAL DIVISION   JAMES FITTON COUCH
BUREAU OF ANIMAL INDUSTRY
WASHINGTON, D. C.

OXIDATION OF THE ALPHA AND BETA FORMS OF THE SUGARS

Sir:

In the course of studies on the oxidation of the sugars with bromine water experimental conditions have been developed by means of which it is possible to follow the oxidation of a single form of a sugar. The crystalline sugar is added to a suspension of barium carbonate in bromine water saturated with carbon dioxide, and the reaction is allowed to continue while stirring the mixture and holding the temperature constant. At intervals samples of the solution are taken and the amount of oxidation is determined by analysis. Through the buffer action of the barium carbonate and carbon dioxide the solution is maintained in a slightly acid condition (P_H 6). As a result the mutarotation of the sugar is relatively slow and the oxidation is relatively rapid. Equilibrium between the various forms of the sugar is not established prior to oxidation and consequently the reaction rates depend largely on the particular forms of the sugars used. There are marked differences in the rates obtained with various sugars and in the rates obtained with different forms of a given sugar.

Thus the oxidation of a sample of beta lactose is about 95% complete in three minutes, while under like conditions the reaction of alpha lactose is

only about 50% complete. This marked difference in the reaction rates affords a new method for ascertaining the approximate amounts of the alpha and beta isomers in solution. Such data should be of value in the study of the mechanism of the oxidation reactions and also for determining whether a given crystalline form of a sugar consists of a single isomer or whether it is a mixture of the alpha and beta forms. The oxidation of the sugar containing a single isomer progresses uniformly, while the oxidation of a mixture of the alpha and beta forms progresses rapidly until one form, usually the beta, is used up, and then more slowly as the oxidation of the other form is continued. Inasmuch as homogeneous crystalline compounds containing the alpha and beta forms of a single sugar have been discovered recently by Hockett and Hudson [THIS JOURNAL, **53,** 4455 (1931)] it is necessary to determine whether or not the known crystalline sugars are substances of this type. This problem may be attacked by determining the rates at which they are oxidized by bromine water.

Since a large number of the sugars are being studied under strictly comparable conditions, the results may be used also in correlating the rate of oxidation with the stereomeric structure of the sugars.

The writer is being assisted in this work by W. W. Pigman.

POLARIMETRY SECTION   HORACE S. ISBELL
BUREAU OF STANDARDS
WASHINGTON, D. C.
RECEIVED MARCH 2, 1932
PUBLISHED APRIL 6, 1932

THE NATURE OF ACTIVATED ADSORPTION

Sir:

In a recently published article [THIS JOURNAL, **54,** 602 (1932)] Taylor and Sickman presented data on the low- and high-temperature adsorption of hydrogen by zinc oxide, from which some information on the two types of adsorption can be secured by statistical methods. From their Fig. 3 on page 612, it is found that equal amounts are adsorbed at 125°K. and 580°K. and 400 mm. pressure, while the heats of adsorption are 1100 and 21,000 cal., respectively. Writing statistical expressions for exp. $(-f/kt)$ (f: free energy at constant pressure in μ space), setting free energy of gas equal to that of adsorbate at each temperature and dividing the square of the expression for 125°K. by that for 580°K. the following equation results

$$e^{(2\Delta\epsilon_1/KT_1) - (\Delta\epsilon_2/KT_2)} = \frac{T_1^3 \, h^3}{T_2^{7/2} \, P2^{5/2} \, \pi^{5/2} \, m^{1/2} \, k^{1/2} J} \cdot \frac{\Omega_{v_2}^6}{\Omega_{v_1}^2} \cdot \frac{N^2}{S^2}$$

The assumptions underlying this expression are that in low temperature adsorption hydrogen molecules have freedom of motion over the surface (two dimensional ideal gas) and that their rotation is unchanged by

adsorption, while at high temperature hydrogen atoms are produced which are held by definite surface atoms. Further, m and J are the mass and the moment of inertia of hydrogen molecules, Ω_{v_1} is the phase space of vibration (in h units) normal to the surface in low temperature adsorption, Ω_{v_2} is the phase space of vibration of adsorbed atoms at higher temperature, P is the gas pressure, S is the surface available for the low temperature adsorption in sq. cm., while N is the number of surface atoms available for the high temperature adsorption. Assuming, in the first approximation, that the zero point energy changes $\Delta \epsilon_1$ and $\Delta \epsilon_2$ are equal to the measured heats of adsorption, the numerical calculation yields

$$\frac{N}{S} = 2 \times 10^{12} \frac{\Omega_{v_1}}{\Omega_{v_2}^3}$$

Since the ratio $\Omega_{v_1}/\Omega_{v_2}^3$ is hardly much larger than unity and the total number of surface atoms per sq. cm. is of the order of 10^{15}, it is seen that only a small fraction of the surface participates in the "activated" adsorption. Other assumptions regarding the state of adsorbed gases lead to still smaller fractions of the surface involved in high temperature adsorption. Thus, if in activated adsorption hydrogen molecules retain their identity and execute a rotational motion in addition to vibration as a whole (Ω_{v_2}) around their position of equilibrium, the expression is obtained

$$\frac{N}{S} = 2 \times 10^{11} \frac{\Omega_{v_1}}{\Omega_{v_2}^3}$$

If, finally, freedom of motion on the surface is accepted for activated adsorption, the ratio of surfaces involved in the two processes is found to be

$$\frac{S_2}{S_1} = 10^{-6} \frac{\Omega_{v_1}}{\Omega_{v_2}}$$

A larger fraction of surface involved in activated adsorption than calculated above, is obtained only if formation of multimolecular layers at low temperature is postulated. These calculations lead to the conclusion that activated adsorption is limited to particular surface atoms only, the adsorbate not forming a freely moving two-dimensional gas on the surface (*cf.* H. S. Taylor, "Catalytic Symposium," Faraday Society, 1931); they indicate at the same time a way for a detailed study of the structure of surfaces by measurements of heat changes in adsorption of varying amounts at low and high temperatures. It should be pointed out also that in calculations of the theoretical adsorption rate, correction must be made for the inactive surface.

DEPARTMENT OF CHEMISTRY   G. B. KISTIAKOWSKY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS

THE SPECIFIC NATURE OF ENERGY EXCHANGE IN UNIMOLECULAR REACTIONS

Sir:

Since the energy of activation in unimolecular reactions is undoubtedly obtained by collision, the velocity constants fall off at low pressures. It is well known that certain inert gases will prevent this falling off by furnishing the necessary collisions. The specific nature of this effect is, however, very remarkable. In general, hydrogen and the products of the reaction are effective, while other inert gases are usually ineffective. Rice has recently discussed the question from the point of view of quantum mechanics [O. K. Rice, *Chem. Reviews*, **10**, 125 (1932)].

In the past most of the inert gases employed have been of comparatively simple structure. It seems desirable to obtain information regarding the behavior of gases which are as complicated as the reactant, and which resemble the reactant as much as possible. The series of ether decompositions investigated by Hinshelwood and his co-workers are ideal for the purpose. Accordingly an investigation has been undertaken on the rate of decomposition of mixtures of aliphatic ethers. Mixtures of dimethyl and diethyl ether have already been investigated. These ethers decompose in an almost identical way, and have a pronounced resemblance in physical properties, and in the manner in which the velocity constants fall off with diminishing pressure. Each might therefore be expected to show a high efficiency in activating the molecules of the other.

The surprising result has been obtained that the two gases have absolutely no activating effect on each other. A mixture of the two (at pressures where the falling-off is large) decomposes at a rate which is exactly the mean of those of its components (within an experimental error of about three per cent.). This appears to be the most pronounced example of the specificity of energy transfer which has yet been observed.

The decomposition of mixtures of methyl ethyl ether with both diethyl and dimethyl ether is being investigated. A full account of the work will appear later.

PHYSICAL CHEMISTRY LABORATORY   E. W. R. STEACIE
McGILL UNIVERSITY
MONTREAL, CANADA

THE PREPARATION OF AN OPTICALLY ACTIVE TRIARYLCARBINOL

Sir:

A survey of the chemical literature shows that many primary and secondary alcohols containing an asymmetric carbon atom have been successfully resolved. However, all previous attempts to resolve asymmetrically substituted tertiary alcohols have failed. In an article published

in the *Proceedings of the National Academy of Sciences*, **16**, 215 (1930), I described a method for preparing an optically active triarylcarbinol in the form of its thioglycolic acid derivative. *l*-Phenylbiphenyl-α-naphthyl-methylthioglycolic acid, $(C_6H_5)(C_6H_5C_6H_4)(C_{10}H_7)CSCH_2COOH$, was prepared and resolved by means of its brucine salt. It was found to have the specific rotation in carbon tetrachloride, $[\alpha]_D^{20}$ −13.63°; in ether, $[\alpha]_D^{20}$ −12.93°. The dextro modification obtained by working up the residues from the fractional crystallization of the brucine salt gave an acid with $[\alpha]_D^{20}$ +10.6° in ether.

Many experiments have been carried out on these compounds in order to convert them into the corresponding optically active triarylcarbinols. This has finally been accomplished. Under proper conditions the levo modification of the acid gives a *d*-phenylbiphenyl-α-naphthylcarbinol of the specific rotation in carbon tetrachloride, $[\alpha]_D^{20}$ +5.8°. The dextro modification of the acid yields a levorotatory-carbinol, $[\alpha]_D^{20}$ −5.4°. The corresponding ethyl ethers have been prepared. The levo acid produces a levorotatory ether, $(C_6H_5)(C_6H_5C_6H_4)(C_{10}H_7)C-OC_2H_5$, $[\alpha]_D^{20}$ −22.7° in ether. The dextro acid gives a dextrorotatory ether, $[\alpha]_D^{20}$ +21.6°. Other asymmetrically substituted tertiary alcohols are being prepared in order to study their possibilities of resolution by this method. Further investigations on the above optically active compounds are in progress with a view of answering the question of the spatial arrangement of the valences of the trivalent carbon atom. At present this is completely unexplained, and has been but superficially investigated. A report of this work will be published later.

FRICK CHEMICAL LABORATORY   EVERETT S. WALLIS
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

BETA-SUBSTITUTED FURANS

Sir:

Absolute orientation studies of nuclear substituted furans are circumscribed by the paucity of simple *beta*-substituted furans, which are uncommonly difficult of synthesis. 3-Furancarboxylic acid is now accessible by the preferential pyrolytic decarboxylation of 2,4-furandicarboxylic acid. Although the halogen in 3-iodofuran is extremely inert, particularly toward magnesium and sodium, 2,5-dimethyl-3-iodofuran readily forms an organomagnesium iodide. The iodofurans were prepared from the furan-mercurials.

DEPARTMENT OF CHEMISTRY   HENRY GILMAN
IOWA STATE COLLEGE   ROBERT R. BURTNER
AMES, IOWA   GEORGE F. WRIGHT

PREPARATION OF 7,7'-DIMETHYL-8,8'-DIQUINOLYL AND OF 5,5',7,7'-TETRA-METHYL-8,8'-DIQUINOLYL

Sir:

The possibility of optical isomerism in substituted diquinolyls has been suggested by Mascarelli [*Gazz. chim. ital.*, **58**, 627 (1928)]. The preparation of such compounds has been under way at this Laboratory for nearly two years.

7,7'-Dimethyl-8,8'-diquinolyl was made by coupling two molecules of 3-nitro-2-iodotoluene by means of copper powder. The resulting dinitrodimethyldiphenyl was reduced and converted by a Skraup synthesis to 7,7'-dimethyl-8,8'-diquinolyl. It is a white solid, melting at 213–215°. It is insoluble in water, but soluble in dilute acids and in alcohol, benzene and ether.

5,5',7,7'-Tetramethyl-8,8'-diquinolyl was made by coupling two molecules of 5-nitro-4-iodo-1,3-dimethylbenzene with copper powder. The resulting dinitrotetramethyldiphenyl was reduced and converted by a Skraup synthesis to 5,5',7,7'-tetramethyl-8,8'-diquinolyl. The substance is a white solid similar in properties to the dimethyldiquinolyl. The preparation of larger quantities of these and other substituted diquinolyls is now under way and attempts are being made to resolve the compounds.

DEPARTMENT OF CHEMISTRY   HENRY P. WARD
THE CATHOLIC UNIVERSITY OF AMERICA   MARY GRACE WARING
WASHINGTON, D. C.
RECEIVED MARCH 11, 1932
PUBLISHED APRIL 6, 1932

THE STRUCTURE OF ALPHA-PENTAACETYLFRUCTOSE AND ALPHA-CHLOROACETYLFRUCTOSE

Sir:

In 1915 Hudson and Brauns [THIS JOURNAL, **37**, 1283, 2736 (1915)] described two crystalline pentaacetates of fructose which they believed to constitute an α,β-stereoisomeric pair.

In 1920 Brauns [*ibid.*, **42**, 1846 (1920)] prepared from tetraacetylfructose two chloro compounds which he assumed to be α- and β-stereoisomers. Subsequently his designation of the two forms was reversed at the suggestion of Dr. Hudson and now the substance showing $[\alpha]_D - 161°$ in chloroform solution is known as β-chloroacetylfructose whereas the one with $[\alpha]_D +45°$ is assigned the α-configuration.

Using the rotations of these chloro compounds to determine the applicability of the principle of optical superposition to derivatives of the ketone sugars, Dr. Hudson [*ibid.*, **46**, 477 (1924)] calculated the rotations of the fructose pentaacetates. From his results he concluded that the compound with the positive rotation is probably not the true α-form. This conclusion is supported by the differences in properties of the two known pentaace-

tates.   However, the extreme dissimilarity of the two chloroacetylfructoses suggests that they, too, may not constitute an α,β-pair.   Dr. Brauns has remarked on their great difference in stability.

We now have experimental evidence that the so-called "α-chloroacetyl-fructose" and the "α-pentaacetylfructose" differ *structurally* from their isomer in that they are derivatives of the open-chain fructose and contain a free ketone group.   The strongest evidence for the presence of a ketone group in "α-pentaacetylfructose" is its catalytic reduction to the alcohol. On account of the new asymmetric carbon atom formed during the reduction, sorbitol and mannitol derivatives should be obtained.   After acetylation two compounds were isolated and identified as hexaacetylmannitol and hexaacetylsorbitol with melting points 121 and 97°, respectively.

Under the same conditions of reduction the "α-chloroacetylfructose" took up hydrogen and there resulted a substance which, like the starting material, contained a very stable chlorine atom.

The chlorine atom in "α-chloroacetylfructose" could not be replaced by heating the substance in acetic anhydride solution with silver acetate. This behavior suggests the presence of a firmly bound, primary chlorine atom.

For these reasons we conclude that the "α-chloroacetylfructose" represents a derivative of the open-chain fructose with a chlorine atom at carbon atom 6.

The details of this investigation will be published within a short time.

FRICK CHEMICAL LABORATORY   EUGENE PACSU
PRINCETON UNIVERSITY   FRANK V. RICH
PRINCETON, NEW JERSEY
RECEIVED MARCH 12, 1932
PUBLISHED APRIL 6, 1932

THE CONSTANT a IN THE DEBYE-HÜCKEL LIMITING EQUATION

Sir:

In THIS JOURNAL for February, 1932 (p. 831), Professor Hall discusses the numerical value of the constant a in the Debye–Hückel limiting equation: $-\log f = aC^{1/2}$, and refers to a publication ("Conductivity of Solutions," 1930) in which I pointed out that attempts to determine a experimentally have always led to values nearer to 0.4 than to the theoretical value 0.5.

In the same place I remarked that further data on the point are needed, and that conductivity measurements probably provide the most accurate way of obtaining them.   Since then, Mr. Banks in this Laboratory has made conductivity measurements on mandelic acid at 25° which agree, after applying Onsager's correction for the mobility changes, with the theoretical value of a.   We had intended to study further weak acids, but abandoned this plan when MacInnes and Shedlovsky [THIS JOURNAL, **53,**

2419 (1931)] announced that their new conductivity measurements on acetic acid were in complete agreement with the Debye–Hückel value $a = 0.505$.

I think that these two independent investigations provide the best possible verification of the theoretical formula, and it is interesting to find that Hall's calculations on hydrochloric acid are also in agreement with them. Incidentally, further support, if that were needed, for the theoretical value is afforded by the most recent solubility measurements [La Mer and Goldman, THIS JOURNAL, **51**, 2632 (1929), on thallous iodate; unpublished measurements in this Laboratory on barium iodate]. I am glad, therefore, to express my agreement with Professor Hall's conclusions, and have already taken an opportunity of replacing the older, misleading figures in the book to which he refers.

BATTERSEA POLYTECHNIC   C. W. DAVIES
LONDON S. W. 11, ENGLAND
RECEIVED MARCH 22, 1932
PUBLISHED APRIL 6, 1932

NEW BOOKS

This is a biographical sketch giving a readable and clear delineation of Svante Arrhenius and his important place in contemporaneous science for a third of a century, accompanied by a bibliography. The author shows a thorough understanding of men and events as well as of the important part played by the dissociation theory in the decade and a half prior to 1900, when the infant science of physical chemistry was going through its growing pains. Students of the history or philosophy of science will gain an insight from this book into the obstacles that ideas in advance of the times frequently and probably quite generally have to overcome before being accepted.

"There are not many scientists who have shaken so deeply the foundations of their science and pointed the way for its future development so far in advance as Svante Arrhenius, the creator of the doctrine of electrolytic dissociation," the author very truly states in the opening paragraph.

The tardy recognition of Arrhenius by scientific men in his own country is regrettable but not unusual, and perhaps we may say even according to the Scriptures. The reader, at least the American reader, is somewhat puzzled by several references to the work of Arrhenius' enemies in retarding his scientific advancement because no reasons are apparent why he should have had enemies, or at least active ones, particularly as the picture painted of him by the author is that of a genial, modest personality without conceit.