as fast as 20° as at 25°, but upon addition of chloroform to prevent freezing and cooling with solid carbon dioxide it appeared to be instantaneous.

The only hypothesis that seems to accord with all of these results is the one suggested by Liebhafsky,[1] that the reactive halogen is in the form of hydrate. If these hydrates contain a number of molecules of water, like the solid $Cl_2 \cdot 6H_2O$, they could involve the large heat of formation required to explain the large negative temperature coefficient of the reaction. There is, of course, ample evidence that the number of "icebergs" in water falls off rapidly from 0° to room temperature.

It has been difficult to secure sufficient reproducibility to give satisfactory quantitative data, and since this may take some time, it seems appropriate to publish the above preliminary results.

(1) H. A. Liebhafsky, *Chem. Rev.*, **17**, 89 (1935).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIF. J. H. HILDEBRAND

RECEIVED APRIL 15, 1946

THE ISOLATION OF LEVOGLUCOSAN FROM THE ENZYMIC HYDROLYSATES OF WAXY CORN STARCH

Sir:

Waxy corn starch[1,2,3] has been subjected to the consecutive action of β-amylase, α-amylase, β-amylase, and an amylase prepared from *Aspergillus oryzae* in order to obtain information on its structure.

The starch, pasted at 80°, was first treated with β-wheat amylase[4] free from α-amylase and maltase. Dextrin A[5] and maltose, the end-products of this hydrolysis, were isolated in yields of 49 and 48%, respectively.

Dextrin A was then subjected to the action of α-malt-amylase,[6] free from β-amylase and maltase, until no further increase in the reducing power of the hydrolysate occurred. From this hydrolysate, dextrin B-1 was separated by the addition of ethanol to a concentration of 85% by volume; after two reprecipitations the new dextrin was dialyzed continuously against distilled water for nine hours. The liquor remaining after dialysis was concentrated and the dextrin B-1a was recovered by precipitation with ethanol; yield, 44% of the weight of dextrin A; $[\alpha]^{25}D$ +160.2° in water; reducing power 3.8 and 8.0% of that of glucose by Shaffer–Hartmann and Gore–Steele methods, respectively.

Dextrin B-1a was next submitted to the action of β-amylase until the rotation and reducing power were constant. The products of this hydrolysis were dextrin B-1a$_1$ and maltose, the yields being 62 and 30% of the weight of dextrin B-1a, respectively. Dextrin B-1a$_1$ rotated +146.0° in water and had a reducing power by the Gore–Steele method equivalent to 12% of that of glucose. On treatment with the amylase of *Aspergillus oryzae*, the reducing power of dextrin B-1a$_1$ increased about sixfold and the rotation decreased to +38°. This hydrolysate after fermentation with yeast did not reduce Fehling solution and was levorotatory. After removal of the yeast and concentration of the solution, a solid was obtained by addition of ethanol; $[\alpha]^{25}D$ −32° in water; yield, 4.2% of the weight of dextrin A. This solid was acetylated and from the resulting product levoglucosan triacetate was isolated; yield, 0.6% of that calculated for levoglucosan on the basis of waxy corn starch; $[\alpha]^{25}D$ −65.5° in $CHCl_3$ (*c*, 1); m. p. 110–111°,[7] (mixed m. p. unchanged). On deacetylation, levoglucosan was obtained in pure crystalline form and characterized. Levoglucosan was also obtained from the hydrolysate resulting from the action of the amylase from *Aspergillus oryzae* on dextrin B-1a without prior fermentation. Isolation was effected both by distillation and by fractional crystallization after acetylation. Further work will have to be carried out to determine whether the 1,6-anhydro linkage is formed during enzymic fission of the substrate or actually occurs in waxy starch.

(1) Hixon and Sprague, *Ind. Eng. Chem.*, **34**, 959 (1942).
(2) MacMasters and Hilbert, *ibid.*, **36**, 958 (1944).
(3) Schopmeyer, Felton and Ford, *ibid.*, **35**, 1168 (1943).
(4) Hanes, *Biochem. J.*, **30**, 174 (1936).
(5) *Cf.* Haworth, Kitchen and Peat, *J. Chem. Soc.*, 619–625 (1943).
(6) Hanes, *Can. J. Research*, **13B**, 185–208 (1935).
(7) Zemplén, Gerecs and Valatin, *Ber.*, **73**, 576 (1940).

CORN INDUSTRIES RESEARCH FOUNDATION
NEW YORK 17, N. Y. EDNA M. MONTGOMERY
NORTHERN REGIONAL RESEARCH LABORATORY
BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY
AGRICULTURAL RESEARCH ADMINISTRATION
U. S. DEPARTMENT OF AGRICULTURE
PEORIA 5, ILLINOIS G. E. HILBERT

RECEIVED MARCH 4, 1946

6-CHLOROVANILLIN FROM THE CHLORITE OXIDATION OF LIGNIN

Sir:

In a fundamental study of the reaction of lignin with sodium chlorite in acid solution, the original filtrate from the preparation of holocellulose from black spruce (*Picea mariana*) by means of sodium chlorite in dilute acetic acid according to Wise and co-workers[1,2] was investigated. The filtrate was further acidified with sulfuric acid and fractionated. The steam non-volatile aldehyde fraction was identified as 6-chlorovanillin, colorless plates from ethanol melting at 167–168°. (*Anal.* Calcd. for $C_8H_7O_3Cl$: C, 51.49; H, 3.78; Cl, 19.00; CH_3O, 16.63. Found: C, 51.34; H, 3.76; Cl, 19.19; CH_3O, 16.70.) The oxime, prepared by heating with a solution of hydroxylamine hy-

(1) Wise, *Ind. Eng. Chem., Anal. Ed.*, **17**, 63–64 (1945).
(2) Wise, Murphy and D'Addieco, *Paper Trade J.*, **122**, No. 2, 35 (1946).

drochloride and sodium hydroxide and recrystallizing the product from dilute ethanol, was obtained as colorless needles melting at 177–178°. Raiford and Lichty[3] synthesized 6-chlorovanillin and its oxime and recorded melting points of 167–168° and 178°, respectively.

Further work on the filtrates from the chlorite treatments of carefully analyzed samples of black spruce (*Picea mariana*), western red cedar (*Thuja plicata*), western hemlock (*Tsuga heterophylla*), aspen (*Populus sp.*), loblolly pine (*Pinus taeda*) and slash pine (*Pinus caribaea*) and on the liquors from the chlorite treatments of a number of isolated lignins of various types from both hardwoods and softwoods is now in progress. The results of these experiments, together with theoretical considerations, will appear in future communications.

THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN IRWIN A. PEARL

RECEIVED APRIL 3, 1946

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[3] Raiford and Lichty, THIS JOURNAL, **52**, 4581 (1930).

NEW BOOKS

Journal of Colloid Science, VICTOR K. LAMER, Editor-in-Chief, *et al.* Academic Press, Inc., Publishers, 125 East 23rd St., New York 10, N. Y. Volume I, No. 1, January, 1946. Published bimonthly at $10.00 a year.

This new publication, with Professor LaMer of Columbia University as Editor-in-chief, will contain original papers, letters to the Editor and book reviews. In addition to Professor LaMer the editors are T. R. Bolam of Edinburgh, E. F. Burton of Toronto, R. M. Fuoss of New Haven, H. R. Kruyt of Utrecht, J. W. McBain of Palo Alto, E. K. Rideal of Cambridge, William Seifriz of Philadelphia, A. W. Thomas of New York, Arne Tiselius of Upsala and Harry B. Weiser of Houston, an impressive list. There is also a consulting committee composed of W. T. Astbury, J. J. Bikermann, W. Clayton, P. Debye, W. Feitknecht, Alexander Frumkin, William D. Harkins, Ernst A. Hauser, Wilfried Heller, J. N. Mukherjee, F. F. Nord and The Svedberg.

The papers in the first number are: "Contraction and the Chemical Structure of the Muscle Fibril" by A. Szent-Györgi; "Polarization and Permeability" by M. Spiegel-Adolf and E. A. Spiegel; "Torsion in Protoplasm" by William Seifriz; "Adsorbed Nitrate Ions in Relation to Plant Growth" by H. Jenny; "Surface Films of Polymers" by D. J. Crisp; "Mono-dispersed Hydrophobic Colloidal Dispersions and Light-Scattering Properties. I." by Victor K. LaMer and Marion D. Barnes; "Monodispersed Hydrophobic Colloid Dispersions and Light-Scattering Properties. II." by Marion D. Barnes and Victor K. LaMer; "The Method of Purifying and Concentrating Colloidal Dispersions by Electrodecantation" by Paul Stamberger; "Structure of Soap Micelles as Indicated by X-Rays and Interpreted by the Theory of Molecular Orientation. II." by William D. Harkins, Richard W. Mattoon and Myron L. Corrin. One wonders why there was not a paper on plastics in the first number and why there were two papers by the Editor-in-Chief. Plastics is a very important field in the colloid science of today.

WILDER D. BANCROFT

Colorimetry for Chemists. By M. G. MELLON, Ph.D., Sc.D., Professor of Analytical Chemistry, Purdue University. The G. Frederick Smith Chemical Company, 867 McKinley Avenue, Columbus, Ohio, 1945. 15.5 × 23 cm. 133 pp. 51 figs. Price, $1.00 for bound copies. Paper copies free on request.

The still growing importance of optical methods for quantitative analysis is exemplified by this compact and suggestive volume. After a careful delineation of the scope of colorimetric methods, there is a description of typical instruments, their manipulation and limitations. Much attention is devoted to tabulation and plotting of experimental data, and the relative advantages of various coördinates are discussed. There is a section dealing with color analysis and psychophysical specification. The final chapter outlines a number of experiments designed for development of technical skill. The bibliography of two hundred and fifty references is well chosen and up to date. Those who digest this booklet can undertake colorimetric and spectrophotometric procedures with added efficiency and confidence.

GEORGE S. FORBES

L'Effet Soret. Diffusion Thermique dans Les Phases Condensées. By S. R. DE GROOT, Doctor of Science. N. V. Noord-Hollandsche Uitgevers Maatschappij, Amsterdam, Holland, 1945. 191 pp. 42 illustrations. 15 × 23 cm.

This book, the author's doctoral thesis, reviews the experimental and theoretical literature on the Soret effect and thermal diffusion in the liquid phase and contains a report of the author's own experimental work on thermal diffusion in aqueous salt solutions.

After an introductory chapter, the experimental procedures and results, which have been obtained in investigations of the pure Soret effect, are discussed in some detail. Then follows a discussion of the thermal diffusion method of Clusius and Dickel, called the thermogravitational procedure by the author. Results of its application to liquid phase separations obtained by the author and other investigators are presented.

The following chapters are devoted to a lengthy review of the theoretical interpretation of the Soret effect and thermal diffusion. The thermodynamic theories, analogous to those of the thermo-electric effect and the relations between thermoelectric potentials and Peltier heats, are presented in some detail. It is shown how the Onsager reciprocal relations, based upon the principle of microscopic reversibility and the theory of fluctuations, may be used to supplement the purely phenomenological theory to yield significant results.

The kinetic theories of the Soret effect are also presented, and the results which can be obtained from them are summarized. Unfortunately, no entirely adequate molecular theory of thermal diffusion exists except that of Chapman and Enskog for gases of low density, to which Maxwell-Boltzmann transport equation is applicable.