This method was applied to the examination of fifteen samples obtained at intervals from three distinct types of silos. We found acetic and propionic acids in the ratio of about ten to one, butyric acid in considerable amount only in samples where some slight indications of spoiling were otherwise apparent and formic acid usually only in traces. By fractionally distilling some 300 cc. of pure acids extracted from silage and identifying the acids by their boiling point, the same results were obtained. We found also ethyl and propyl alcohols in the proportion of about ten to one, but no evidence whatever of methyl alcohol. Our average for the total volatil acid was 1% formic, 87% acetic, 8.7% propionic, 3% butyric, and 0.3% valeric, and for the total alcohols, 90% ethyl and 10% propyl. Although, as Hart and Willaman maintain, no two silages are exactly alike in composition, the differences between our results and theirs, with regard to the presence of relatively large amounts of formic acid and methyl alcohol, can hardly be explained on this assumption.

IOWA AGRICULTURAL EXPERIMENT STATION,
AMES, IOWA.

## NOTES.

*Ethyl Ether by Catalysis.*[1]—Sabatier and Mialhe[2] have shown that several metallic oxides (thoria, alumina, and tungsten) exercise a "catalytic action" on alcohols between 300° and 350°. It would appear from their investigations that this action is almost entirely that of dehydration with the separation of ethylene, although, when operating at a lower temperature, the dehydration is said to be incomplete and to be capable of limitation to the production of ethyl oxide.

The dehydration of ethyl alcohol in the presence of thoria has been studied in this laboratory[3] and the results obtained show some variance with those of Sabatier and Mialhe. The contributions of these authors are not very explicit as to experimental details, but we endeavored to observe all the conditions necessary for the production of ethyl ether by partial dehydration, according to the reactions:

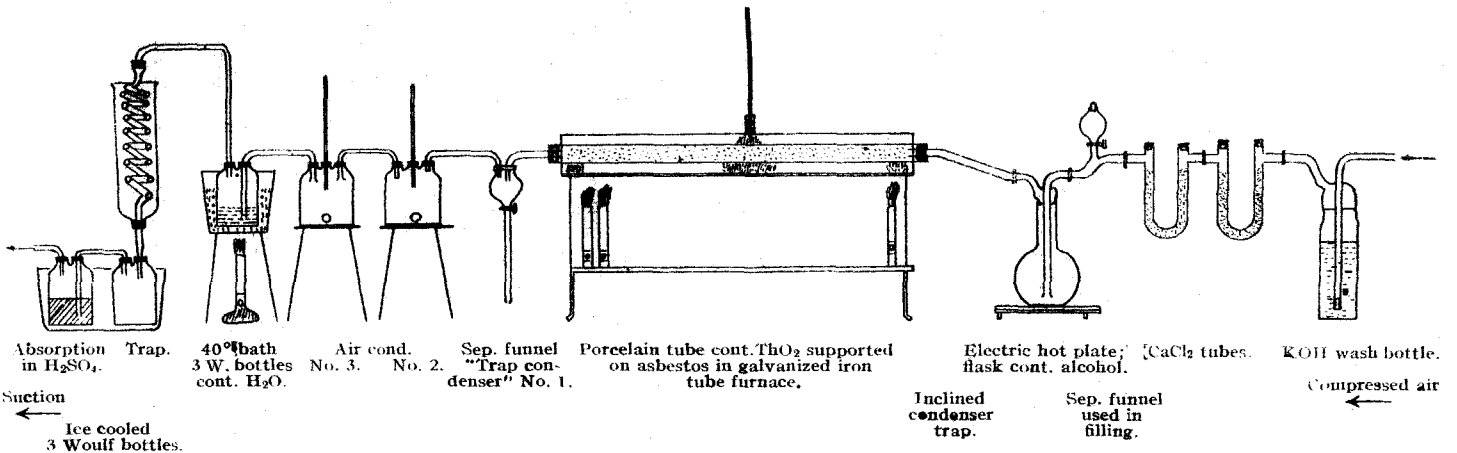
$$2C_nH_{2n+1}OH + ThO_2 = H_2O + ThO(OC_2H_{2n+1})_2;$$
$$ThO(OC_nH_{2n+1})_2 = ThO_2 + (C_2H_{2n+1})_2O.$$

The apparatus used in our experiments, illustrated herewith, consisted essentially of a jacketed porcelain tube containing glass beads covered with pure thoria, heated in a combustion furnace, and over which

[1] Read at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[2] *Compt. rend.*, **150**, 823; see also *Idem.*, **149**, 995; **150**, 1217; **161**, 359, 492.

[3] The experimental work was carried out by Messrs. Barnett Cohen and Alfred V. Salamon.


Absorption Trap.
in $H_2SO_4$.
40°C bath
3 W. bottles
cont. $H_2O$.
Air cond.
No. 3.
No. 2.
Sep. funnel
"Trap condenser" No. 1.
Porcelain tube cont. $ThO_2$ supported on asbestos in galvanized iron tube furnace.
Electric hot plate; flask cont. alcohol.
$CaCl_2$ tubes.
KOH wash bottle.
Compressed air
Suction
Ice cooled
3 Woulf bottles.
Inclined condenser trap.
Sep. funnel used in filling.

vaporized absolute ethyl alcohol was conducted by means of a purified air current. Suitable means were provided for recovering products of dehydration and oxidation, and excess of ethyl alcohol was absorbed in water kept at 40°. No difficulty was experienced in maintaining the desired temperatures throughout the train of apparatus.

In experiments 1 (length, 1 hr. 20 min.; average temperature 245°), 2 (2 hrs. 45 min.; 233°), and 3 (5 hrs. 15 min.; 228°), in all of which 375 cc. of ethyl alcohol were used, no reliable results were obtained, although it was found that the ethyl alcohol had evidently undergone oxidation.

In experiment 4, in which 390 cc. of ethyl alcohol were used during 3 hrs. 20 min., and in which the thoria tube was maintained at 250°, a small amount of a heavy yellow oil condensed in the tube leading from the thoria tube, and it was found that this formed at about 200°. The sulfuric acid, kept in absorption bottles in ice at the end of the train, became discolored, but no indications of the formation of ethyl ether were had. On the conclusion of the experiment, the thoria was found to possess a brownish black color and fruity odor, but upon ignition in air it regained its original color, and this revivified thoria was used in the following experiment.

In experiment 5, the time of the run was 4 hrs. 30 min., and 390 cc. of ethyl alcohol were passed over thoria heated to 245°. During this experiment, tests were made for the formation of ethylene,[1] and indications were had of the presence of unsaturated hydrocarbons and carbon dioxide in the gas issuing from the last sulfuric acid bottle. Upon the conclusion of the run, the first trap was found to contain a very small amount of ethyl ether, and the sulfuric acid at the end of the train was darkened and had a pungent ethereal odor. The water solutions in the baths maintained at 40° for the absorption of alcohol were fractionated; considerable amounts of acetaldehyde were found, also small amounts of acetic acid.

In experiment 6, the average temperature was 253° and the period of the run was 3 hr. 25 min. Care was exercised to establish the dehydration observed by Sabatier and Mialhe, and the formation of ethylene and carbon dioxide was shown; however, the amounts formed were small under the conditions of the experiment. No ethyl ether was found in the traps, receivers or absorption vessels; but the heavy yellow oil noted in experiment 4 was again found, this time being condensed in the receivers. Not sufficient of this oil was obtained for examination. The alcohol absorption vessels were found to contain an alcohol solution giving a strong acetaldehyde reaction.[2]

[1] By means of iodine and starch solution, bromine water, and palladium chloride solution (see Phillips, *Am. Chem. J.*, 16, 4, 266).

[2] The acetaldehyde present was of such an amount as to lead us to believe that it

The above experiments warrant the conclusion that, under the experimental conditions described, no satisfactory yield of ethyl ether is obtained in the neighborhood of 250°. It is planned to extend these experiments, using other rare earth oxides and working at lower temperatures.

CHARLES BASKERVILLE.

DEPARTMENT OF CHEMISTRY,
COLLEGE OF THE CITY OF NEW YORK.

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*The Melting Point of Ethyl Gallate.*—In the July number of THIS JOURNAL[1] we suggested tentatively that the peculiar behavior of ethyl gallate on melting might possibly be due to the existence of two crystallin forms of the substance. Further study of the ester in conjunction with one of my students, Mr. R. C. Lyons, has shown that continued purification eventually leads to a substance of constant melting point.

If, for example, an ethereal solution of ethyl gallate is repeatedly shaken up with a solution of sodium bicarbonate (a 0.2 *N* solution was used), as suggested by Manning and Nierenstein,[2] the product obtained still shows a variation in melting point. If this product, however, is now subjected repeatedly to fractional crystallization from a mixture of ether and petroleum-ether, the ethyl gallate finally obtained crystallizes in long, colorless needles and melts fairly sharply at 160°, or two degrees higher than the highest melting point hitherto observed for this substance.

H. C. BIDDLE.

UNIVERSITY OF CALIFORNIA,
BERKELEY, CAL.

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## NEW BOOKS.

**Recent Advances in Physical and Inorganic Chemistry.** By A. W. STEWART, D.Sc., Lecturer on Organic Chemistry in the University of Belfast, &c. With an introduction by Sir William Ramsay, K.C.B., F.R.S. Second edition. London: Longmans, Green & Co. 1912. pp. xvi + 272. Price, $2.50 net.

This book represents a type, as rare as it is valuable. The difficulty of keeping abreast of the rapid advances of chemistry in its multifarious fields, buried in thousands of pages of periodical literature, must impress itself upon all chemists, and especially upon the teacher. A book which presents an authoritative, critical, and suggestive review of the work in a number of fields, and prepared by one as competent as Dr. Stewart, is, therefore, a welcome addition to the library of any chemist, and forms an excellent companion volume to the author's "Recent Advances in Organic Chemistry".

did not arise from the auto-oxidation of the ethyl alcohol, which originally contained bu a mere trace of acetaldehyde. The water solutions were carefully stored, up to the tim of fractionation.

[1] Biddle and Kelley, THIS JOURNAL, 34, 923 (1912).

[2] *Ber.*, 45, 1548 (1912).