[CONTRIBUTION FROM BEACON LABORATORY OF THE TEXAS COMPANY]

An Azeotropic Mixture of Acetylene and Ethane at Atmospheric Pressure

BY WALLACE A. MCMILLAN

During work on the development of precision methods for the analysis of complex hydrocarbon gases, considerable difficulty was encountered occasionally in the separation of ethylene from ethane by ordinary low temperature fractional distillation methods. Continued work on such separations resulted in the isolation of an azeotropic mixture of acetylene and ethane of minimum boiling point. The existence of such a mixture has been established previously[1] for high but not for low pressures. With the increasing use of low temperature fractionation as an analytical method it was felt that constants for the mixture, at atmospheric pressure and low temperature, should be established.

Experimental

Acetylene.—Commercial acetylene was washed successively with distilled water, 40% potassium hydroxide, and 30% sulfuric acid, then passed through soda-lime and dried with anhydrous magnesium perchlorate. The dried gas was condensed by liquid air in the kettle of a special low temperature fractionating column,[2] the fixed gases pumped off, and the acetylene distilled at 1.5 atmospheres, discarding both end fractions. Two subsequent distillations, discarding heads and tails, were made before use. Hydrogenation of the pure material gave a value of 100% for the unsaturation.

Ethane.—Commercial ethylene-free ethane was purified by successive washings through 30% fuming sulfuric acid, and 98 and 79% sulfuric acid, followed by two washings with 43% potassium hydroxide, a soda-lime tower, and dried by anhydrous magnesium perchlorate. It was likewise distilled through a special low temperature column, retaining only the middle portion each time. After four redistillations, the purified material showed a constant boiling point (−88.3°) and the end fractions showed constant vapor pressures when tested in a Shepherd differential manometer.[3] Hydrogenation of the pure material showed no unsaturation.

Mixtures.—Mixtures of the two components were made by blending in the gas phase in an evacuated all-glass system. They were then condensed into the kettle of a special low temperature fractionating column[2] and distilled. The first mixture, containing 70% ethane and 30% acetylene, distilled at −94.5° until 73.5% had come over, at which point the temperature broke sharply to −88.3° and the remainder of the ethane came over at that temperature. In the case of a 70% acetylene–30% ethane mixture, 50.2% distilled at −94.5° at which point the column froze solid with acetylene and it was necessary to go to 1.5 atmospheres to continue the distillation.

When analyzed by catalytic hydrogenation of the acetylene over a reduced nickel catalyst,[4] each of the azeotropic mixtures boiling at −94.5° gave 40.8% acetylene and 59.2% ethane. Check determinations on five additional samples distilled at pressures from 752 to 766 mm. gave a boiling range of −94.5 ± 0.1° and a composition range of: acetylene, 40.75 ± 0.25%; ethane, 59.25 ± 0.25%.

Redistillations of the constant boiling mixtures did not change either the boiling points or compositions.

An azeotropic mixture isolated from reformed refinery gases gave, after redistillation, a boiling point of −94.4° and a composition of: acetylene, 40.7%; ethane, 59.3%; thus checking the existence and identity of the mixture.

Discussion

The isolation and identification of this mixture is of interest inasmuch as reports in the technical literature show acetylene determined by auxiliary reagent methods even though no acetylene had been observed on fractional distillation of the sample.[5] This phenomenon can be accounted for by the analysts disregarding irregularities usually found in Podbielniak distillations, especially when run at accelerated rates. It also explains, at least in part, the appearance of so-called "carbon dioxide plugs" which develop from time to time during ethane separations even though the original gases have been scrubbed with fresh caustic. The white solid which separates in such cases is usually not carbon dioxide but acetylene and can be identified by Ilosvay solution[6] or some other acetylene reagent.

Summary

The existence and composition of an azeotropic mixture of acetylene and ethane at atmospheric pressure have been determined.

BEACON, N. Y. RECEIVED MAY 12, 1936

(1) Kuenan, *Phil. Mag.*, **40**, 173 (1895); **44**, 174 (1897); *Z. physik. Chem.*, **24**, 667 (1897).

(2) McMillan, U. S. Patent 2,005,323.

(3) Martin Shepherd, *Bur. Standards J. Research*, **2**, 1156 (1929).

(4) McMillan, Cole and Ritchie, *Ind. Eng. Chem., Anal. Ed.*, **8**, 105 (1936).

(5) Groll, *Ind. Eng. Chem.*, **25**, 784 (1933); Frey and Hepp, *ibid.*, **25**, 441 (1933); *et al.*

(6) Pietsch and Kotowski, *Z. angew. Chem.*, **44**, 509 (1931).