hydrogen fluoride, (d) polymerization, and (e) fragmentation, either concurrently or successively.

All of the new products just mentioned and a number of other related derivatives have been adequately characterized with respect to both composition and molecular weight, but not necessarily with respect to such structural or stereoisomeric forms as may have been present.

DURHAM, NORTH CAROLINA RECEIVED JULY 18, 1949

[CONTRIBUTION FROM THE PULP MILLS RESEARCH PROJECT AND THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

Vapor–Liquid Equilibrium of Pyridine–Acetic Anhydride Solutions[1]

BY PHILIP A. NELSON[2] AND AARON E. MARKHAM

Certain analytical methods for hydroxyl in organic compounds, such as that of Verley and Bölsing[3] and its modifications, *e.g.*, that of Freed and Wynne,[4] involve esterification using acetic anhydride in pyridine solution. The analyses are usually carried out under such conditions that even a small loss of acetic acid or anhydride vapors from the refluxing mixture would introduce serious errors into the result. Vapor–liquid equilibrium data for the systems acetic acid–pyridine, and acetic anhydride–pyridine, would be helpful in indicating the magnitude of the error introduced by the loss of a small amount of vapor. Data have been presented on the acetic acid–pyridine system by Swearingen and Ross.[5] The present investigation was undertaken to obtain data on the acetic anhydride–pyridine system.

Experimental

Reagents.—Analytical grade reagents were used throughout. The acetic anhydride was fractionally distilled in a packed column before use, the first third, before the boiling point became constant, being discarded. Boiling points of 139.2° at 760.9 mm. and 138.2° at 756.6 mm. were observed, as compared with the value of 139.55° at 760 mm. reported by Orton and Jones.[6] Analysis of the anhydride for acid by the method of Rott[7] showed no acid, within the estimated limit of error of the method (0.2%). This method depends on a freezing point determination of the acetic acid produced by hydrolysis of the anhydride with a measured amount of water, and consequently should be quite sensitive to other impurities as well.

The pyridine had a boiling point of 115.6° at 756.6 mm., as compared to 115.5° at 760 reported by Timmermans.[8] The fraction used boiled over a range of less than 0.05°. The densities of two different materials used were 0.97797 and 0.97781, respectively, as compared to 0.9776 reported in the literature.[9] Distillation over barium oxide did not change the density of the pyridine.

Apparatus.—The equilibrium still used was a modification of that described by Jones, Schoenborn and Colburn.[10] A central tube, characteristic of the Othmer still,[11] was installed in the upper part of the boiling chamber to provide adiabatic insulation for the vapors and thus prevent reflux. A vent was provided to remove non-condensable gas from the space outside the central tube. When the apparatus was applied to the ethanol–water system to check its performance, with 16.5 mole per cent. ethanol in the liquid, the vapor composition was found to be 50.1% ethanol and the boiling point 83.5° at 756.3 mm. as compared with 50.3% ethanol and 83.9° at 760 mm. interpolated from the data of Jones, *et al.*[10]

Analysis.—The samples of liquid and condensed vapor withdrawn from the still were analyzed by hydrolyzing the acetic anhydride with water and titrating the product with carbonate-free sodium hydroxide to the phenolphthalein end-point.

Equilibrium and Boiling Point Data

The experimental boiling point and vapor–liquid composition data are presented in Fig. 1, in which the solid line is the composition curve according to Raoult's law. The water content was ignored in the calculation of the mole fractions. For the vapor pressures of the pure materials required in the calculations, the equation of Van der Meulen and Mann[12]

$$\log p = 6.8827 - (1281.3/(t + 203))$$

was used for pyridine, and the equation

$$\log p = 8.2899 - 2232.4/(t + 273.2)$$

obtained from vapor pressure data at 100°[13] and 139.55°[4] was used for acetic anhydride.

Discussion

The solutions were observed to darken on boiling due to the formation of a small amount of tar. This tar formation was observed by Wilson and Hughes,[14] who reported that it resulted from the use of anhydrous pyridine and could be prevented by the addition of about 0.5% of water to the pyridine before mixing with the acetic anhydride. A sample of a mixture, which had been boiled for several hours in the still while being

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[1] From a thesis submitted by Philip A. Nelson in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemical Engineering.

[2] Seattle Gas Co., Seattle, Wash.

[3] Verley and Bölsing, *Ber.*, **34**, 3354 (1901).

[4] Freed and Wynne, *Ind. Eng. Chem., Anal. Ed.*, **8**, 278 (1936).

[5] Swearingen and Ross, *J. Phys. Chem.*, **39**, 821 (1935).

[6] Orton and Jones, *J. Chem. Soc.*, **101**, 1720 (1912).

[7] Rott, *Chem. Ztg.*, **54**, 954 (1930).

[8] Timmermans, *Bull. soc. belg. chim.*, **24**, 244 (1910).

[9] Jones and Speakman, THIS JOURNAL, **43**, 1867 (1921); Müller and Brenneis, *Z. Elektrochem.*, **38**, 450 (1932).

[10] Jones, Schoenborn and Colburn, *Ind. Eng. Chem.*, **35**, 666 (1943).

[11] Othmer, *Ind. Eng. Chem., Anal. Ed.*, **20**, 763 (1948).

[12] Van der Meulen and Mann, THIS JOURNAL, **53**, 451 (1931).

[13] Beckmann and Liesche, *Z. physik. Chem.*, **88**, 419 (1914).

[14] Wilson and Hughes, *J. Soc. Chem. Ind.*, **58**, 74 (1939).

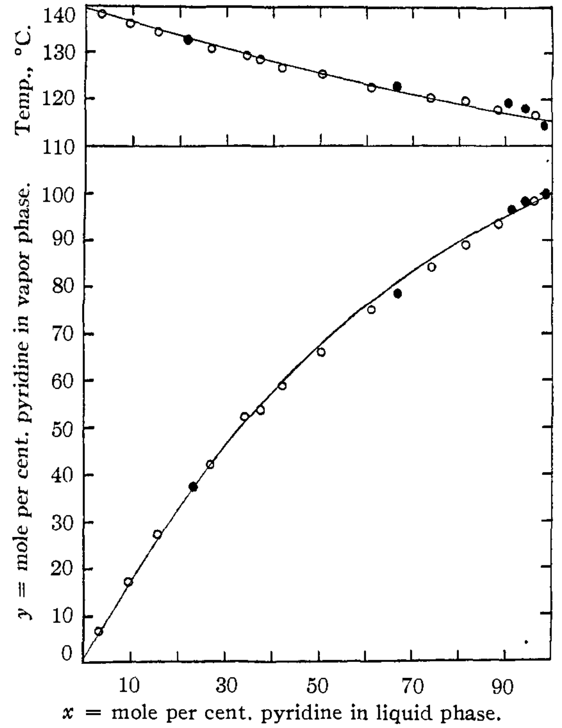

Fig. 1.—x–y and x-temperature diagram for the system pyridine–acetic anhydride, at atmospheric pressure: —, Raoult's law; O, experimental points with anhydrous reagents; ●, experimental points with water added to pyridine.

used for three vapor–liquid equilibrium determinations, was evaporated on a steam-plate over a period of seventy-two hours and found to leave a residue of 0.2% by weight. Thus, the weight per cent. of such tar present during the experiments, in which the liquid was boiled for a much shorter time, must have been quite small, and if the molecular weight of the tar was large its mole fraction and effect on the equilibrium could be expected to be negligible.

In an effort to avoid tar formation, water was added in several experiments to the pyridine to the extent of 0.5% as recommended by Wilson and Hughes. Tar formation was thus prevented when the pyridine content of the mixture was high, and greatly decreased when it was low. The content of acetic anhydride in the vapor was considerably reduced by the use of wet pyridine when the pyridine content was high, as would be expected from the formation of relatively nonvolatile pyridinium acetate from the acetic acid formed on hydrolysis. Through most of the range of composition, the effect of 0.5% of water on the equilibrium is within the experimental error.

The data fit Raoult's law quite closely over most of the range of composition. It is evident that the vapors contain substantial amounts of acetic anhydride at all concentrations and that any vapor loss from this system would have a serious effect on analytical results.

Summary

The equilibrium vapor–liquid compositions over the whole range at atmospheric pressure have been obtained for the system pyridine–acetic anhydride. The system was found to obey Raoult's law quite closely.

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[CONTRIBUTION FROM THE RESEARCH SECTION, DIVISION OF CHEMICAL ENGINEERING, TENNESSEE VALLEY AUTHORITY]

High-Temperature Heat Content of Hydroxyapatite

BY EDWARD P. EGAN, JR., ZACHARY T. WAKEFIELD AND KELLY L. ELMORE

Thermodynamic data for only a few compounds of interest in phosphatic fertilizer technology appear in the literature. Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, plays an important part in the physical chemistry of the calcium phosphates. In a review of the basic calcium phosphates, Eisenberger, Lehrman and Turner[1] concluded, "...it is only a fortuitous occurrence when the composition of any apatite may be expressed by small whole number ratios of atomic species suggesting a definite chemical compound." The preparations described in the present paper are believed, however, to represent as close an approach to the composition, $Ca_{10}(PO_4)_6(OH)_2$ as reasonably could be expected.

This paper is expected to be the first of a series on the thermal properties of calcium phosphates; hence, significant details of the construction of the calorimeter are presented. The calorimeter was calibrated primarily with electrical energy. Alumina and silica glass were used to test the calorimeter system, and the observed heat contents for these substances are included and compared with values from the literature.

Apparatus

The basic design of the high-temperature calorimeter was patterned after that of Southard.[2] Ready access to the receiving well in the gold-plated copper block was obtained by mounting the furnace on a hydraulic lift that permitted the furnace to be swung through an arc of 90° in the raised position.

The furnace temperature was controlled by means of a four-junction platinum–platinum + 10% rhodium ther-

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[1] S. Eisenberger, A. Lehrman and W. D. Turner, *Chem. Rev.*, **26**, 257-296 (1940).

[2] J. C. Southard, THIS JOURNAL, **63**, 3142-3146 (1941).