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No. 1]

# THE VAPOR PRESSURE OF ISOPROPYL ACETATE[1]

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## Introduction

While conducting some experiments recently on the physical properties of binary mixtures of ethyl, *n*-propyl and *iso*propyl acetates with acetic acid,[2] in order to make certain calculations with these mixtures it was necessary to know the vapor pressures of the esters. In searching through the literature we were able to find such data on the ethyl and *n*-propyl acetates,[3] but were unable to discover any vapor pressure work on the *iso*propyl acetate. In the absence of such data the following investigation was undertaken.

## Experimental

The apparatus employed in this work was essentially the same as that recommended by Smith and Menzies,[4] mercury serving as the confining liquid in the U-tube. The thermostat was a glass vessel of about six liters' capacity, provided with a propeller type stirrer and a nichrome wire heating element which was so connected through a lamp bank that the current could be varied at will, and in addition, a small fraction of current operated through a thermoregulator and relay, maintaining the temperature to within ±0.01°. Small Anschütz thermometers were employed along with a Beckmann, which served to denote the variation of temperature of the water-bath. The small thermometers were calibrated against a Bureau of Standards thermometer at the temperatures employed in this work. The manometer was of the ordinary type used in vapor pressure measurements. With the usual precautions it was accu-

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[1] This paper is constructed from a thesis submitted by Joseph F. Weiler to the Faculty of Holy Cross College in partial fulfilment of the requirements for the degree of Master of Science.

[2] Work to be published later.

[3] Young and Thomas, *J. Chem. Soc.*, **63**, 1191 (1893).

[4] Smith and Menzies, THIS JOURNAL, **32**, 1419 (1910).

rate to within 0.2 mm. The bulblet and U-tube part of the apparatus were baked at 150° for twenty-four hours in order to remove as much adsorbed water as possible. It was then cooled in a desiccator over sulfuric acid and used immediately when cool.

**Preparation of Materials.**—*Iso*propyl acetate from the Eastman Kodak Company served as a starting point. This was treated with a solution of potassium carbonate (50 g. in 100 cc.) in order to remove any acid which might be present, and then with a strong solution of calcium chloride (100 g. in 100 cc.) to remove any alcohol. It was allowed to stand over anhydrous calcium chloride overnight and then carefully distilled. Only that fraction which boiled within 0.1° was taken. It is very difficult to purify an ester beyond this point, so this fraction served as a stock solution and the samples employed in the isoteniscope were freshly distilled from it each time. We did not attempt to obtain the boiling point of this fraction accurately for we expected to obtain the true boiling point from the vapor pressure data. The mercury used in the manometer was distilled several times according to the method of Hulett.[5]

**Discussion of Error.**—At the lower temperatures the main error is due to the variation in reading the manometer. This amounts to about 0.2 mm. At temperatures above 60° the error due to temperature variation should become noticeable and gradually increase up to the maximum temperature employed in this work. The maximum absolute deviation was 0.5 mm. This indicates that providing sufficient readings are made on the manometer the error due to temperature variation may be maintained within the error due to reading the manometer. In order to make sure that these errors were not larger than we anticipated, we ran a determination of the vapor pressure of water and compared the results with those of Smith and Menzies.[6] These results deviated at most by an absolute error of 0.3 mm. The average deviation from the mean of values at 5° intervals from 50 to 80° was 0.2 mm. This shows that our values on the vapor pressure of *iso*propyl acetate are probably correct to within 0.2 mm. The largest percentage error obtains at the lower temperatures, where it may amount to as much as 1.5%. This percentage error falls off gradually as the temperature is raised.

**Method of Procedure.**—After the bulblet and U-tube were removed from the desiccator, the bulb was charged with 5–6 cc. of *iso*propyl acetate and the mercury placed in position in the limb of the U-tube. This part of the apparatus was connected to the manometer and vacuum pump and the whole system evacuated with continuous pumping for about an hour, reducing the volume of *iso*propyl acetate to about 1–1.5 cc. The mercury was then tipped into position in the U-tube with the pump

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[5] Hulett, *Z. physik. Chem.*, **33**, 611 (1900).

[6] Ref. 4, p. 1430.

still running. The system was disconnected from the pump and the usual procedure followed for determining vapor pressure.

## Experimental Data

The vapor pressure measurements on *iso*propyl acetate are given in Table I. The values in the second column are the average of several readings at the indicated temperatures, while those in Col. 3 are on a different sample and with a different U-tube and bulblet. The fourth column gives the average of the values in 2 and 3, and the last column the calculated values. The experimental readings at each temperature were all taken within a fifteen-minute interval along with the barometric pressure. All pressures are corrected to 0°.

Table I

Vapor Pressures of *Iso*propyl Acetate

| Temp., °C. | Vapor press., I | Obs., mm., II | Av. mm. | Calcd. mm. | Temp., °C. | Vapor press., I | Obs., mm., II | Av. mm. | Calcd. mm. |
|---|---|---|---|---|---|---|---|---|---|
| 0.00 | 15.8 | 15.6 | 15.7 | 15.7 | 50.20 | 189.4 | 189.4 | 189.4 | 188.8 |
| 5.00 | 21.3 | 20.9 | 21.1 | 21.0 | 55.20 | 234.2 | 233.9 | 234.1 | 232.0 |
| 10.00 | 27.9 | 27.8 | 27.9 | 27.8 | 60.20 | 284.4 | 284.2 | 284.3 | 281.7 |
| 15.00 | 36.5 | 36.3 | 36.4 | 36.4 | 65.20 | 344.1 | 344.1 | 344.1 | 340.3 |
| 20.00 | 47.2 | 47.0 | 47.1 | 47.2 | 70.20 | 413.6 | 413.7 | 413.7 | 409.6 |
| 25.00 | 60.8 | 60.5 | 60.7 | 60.6 | 75.20 | 493.8 | 494.0 | 493.9 | 490.0 |
| 30.00 | 77.3 | 77.2 | 77.3 | 77.0 | 80.20 | 585.4 | 585.8 | 585.6 | 582.5 |
| 35.05 | 98.0 | 97.7 | 97.9 | 97.9 | 85.20 | 689.8 | 690.0 | 689.9 | 689.1 |
| 40.10 | 122.9 | 122.7 | 122.8 | 122.6 | 90.20 | 810.6 | 810.9 | 810.8 | 811.0 |
| 45.15 | 152.6 | 152.8 | 152.7 | 152.7 | | | | | |

**Discussion of Results.**—By substitution of the proper constants in the empirical equation of Kirchhoff[7]

$$\log_{10} P = A + B \log_{10} T + C/T$$

we obtained the following equation

$$\log_{10} P = 14.2517 - 2.0972 \log_{10} T - 2170.1/T$$

The values in Col. 5 of Table I were obtained from this equation by substituting the proper temperatures and solving for the vapor pressure. It will be seen that the calculated values agree fairly well with the observed, the maximum percentage error occurring at 65.20°, where it is a little over 1%. This equation may also be used to calculate the boiling point, which is found to be 88.2°.

We have also employed this equation along with the expression $\mathrm{d} \ln P/\mathrm{d}T = L/RT^2$ in order to determine the molal heat of vaporization at the boiling point. The value so obtained was corrected by deducting 4% according to Parks and Barton,[8] giving a final value of 7900 cal. per mole. This quantity substituted in the Trouton equation gives a molal

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[7] Kirchhoff, *Pogg. Ann.*, **103**, 185 (1858).

[8] Parks and Barton, This Journal, **50**, 26 (1928).

entropy of vaporization of 21.8 cal. per degree, indicating that *iso*propyl acetate is a normal liquid.

Following Hildebrand,[9] we have also calculated the molal entropy of vaporization at that temperature (35.0° in the case of *iso*propyl acetate) at which the concentration of the vapor is 0.00507 mole per liter and obtained a value of 27.6 cal. per degree. As 27.4 cal. per degree is the mean value obtained by Hildebrand for normal liquids, this value also indicates that *iso*propyl acetate is a normal liquid.

## Summary

Vapor pressure measurements have been made on *iso*propyl acetate from 0 to 90°, inclusive.

An equation has been obtained for the vapor pressure curve from which the boiling point has been determined.

From this equation the molal heat of vaporization has been determined.

The molal entropy of vaporization has been determined at the boiling point and also at that temperature at which the vapor concentration is 0.00507 mole per liter.

These molal entropies indicate that *iso*propyl acetate is a normal liquid.

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# EQUILIBRIUM BETWEEN THE CARBONATES AND BICARBONATES OF SODIUM AND POTASSIUM IN AQUEOUS SOLUTION AT 25°

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A phase-rule study of the reactions between the carbonates and bicarbonates of sodium and potassium does not appear to have been published heretofore. Such a study may be regarded as including the more important part of the possible reactions of the two bases with carbonic acid, between the limits in which the carbonic acid varies from an amount just sufficient to form normal carbonates with all the base present and an amount sufficient to form bicarbonates with all the base present. For such a four-component study, four three-component studies are a preliminary essential; these are listed below. Three of them have been studied with more or less completeness at a number of times and places, and more recently at this

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[9] Hildebrand, "Solubility," American Chemical Society Monograph, Chemical Catalog Company, New York, **1924**, p. 94.

[1] The material of this paper was presented by Sterling B. Smith in partial fulfilment of the requirements for the degree of Doctor of Philosophy at New York University, June, 1927.