the electrodes. Iodimetric titrations can be made in the weaker of the two solutions without the use of a battery.

Columbus, Ohio

[Contribution from the Cryogenic Laboratory, Bureau of Mines, United States Department of Commerce]

THE VAPOR PRESSURE OF ETHANE NEAR THE NORMAL BOILING POINT[1]

By A. G. Loomis and J. E. Walters

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Introduction

For the design of an efficient plant to extract helium from natural gas it is necessary to know the thermodynamic properties of the several components of the gas. This investigation supplies the vapor pressure of ethane in the neighborhood of the normal boiling point, and is one of a series of investigations now being undertaken on the thermodynamic properties of the pure components of natural gas, and of their binary mixtures. The pressures recorded in this paper cover the range from 0.0245 atmospheres to 2.1441 atmospheres; Dr. Porter (see the following paper) has extended these measurements to the critical pressure.

Previous Investigations

Olszewski[2] reports the normal boiling point of ethane prepared from zinc ethyl as —93°.

Burrell and Robertson[3] measured the vapor pressure from 1 mm. to 760 mm., giving 183.8°K. as the normal boiling point. Temperatures were measured by means of a pentane thermometer, and two observers could check readings to 0.2° and in most cases to 0.1°. The cryostat of the Henning type could be held constant to 0.04° for the period of measurement of a vapor pressure. Pressure readings were reproducible to 1 mm. The limit of accuracy of reading the thermometers (0.2°) corresponds to 7.5 mm. near the normal boiling point. The ethane used was prepared from sodium acetate solution by electrolysis, purified chemically, fractionated and pumped free from traces of foreign gases. Moreover, portions were removed from time to time, so that the purity of their ethane was all that could be desired.

Maass and McIntosh[4] measured the vapor pressure from 288 mm. to 765 mm. and found 184.6°K. as the normal boiling point. Temperatures were read on a hydrogen gas thermometer; the cryostat could be held con-

[1] Published with the permission of the Director of the Bureau of Mines.

[2] Olszewski, *Berl. Ber.*, **27**, 3305 (1894).

[3] Burrell and Robertson, This Journal, **37**, 1893 (1915).

[4] Maass and McIntosh, *ibid.*, **36**, 737 (1914).

stant to 0.1°. Their ethane was prepared from methyl iodide by means of a zinc-copper couple, chemically purified, cooled in spirals at —78°, and the middle fraction of several distillations accepted as pure. However, it has been shown by Kuenen[5] that ethane prepared from methyl iodide by means of a zinc-copper couple contains a heavier constituent, presumably butane, and since the latter has an appreciable vapor pressure at —78° a limited number of fractionations at this temperature would not remove all of it from the ethane, a circumstance which may explain their somewhat high value of 184.6°K. for the normal boiling point of ethane.

Experimental Part

Preparation of Ethane.—Ethane was prepared by the electrolysis of potassium acetate solution, following the methods of Murray.[6] The impure ethane was repeatedly circulated between two reservoirs of potassium hydroxide solution and allowed to remain in contact with this solution for several days. It was then allowed to bubble at a slow rate through fuming sulfuric acid to remove unsaturated gases, through sulfuric acid, and finally through potassium hydroxide solution; this procedure was repeated a number of times. The gas was finally dried over solid potassium hydroxide and phosphorus pentoxide, and frozen with liquid air. The solid ethane was pumped free from uncondensed gases by means of a mercury diffusion pump, the ethane then distilled to another bulb and pumped again, this procedure being repeated until no more gas was given off. The ethane was then repeatedly fractionated while being stirred with a small magnetic stirrer, only the middle portions being retained, and finally condensed into the vapor-pressure bulb. The temperature of the cryostat was adjusted so that the pressure was about one atmosphere, and it was found that repeated removals of small fractions of the sample did not change the pressure reading, proving that the ethane was pure.

Ethane prepared by the action of water on ethylmagnesium iodide and purified in the same manner as described above showed the same vapor pressure as ethane prepared by the first method.

Auxiliary Apparatus.—The cryostat employed was that described by Walters and Loomis,[7] and the temperature was maintained constant to 0.01° during the period of measurement.

For measurement of temperature we used platinum-resistance thermometer No. 2, made and calibrated as described by Loomis and Walters.[8] The temperature scale was defined by the Henning equation based on the calibration points; the observed and calculated temperature of the carbon dioxide point checked to 0.01°.

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[5] Kuenen, *Proc. Roy. Soc. Edinburgh*, **21**, 433 (1897).

[6] Murray, *J. Chem. Soc.*, **61**, 10 (1892).

[7] Walters and Loomis, THIS JOURNAL, **47**, 2302 (1925).

[8] Loomis and Walters, *ibid.*, **47**, 2851 (1925).

The bridge was of the Mueller type and had been calibrated by the Bureau of Standards.

Pressures were read on a manometer of wide inside bore by means of a Geneva Society cathetometer, calibrated by the Bureau of Standards; the cathetometer read directly to 0.001 cm. A Geneva Society standard meter was suspended near the mercury column for comparison on the cathetometer. At any particular temperature a series of readings was obtained, the temperature of the cryostat being temporarily varied so that the equilibrium pressure was approached from both sides. The containing bulb was shaken repeatedly to hasten the attainment of equilibrium. All pressures are expressed in terms of the normal atmosphere.[9]

Results

In Table I are given the results, each pressure being the mean of at least four readings with rising and falling meniscus. The data are well represented by the following equation; $\log_{10} P_{(\text{atm.})} = -(780.24/T) + 4.2563 - 0.000103T - 9.3 \times 10^{-10}(T - 238)^4$. From the equation the normal boiling point of ethane is found to be 184.467°K.

TABLE I

VAPOR PRESSURE OF ETHANE

T,°K.	$P_{\text{atm.}}$ (calcd.)	$P_{\text{atms.}}$ (obs.)	P(obs.) − P(calcd.)
167.836	0.3695	0.3693	−0.0002
165.529	.3162	.3160	− .0002
162.629	.2582	.2573	− .0009
158.385	.1890	.1886	− .0004
154.546	.1402	.1400	− .0002
147.324	.0762	.0759	− .0003
143.267	.0526	.0522	− .0004
135.736	.0247	.0245	− .0002
169.175	.4036	.4033	− .0003
171.700	.4747	.4743	− .0004
170.602	.4427	.4430	+ .0003
174.062	.5499	.5498	− .0001
175.708	.6076	.6073	− .0003
177.623	.6807	.6804	− .0003
178.621	.7215	.7210	− .0005
179.750	.7698	.7696	− .0002
181.506	.8500	.8499	− .0001
182.463	.8964	.8963	− .0001
183.778	.9633	.9634	+ .0001
184.539	1.0038	1.0040	+ .0002
185.137	1.0365	1.0366	+ .0001
185.914	1.0803	1.0800	− .0003
186.609	1.1206	1.1208	+ .0002
187.302	1.1620	1.1619	− .0001

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[9] The acceleration of gravity at the place of measurement was taken as 980.111 cm. sec.$^{-2}$.

TABLE I (*Concluded*)

T,°K.	P_{atm}. (calcd.)	P_{atms}. (obs.)	P(obs.) − P(calcd.)
187.72_6	1.1878	1.1881	+ .0003
188.37_9	1.2286	1.2289	+ .0003
189.11_4	1.2757	1.2761	+ .0004
189.85_8	1.3248	1.3264	+ .0016
190.79_1	1.3885	1.3900	+ .0015
191.43_0	1.4334	1.4347	+ .0013
192.28_6	1.4953	1.4974	+ .0021
192.77_7	1.5318	1.5340	+ .0022
199.90_9	2.1417	2.1441	+ .0024
196.24_4	1.8088	1.8110	+ .0022

The latent heat of vaporization of ethane at the normal boiling point is calculated to be 3642.4 cal. per mole from the thermodynamic equation $(\partial \ln P/\partial T)_p = \Delta H/RT^2$, using the equation given above to express P as a function of T. This value for ΔH is, of course, somewhat high resulting from the assumption of the perfect gas law in the thermodynamic equation.[10]

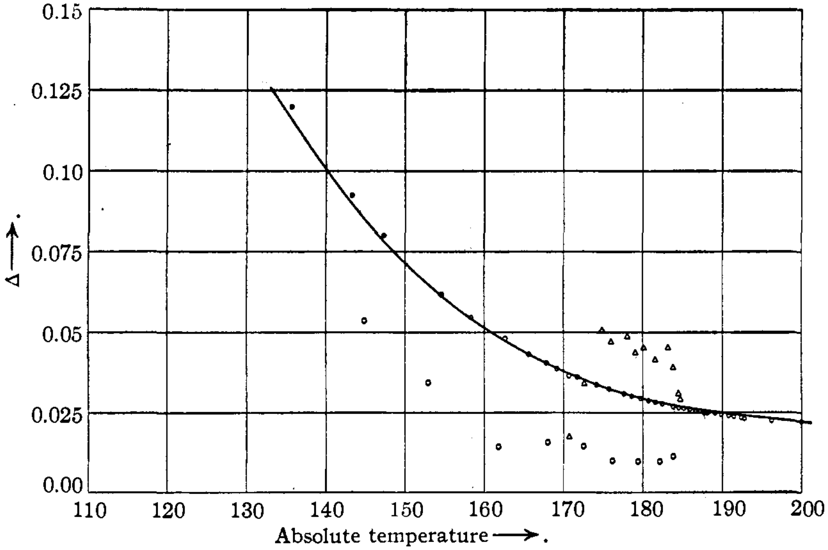

Fig. 1.—ΔT plot. Curve calculated from $\log P_{\text{atm}} = -0.000103T - 9.3 \times 10^{-10} (T - 238)^4$. ○—Loomis and Walters. △—Maass and McIntosh. □—Burrell and Robertson.

For a comparison of the data of the several observers a plot is given representing the deviation Δ as a function of T, where Δ is $\log P_{\text{obs.}} - \log P_{\text{calcd.}}$, the values of $\log P_{\text{calcd.}}$ being obtained from the equation $\log P_{\text{calcd.}} = -(780.24/T) + 4.2563$, the first three terms of our equation representing

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[10] See the paper by Porter and Perry for the calculated value of ΔH based on specific volumes experimentally determined. THIS JOURNAL, **48**, 2059 (1926).

the data. It is seen that our observations fall on a smooth curve lying between the somewhat scattered data of Maass and McIntosh and of Burrell and Robertson. The two remaining terms of the equation [$-0.00010\ T - 9.3 \times 10^{-10}(T - 238)^4$] are calculated for several values of T and, as shown on the plot, fit the curve very closely.

Summary

The vapor pressure of pure ethane has been measured from a pressure of 0.0245 to 2.1441 atmospheres.

The equation derived from the data representing P as a function of T is $\log_{10} P_{\text{atm.}} = -(780.24/T) + 4.2563 - 0.000103T - 9.3 \times 10^{-10}(T - 238)^4$. The normal boiling point is calculated to be 184.46$_7$°K. from this equation.

A deviation plot is given which compares the data of the several observers.

The latent heat of vaporization at the normal boiling point of ethane is calculated to be 3642.4 calories per mole.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE]

THE VAPOR PRESSURES AND SPECIFIC VOLUMES OF THE SATURATED VAPOR OF ETHANE[1]

BY FRANK PORTER

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The present work represents a part of a series of investigations that are being carried out on the properties of this substance. Measurements on the vapor pressure of ethane have been made by Hainlen,[2] Kuenen and Robson,[3] Maass and McIntosh,[4] Burrell and Robertson,[5] and Loomis and Walters.[6] Of these, only Kuenen and Hainlen extended their work to the higher pressures. The character of Hainlen's work does not conform to the present-day standards along this line. Kuenen did not succeed in getting his ethane completely pure, the variation in pressure at a constant temperature being as much as 1%.

Specific volumes of the saturated vapor have been measured only by Kuenen.[7] Only a short range below the critical was covered by this work.

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[1] Published with the permission of the Director of the Bureau of Mines.

[2] Hainlen, *Ann.*, **282**, 229 (1894).

[3] Kuenen and Robson, *Phil. Mag.*, [6] **3**, 149 (1902).

[4] Maass and McIntosh, THIS JOURNAL, **36**, 737 (1914).

[5] Burrell and Robertson, *ibid.*, **37**, 1893 (1915).

[6] Loomis and Walters, *ibid.*, **48**, 2051 (1926).

[7] Kuenen, *Phil. Mag.*, **40**, 173 (1895).