

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 184.467°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.

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THE VAPOR PRESSURES AND SPECIFIC VOLUMES OF THE SATURATED VAPOR OF ETHANE¹

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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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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).

More accurate and complete data were considered desirable, especially for the calculation of the heats of vaporization over this range.

Ethane was generated by the electrolysis of a 60% solution of potassium acetate. It was allowed to stand over a solution of sodium hydroxide for some time and was then bubbled slowly several times through a train in which it successively passed through fuming sulfuric acid, ordinary concd. sulfuric acid, potassium hydroxide solution and phosphorus pentoxide. About 20 liters so treated was freed from air by freezing down with liquid air and evacuating several times, and then fractionated in a bead column of the Hempel type, the top of the column being refrigerated by a bath cooled to about -100° . Only a very small fraction of the ethane vaporized was removed, the remainder being refluxed down the column. About 3 liters of vapor from the middle portion was collected for the measurements. It was found to liquefy completely at a constant pressure within the limit of our measurements described below.

Temperature measurements were made with a platinum resistance thermometer, the calibration of which is described by Loomis and Walters.⁸ The cryostat employed was also of the same type as used by those investigators.⁹

The pressure gage was of the type that was described by Keyes and Brownlee.¹⁰ It had previously been calibrated against a mercury column of about 8 meters.

The dilatometer was made of heavy-walled Pyrex tubing, and had a volume of nearly 20 cc. A small capillary tube led from the lower end of the dilatometer up over the side of the cryostat and thence to the pressure gage. A small T connected this line through a steel valve to the volumenometer.

The volumenometer was a straight tube about 1 meter long with a total volume of 100 cc.

The dilatometer and volumenometer were calibrated in place. The heights of the mercury above reference marks were read with a cathetometer and the volumes of mercury removed were related to the readings on the cathetometer scale.

The filling of the dilatometer was accomplished by cooling it below the boiling point of ethane and allowing a suitable measured volume to flow in from the volumenometer.

The temperature of the volumenometer was kept very close to 25° and the pressure at one atmosphere. In order to arrive at the density of ethane under these conditions, for the purpose of determining the mass of ethane employed, an experimental method was used. The expansion

⁸ Loomis and Walters, *THIS JOURNAL*, **47**, 2851 (1925).

⁹ Walters and Loomis, *ibid.*, **47**, 2302 (1925).

¹⁰ Keyes and Brownlee, *ibid.*, **40**, 25 (1918).

on raising a certain volume from 0° to 25° was measured. The accepted density at 0° and 1 normal atmosphere is 0.0013562 g. per cc., and from this and our measurements the density at 25° and 1 normal atmosphere was found to be 0.0012383.

The exact volume of ethane vapor at a point of saturation was determined by holding the temperature constant and measuring the volumes and pressures at a series of points not far removed from the saturation point. By plotting these values on a large scale, the intersection of the curve with the vapor-pressure line could be readily ascertained and the volume of this point was taken as the saturated volume. The manipulation to obtain the part of the isotherm needed was comparatively simple. Starting with a small amount of liquid in the dilatometer, the vapor pressure was read. Then weights equivalent to about 0.001 atmosphere were removed from the pan of the gage and the mercury injector was backed up slowly until the gage was again in equilibrium with the pressure in the dilatometer. The volume occupied by the ethane in the dilatometer was then read and the process repeated until a sufficient number of observations were obtained to establish the curve.

The data of Latimer and Buffington¹¹ were used to correct for the thermal expansion of the Pyrex dilatometer. In calculating expansion due to pressure the Young's modulus of 0.6230 kg./sq. mm. was used. For temperatures below the freezing point of mercury, the mercury was kept at a position just above the level of the cryostat, and while the volume of the ethane was thus kept constant, the temperature and pressure were varied, with the vapor just above the condition of saturation. The isochor was then plotted and the break observed as before. The manipulation is not nearly so simple, because it is not so easy to change the temperature as it was to change the volume in the previous case.

The volume at the boiling point was obtained by connecting the dilatometer through the small capillary to the volumenometer and obtaining the isotherm near the saturation point.

The vapor pressures were found to be fairly well represented by the equation, $\log_{10} P_{\text{atm.}} = -780.24/T + 4.2563 - 0.000103T + 1.4 \times 10^{-11}(T - 238)^5$, in which the pressure is expressed in normal atmospheres. This equation, when applied at low temperatures, fits very approximately but not exactly to the data of Loomis and Walters.⁶

Table I gives the data obtained. The heats of vaporization given in Col. 5 are calculated from the exact thermodynamic equation, $dP/dT = \Delta H/T(V - v)$, where P is vapor pressure, T the temperature, ΔH the heat of vaporization, V the saturated vapor and v the volume of the liquid. The data of Maass and McIntosh⁴ and of Kuenen⁷ for the liquid densities were plotted and the values needed were read from the

¹¹ Unpublished work from University of California.

smoothed curve. The values for dP/dT were obtained from differentiation of the above vapor-pressure equation, with the exception of that at the boiling point, which was obtained by differentiating the equation of Loomis and Walters.⁶

TABLE I
VAPOR PRESSURE OF ETHANE

$T, ^\circ\text{K.}$	$P_{\text{atm.}}$	$P_{\text{obs.}} - P_{\text{calcd.}}$ atm.	$V, \text{cc./mole}$	$\Delta H, 15^\circ \text{ calories}$ per mole
288.26	33.468	+0.011	414.68	1739
283.58	30.106	+ .009	479.33	1890
278.84	26.837	- .073	552.23	2019
273.09	23.544	+ .003	649.24	2166
268.73	21.185	+ .023	736.84	2277
263.28	18.448	+ .009	861.23	2400
258.80	16.421	+ .020	968.6	2469
253.03	14.043	+ .026	1158.1	2624
248.65	12.354	- .027	1320.7	2692
243.22	10.536	- .014	1555.7	2789
238.90	9.229	- .013	1771.9	2849
234.58	8.044	- .010	2026.2	2907
226.18	6.073	.000	2652.2	3005
225.10	5.838	- .008
221.88	5.207	- .004
216.31	4.225	- .011
210.96	3.414	+ .011
205.62	2.733	+ .003
203.49	2.496	+ .005
184.47	0.9994	+ .005	14511	3325

An equation to represent the volumes was not found. Dieterici's equation of state was found to be the best simple equation of state to represent the values approximately. Using the data of Kuenen at the critical point to evaluate the constants, the calculated values were found to have a maximum deviation of 2.5% from observed values, with an average deviation of 1.3%.

Summary

The vapor pressures and specific volumes of the saturated vapor of ethane have been measured over the range from the normal boiling point to 288°K.

The data were used in the calculation of the heats of vaporization.

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