

[CONTRIBUTION FROM THE MOTOR FUELS EVALUATION DIVISION, NORTHERN REGIONAL RESEARCH LABORATORY]¹Pressure-Volume-Temperature Relationships of Alcohol Vapors²

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Vapor densities of methyl, ethyl and isopropyl alcohols have been measured at 40 to 120° and at pressures up to 760 mm. or half the saturation pressure, whichever is smaller. The uncertainty of the measurements was of the order of 3 parts in 10⁵ in $(pV)/(RT)$ at 760 mm., and was greater at lower pressures, being approximately inversely proportional to pressure. The equation $V = RT/p + B + Dp^2$, used by Weltner and Pitzer, and Barrow, was found to fit our results and to give satisfactory agreement with vapor heat capacities measured by these authors and by DeVries and co-workers, and also gave satisfactory agreement with saturated vapor densities calculated from the heats of vaporization measured by Flock, Ginnings and Holton.

In spite of the theoretical importance of the second and higher virial coefficients of gases, comparatively few direct measurements of these quantities have been made for substances with normal boiling points above room temperature. This fact may be ascribed to the experimental difficulties involved in making accurate pressure and volume measurements on a mass of vapor which must be kept in its entirety at an elevated temperature to avoid condensation.

For the alcohols the only direct measurements on record are those of Eucken and Meyer³ and Lambert, *et al.*,⁴ for methanol. Pressure-volume-temperature relationships have been deduced from vapor-heat capacity measurements for methanol by Weltner and Pitzer⁵ and for ethanol by Barrow.⁶ We felt that it would be desirable to make direct measurements on several alcohols, of greater accuracy than those in references 3 and 4, since the vapor-heat capacity measurements do not determine the vapor volume directly, but only its second derivative with respect to temperature. The present paper reports measurements on methanol, ethanol and isopropyl alcohol in the temperature range from 40 to 120°.

Experimental Method

Apparatus.—Figure 1 is a diagram of the apparatus. It was connected to the atmosphere through a drying tube at A, to a mercury diffusion pump at B, to a separate rough vacuum system at I, and to a manometer and ballast vessel at E. Vapor was generated in the boiler P and condensed by the reflux condenser G to be returned to the boiler through the fractionating column O. Thus the portion of the system from the condenser to the manometer at E could be filled with air and did not need to be maintained at an elevated temperature.

On opening valve 9, vapor was admitted to the previously evacuated bulb Q. After pressure and temperature equilibrium had been reached, this bulb contained a known volume of vapor at the temperature of the thermostat R and at the pressure indicated by the manometer at E. This sample of vapor was isolated by closing valve 9, and after opening valve 8, it was condensed in one of the ampoules L, sealed off, and weighed.

Boiler P was operated as a flash boiler, since the ordinary process of ebullition from a mass of liquid would have caused undesirable pressure fluctuations, especially at the

lower pressures. It was made of 16 mm. i.d. tubing with a layer of powdered glass fused to the inside surface, and was immersed in a small electrically heated oil-bath. The rate of vapor generation was controlled by the rate at which liquid passed from reservoir N through the 1/8-inch Hoke needle valve 7 into the fractionating column.

The fractionating column O was also of 16-mm. i.d. tubing. The section above the vapor outlet to bulb Q was designed to remove permanent gases from the liquid without introducing any appreciable pressure drop. It contained no packing except a nichrome wire helix 40 cm. long, snugly fitting the inside surface of the tube. Below the vapor outlet was a short section packed with single-turn glass helices to remove any impurities of lower volatility which might be present in the liquid, and concentrate them in the boiler. The fractionating column, reservoir and connecting tube were covered with heavy thermal insulation, since excessive condensation in these parts of the apparatus would have necessitated an increased rate of vapor generation in the boiler, with an increased pressure drop through the column.

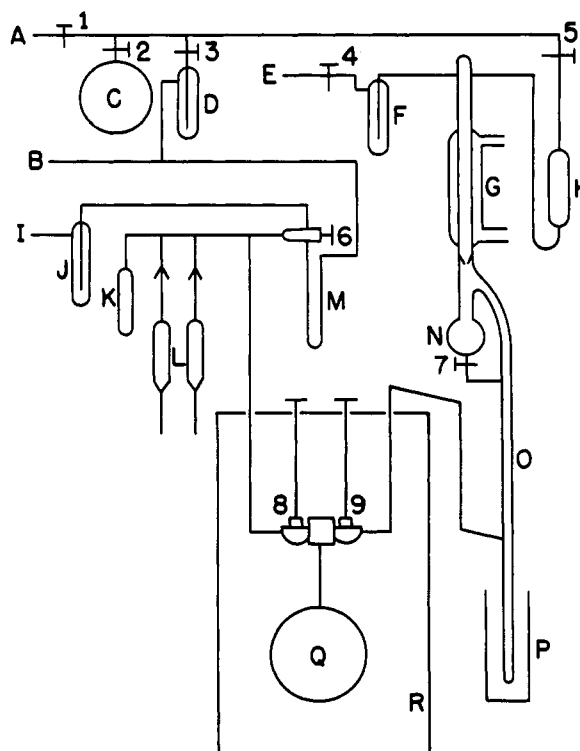


Fig. 1.—Apparatus; see text for explanation.

Bulb Q was constructed from a 1-liter, Pyrex distilling flask. Valves 8 and 9 were Hoke, type 431, miniature, packless needle valves with bronze bellows. The actuating caps on these valves were replaced with threaded bushings accommodating long, threaded control rods which extended through the cover of the bath. When these rods were screwed into the bushings, they pressed the valve

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(2) Presented at the Regional Conclave of the American Chemical Society at New Orleans, Louisiana, December 10-12, 1953.

(3) A. Eucken and L. Meyer, *Z. physik. Chem.*, **55**, 452 (1929).

(4) J. D. Lambert, G. A. H. Roberts, J. S. Rowlinson and V. J. Wilkinson, *Proc. Roy. Soc. (London)*, **A196**, 113 (1949).

(5) W. Weltner, Jr., and K. S. Pitzer, *THIS JOURNAL*, **73**, 2606 (1951).

(6) G. M. Barrow, *J. Chem. Phys.*, **20**, 1739 (1952).

stems into contact with their seats. The valves were screwed and soft-soldered into a brass T-block, with their bellows sides away from the block. Kovar-to-Pyrex seals, soft-soldered into the valves and block, were used to join bulb Q to the block and valves 7, 8 and 9 to the remainder of the apparatus. Valves 8 and 9 were easy to close tightly enough so that leakage was undetectable for a period of several hours, with a pressure difference of one atmosphere across the valve. Since the bronze bellows develop cracks if exposed to mercury vapor, stopcocks 3 and 6 were never opened to the mercury diffusion pump unless traps D and M were cooled to -78° .

The volume confined within the bulb when both valves were closed was determined before assembly of the apparatus by weighing the bulb when filled with air and when filled with distilled water at 35° .

The bulb was supported in the constant temperature oil-bath R. This consisted of a stainless steel tank of 30-liters capacity, insulated at the top and bottom with 2 inches of corkboard, and at the sides with 1.5 inches of silica aerogel insulating powder. A continuous heating coil was wound over the entire outer cylindrical surface of the stainless steel tank. The intermittent heater was a bare nichrome coil immersed directly in the oil. The bath was filled with Dowtherm A to above the tops of the valves. This heat-transfer medium was chosen because it is sufficiently volatile to be removed by pumping, in case leakage of the valve assembly should allow it to enter the apparatus.

The bath liquid was stirred with an efficient propeller. Its temperature was controlled to 0.001° with a platinum resistance thermometer in a bridge circuit which actuated a galvanometer and photoelectric cell relay, switching the intermittent heater on and off. It was found that the performance of this type of controller could be considerably improved by placing in front of the light source a suitably shaped shutter rotated once every several seconds by a small synchronous motor. The shutter was shaped so that the light was completely interrupted during a small fraction of each revolution, and during the remainder of each revolution one defining edge of the light beam was moved back and forth over the photocell cathode. This arrangement constitutes a Gouy modulator⁷ and achieves a form of proportional control. The scheme is used in some commercial controllers. The complete interruption of the light once each cycle eliminates the differential in photocell illumination required to open and close the relay.

The temperature of the bath was measured with a calibrated platinum resistance thermometer and Mueller bridge.

Ampoules L were made of 14-mm. tubing and were connected to the manifold with 10/30 ground joints. They were provided with sealing constrictions below the joints. The bottoms of the ampoules were drawn out into capillary tails of about 1.5-mm. outside and 0.3-mm. inside diameter. After a sealed ampoule, containing a condensed vapor sample, was weighed, a fine scratch completely encircling the capillary tail near its closed end was made with a tungsten carbide knife mounted in a suitable jig and the tip was broken off. This operation could be performed without losing any glass particles. Most of the liquid was removed by placing the ampoule in a vacuum desiccator, tail pointing downward, and applying suction. The ampoule was then connected to a vacuum system by inserting the tail through a hole pierced in a rubber serum stopple on the end of a tube which communicated with the vacuum system. The ampoule was flamed and pumped out, and then the tail was sealed off with a small flame, leaving a small length inserted in the serum stopple. The ampoule, with the two small lengths of capillary resulting from the opening and resealing operations, was again weighed.

Since the ampoule contained no air during either weighing, the buoyancy corrections were greatly simplified. It was not necessary to determine the internal volume of the ampoule, and a very rough measurement of the external volume, obtained by observing the change in level on immersing the ampoule below the surface of water in a graduated cylinder, was sufficient to compute the small correction resulting from the change in air density between the two weighings. Tests made with empty ampoules established that the opening, evacuating and resealing operations did not change the weight of an ampoule by more than a few micrograms.

(7) T. S. Sligh, Jr., *THIS JOURNAL*, **42**, 60 (1920).

The weighings were performed by the substitution method on a microchemical balance with recently calibrated weights. A rigid schedule of wiping the ampoules and letting them come to equilibrium with the air in the balance case was adhered to. The barometric pressure and the temperature and humidity of the air in the balance case were observed at the time of each weighing, in order to compute the buoyancy corrections. Weighings of the ampoules were reproducible to less than 10 micrograms.

The pressure measuring system connected at E consisted of a 20-liter ballast vessel enclosed in heavy thermal insulation, the manometer, and suitable valves for setting the pressure of air in the system to any desired value. The manometer was made of 17-mm. i.d. tubing selected for uniformity of bore. It was built inside a closed wooden case with plate-glass windows. Air from the bottom of the case was drawn, by a fan, into a duct running up one side of the case and was discharged into the top of the case to flow down over the manometer and scale. Tests with thermocouples showed that the uniformity of temperature within the case was more than sufficient for the accuracy with which the manometer could be read. The temperature of the manometer was measured with a calibrated thermometer immersed in mercury in a test-tube of the same diameter as the manometer tubing, located with its bulb 300 mm. above the lower mercury level.

The manometer was filled with mercury which had been treated with 5% $\text{Hg}_2(\text{NO}_3)_2$ solution and distilled. The vacuum arm was attached to a Pirani gage and could be connected to the high vacuum system and pumped out whenever necessary. A Gaertner stainless steel meter bar of rectangular cross section was suspended next to the manometer. The rulings on this scale were 0.01 mm. wide. Calibrations by the maker and by the National Bureau of Standards indicated that no errors greater than 0.01 mm. were present. A Gaertner, model M901, cathetometer with two carriages was used as the comparator. The telescopes were fitted with filar micrometer eyepieces and microscope objectives giving a magnification of 10 diameters. The scale and the tops and bottoms of the mercury menisci were illuminated by methods similar to those described by Beattie.⁸

Materials.—Methanol and isopropyl alcohol were purified as described previously⁹ and ethanol was purified by the method used for isopropyl alcohol. The final drying with freshly cleaned magnesium ribbon was carried out in flasks C (Fig. 1) attached to a manifold which was part of the apparatus. The alcohols were stored in these flasks over excess magnesium alcoholate and never came in contact with the atmosphere. Densities in g./ml. at 25.00° were: methanol, 0.78653; ethanol, 0.78506; isopropyl alcohol, 0.78083; all ± 0.00002 . These values are in close agreement with other reliable measurements,¹⁰⁻¹² and indicate water contents of less than 0.01%.

Procedure.—To begin a determination, the entire apparatus was evacuated to a pressure of less than 1μ . Alcohol vapor from the storage bulb C was condensed in trap H at -78° . After a sufficient amount had accumulated, it was forced through the capillary connecting tube into the vapor generating system by admitting dry air through stopcock 1. Stopcock 4 was then opened to connect the vapor generator with the pressure measuring system, which had been set to the desired pressure. The liquid was refluxed in the vapor generator long enough to free it of dissolved air. To remove the air from the connecting tube leading from O to valve 9, bulb Q was filled with vapor from O several times, each filling being pumped out through 8 and 6 and condensed in trap J. In filling the bulb, care had to be taken that the rate of withdrawal of vapor into Q was always less than the rate at which it was being generated in P; otherwise, air would have entered the bulb. This point was checked by observing that drops continued to fall from the drip tip below condenser G.

When all air had been eliminated from the connecting tube, as above described, bulb Q was pumped to as low a

(8) J. A. Beattie, D. D. Jacobus, J. M. Gaines, Jr., M. Benedict and B. E. Blaisdell, *Proc. Am. Acad. Arts Sci.*, **74**, 327 (1941).

(9) C. B. Kretschmer and R. Wiebe, *THIS JOURNAL*, **74**, 1276 (1952).

(10) G. Jones and H. J. Fornwalt, *ibid.*, **60**, 1683 (1938).

(11) N. S. Osborne, E. C. McKelvy and H. W. Bearce, *Bull. Bur. Standards*, **9**, 327 (1913).

(12) R. F. Brunel, *THIS JOURNAL*, **45**, 1334 (1923).

pressure as possible and then filled with vapor. Valve 9 was left wide open for 15 minutes to allow the vapor in Q to reach equilibrium with respect to temperature and pressure. One telescope was set on the upper meniscus in the manometer, valve 9 was tightly closed, and the other telescope was set on the lower meniscus. The bath temperature was read. Valve 8 was opened and the vapor was condensed in one of the ampoules L at -78° . While this was occurring the pressure measurement was completed by setting the telescope cross hairs to the nearest rulings on the standard scale.

The progress of condensation was followed by means of Pirani gage K. Success in eliminating all permanent gas from the vapor was demonstrated by a fairly rapid decrease of pressure to the vapor pressure of the alcohol at -78° . This residual pressure was measured at each determination. The Pirani gage had been calibrated against a McLeod gage for each vapor studied, the McLeod gage being operated in such a way that the vapor could not condense within it. When condensation was complete, the ampoule was sealed off. The apparatus was now ready for another determination, after setting the pressure in the vapor generator to a new value. At the end of each day's operation, liquid remaining in the vapor generator was pumped into trap F and discarded.

For measurements at pressures below the room temperature vapor pressure of the compound studied, the bulb, vapor generator and manometer were filled with vapor from an outgassed sample of liquid in a small container attached to the ampoule manifold.

The ground joints and stopcocks of the apparatus were lubricated with Apiezon grease L, in which the alcohols studied are insoluble.

Treatment of Data. Accuracy

Weighings were corrected for the buoyancy of the weights and for the change in air density between the two weighings of each ampoule. Pressures were corrected for local gravity, thermal expansion of the mercury and scale, capillary depression, the pressure indicated by the Pirani gage attached to the low pressure arm of the manometer, the residual pressure of vapor indicated by Pirani gage K and the head of vapor and air from the center of the bulb to the lower meniscus in the manometer. Capillary depressions were computed from meniscus heights measured at the time of each pressure determination, using the table of Cawood and Patterson.¹³ For methanol the weight of vapor remaining uncondensed was computed from the residual pressure and added to the observed weight. For ethyl and isopropyl alcohols the residual pressure was so small that a sufficiently accurate correction was obtained by merely subtracting it from the observed pressure. The rate of generation of vapor was always kept so small that the pressure drop, due to its passage through the fractionating column, was negligible.

The volume of the bulb at the temperature and pressure of each measurement was calculated from its measured volume at 35° and 1 atmosphere by assuming a coefficient of cubical expansion of 1.00×10^{-6} per degree¹⁴ and a "stretch" of 1×10^{-4} per atmosphere. This latter figure is based on results for similar bulbs¹⁵ and is sufficiently accurate since the correction for stretch scarcely exceeds the uncertainty with which we could determine the virial coefficients in the most favorable case.

The atomic weight of carbon was taken as 12.011, instead of the presently accepted value of 12.010, since the most recent report¹⁶ of the Commission on Atomic Weights indicates that such a change is likely in the future. The value 1.0080 for hydrogen, recommended in that report, was used. The values¹⁷ 0.0820544 ± 0.0000034 l. atm. deg.⁻¹ mole⁻¹ for the gas constant and $273.160 \pm 0.010^{\circ}$ for the temperature of the ice point were used.

No correction was made for adsorption of vapor on the

(13) W. Cawood and H. S. Patterson, *Trans. Faraday Soc.*, **29**, 514 (1933).

(14) C. B. Kretschmer, *J. Phys. Chem.*, **55**, 1351 (1951).

(15) G. Dietrichson, L. J. Bircher and J. J. O'Brien, *THIS JOURNAL*, **55**, 1 (1933); G. Dietrichson, C. W. Orleman and C. Rubin, *ibid.*, **55**, 14 (1933).

(16) E. Wichers, *ibid.*, **74**, 2447 (1952).

(17) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

wall of the bulb. Emmett¹⁸ found that glass spheres which had been cleaned once with chromic acid had an actual surface some 40% greater than their geometric surface and van Itterbeek and Vereycken¹⁹ obtained close agreement between the geometric surface of glass plates and that found by gas adsorption. Accordingly, we believe that our bulb, which had never been treated with any reagent more powerful than water, possessed an actual surface very little greater than its geometric surface. At half-saturation, which was the upper limit of pressure in our measurements, the adsorbed alcohol layer would have a thickness of less than 6 Å. Coverage of the geometric surface of the bulb with a layer this thick would cause errors in the determination of the virial coefficients, which would be less than those caused by the random errors of the measurements. If the value we have chosen for the atomic weight of carbon is slightly too high, this will partially compensate the effect of adsorption.

The error due to adsorption was studied experimentally by measuring the isotherm of ethanol at 80° in a bulb identical with the one used for the body of the work, except that it was packed with Pyrex tubing to give twice the surface of the empty bulb. The virial coefficients determined in the packed bulb were the same, within the experimental error, as those found when using the empty bulb.

The expected uncertainty of a single determination of $(pV)/(RT)$ was calculated by taking the square root of the sum of squares of the following random errors: 0.01 mm. in the height of each mercury surface in the manometer, 10 micrograms in each of the two weighings, and 0.003° in the temperature. The resulting uncertainty was a little less than 3 parts in 10^5 at 760 mm. It was greater at lower pressures, being approximately inversely proportional to the pressure. The deviations of the individual determinations from the equations fitted to them were often less than, and never more than twice as great as the expected deviations, showing that the measurements were in fact being made with the expected precision.

The number of determinations of vapor density at each temperature varied from 3 to 10, 5 being the usual number. The upper limit of pressure was one atmosphere or half the saturation pressure, whichever was smaller, because adsorption would have started to increase rapidly at some pressure greater than half the saturation pressure. The lowest pressure for each isotherm was about half the maximum. Measurements at still lower pressures would have had such large uncertainties that they would have carried practically no weight in determining the virial coefficients.

Results and Discussion

The equation of state of an imperfect gas may be written

$$V = RT/p + B + Cp + Dp^2 + \dots \quad (1)$$

where B , C and D are the second, third and fourth virial coefficients. Weltner and Pitzer⁵ and Barrow⁶ found that the variation of their heat-capacity results with temperature and pressure required an equation of state of the form

$$V = RT/p + B + Dp^2 \quad (2)$$

having a fourth but no third virial coefficient. We were very reluctant to use this equation rather than the simpler form

$$V = RT/p + B + Cp \quad (3)$$

because it did not seem plausible on the basis of statistical mechanics that the term Dp^2 in equation 1 should be more important than the term Cp , at low pressures. Although equation 2 appeared to fit our data slightly better than equation 3, the precision of our data and the pressure range they covered were not sufficient to distinguish definitely be-

(18) P. H. Emmett in "Advances in Colloid Science," Vol. 1, edited by E. O. Kraemer, Interscience Publishers, Inc., New York, N. Y., 1942, p. 25.

(19) A. van Itterbeek and W. Vereycken, *Z. physik. Chem.*, **B48**, 131 (1941).

tween equations 2 and 3 or to determine more than one other virial coefficient besides the second.

The question was settled with the aid of the extensive vapor heat-capacity measurements of DeVries and co-workers,^{20,21} covering all three of the alcohols studied in the present work. Equations 2 and 3 were fitted to our data, and the resulting expressions were used to calculate $C_p - C_p^0$ according to the relationship

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p \quad (4)$$

It was found that equation 2 gave much better agreement with the experimental heat capacities than equation 3. At the lowest temperatures, equation 3 gave only about half the experimental value of $C_p - C_p^0$.

This comparison involves a form of extrapolation of our p - V - T data, since $(\partial^2 V/\partial T^2)_p$ was evaluated at 750 mm., and our data extend only to a fraction of this pressure at the lower temperatures. Therefore, the calculated values of $C_p - C_p^0$ are sensitive to the form of equation used to express the dependence of vapor volume on pressure.

Figure 2 shows the comparison of observed and calculated heat capacities. The curves are calculated from our p - V - T data using equation 2, and the points are the experimental values of DeVries and co-workers,^{20,21} Weltner and Pitzer⁵ and Barrow.⁶ Values of C_p^0 used in the calculation and plotted in Fig. 2 were taken from Weltner and Pitzer's paper for methanol⁵ and from Barrow's paper for ethanol.⁶ The C_p^0 curve for isopropyl alcohol was calculated from our p - V - T data and Sinke and DeVries' heat capacities.²¹

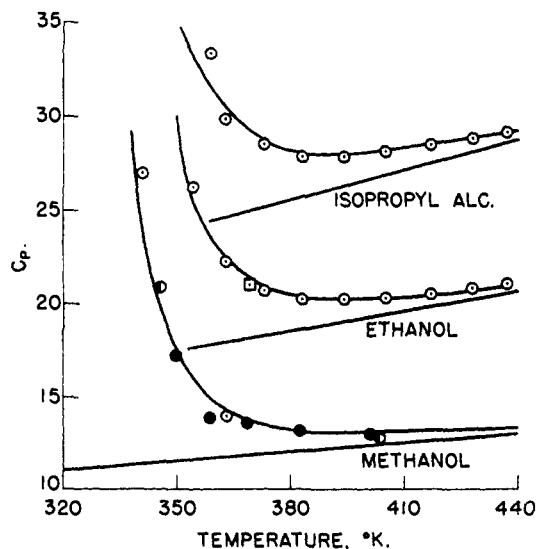


Fig. 2.—Heat capacity of vapor in the ideal gas state and at 750 mm.—calculated from our equations of state with fourth virial coefficient: \circ , experimental values of Sinke and DeVries; \bullet , DeVries and Collins; \circ , Weltner and Pitzer; \square , Barrow.

The agreement between observed and calculated heat capacities at 750 mm. is satisfactory.

- (20) T. DeVries and B. T. Collins, *THIS JOURNAL*, **63**, 1343 (1941).
 (21) G. C. Sinke and T. DeVries, *ibid.*, **75**, 1815 (1953).

The observed values increase more rapidly than the calculated ones as the temperature decreases toward the boiling point. This may mean that higher terms than Dp^2 in the equation of state are beginning to assume significance.

Table I gives the values of B and D in equation 2, which fit our vapor densities. The uncertainty of B is about 5 ml. at 120 and 100°, and increases to about 100 ml. for methanol and ethanol at 40°, and to about 70 ml. for isopropyl alcohol at 60°.

TABLE I
SECOND AND FOURTH VIRIAL COEFFICIENTS IN THE EQUATION $V = RT/p + B + Dp^2$

Temp., °C.	$-B$, ml./mole	$-10^5 D$, ml./mm. ² mole
Methanol		
40	1463	938
60	926	159
80	701	21.2
100	543	4.31
120	433	1.14
Ethanol		
40	2134	2160
60	1285	260
80	938	37.9
100	723	8.00
120	578	2.54
Isopropyl alcohol		
60	1609	329
80	1137	75.8
100	890	12.6
120	721	2.88

The following empirical equations reproduce our values of B and D within their uncertainties

Methanol:

$$B = -100 - 2.148 \exp(1986/T) \quad (5)$$

$$D = -1.445 \times 10^{-17} \exp(10750/T) \quad (6)$$

Ethanol:

$$B = -290 - 0.284 \exp(2730/T) \quad (7)$$

$$D = -1.00 \times 10^{-5} - 7.58 \times 10^{-18} \exp(11144/T) \quad (8)$$

Isopropyl alcohol:

$$B = -300 - 0.755 \exp(2483/T) \quad (9)$$

$$D = 2.70 \times 10^{-5} - 3.16 \times 10^{-16} \exp(9215/T) \quad (10)$$

Eucken and Meyer³ measured the vapor density of methanol at about 760 mm. in the range 80 to 100°. Values of $(RT/p) - V$, calculated from our data for the same concentration, are about 50 ml. higher than theirs at both 80 and 100°. (The uncertainty in our values is about 5 ml. at 80° and 2 ml. at 100°.) Lambert and co-workers⁴ reported second virial coefficients for methanol, which are several hundred ml. more negative than ours, but they did not take account of any higher virial coefficients than the second.

Our values of $-B$ for methanol are somewhat larger than those of Weltner and Pitzer,⁵ and our values of $-D$ are somewhat smaller than theirs. Values of $(RT/p) - V$ calculated from their equations are in substantial agreement with our measured values at the highest pressure at which we measured the vapor density at each temperature. The agreement is within 100 ml. at all tempera-

tures. (The uncertainty in our measurements ranges from 2 ml. at 120° and 100° to 30 ml. at 40°.) Barrow's⁸ equations for ethanol give values of $(RT/p) - V$ which are within 200 ml. of our observed values at the highest pressures reached by our measurements.

Flock, Ginnings and Holton²² used their accurate measurements of the heat of vaporization of methanol and ethanol, together with the vapor pressures of Ramsay and Young, to calculate the volume of the saturated vapors by means of the Clausius-Clapeyron relationship. In Fig. 3 the values they calculated in this way (open circles) are compared with values calculated from our equations of state (curves). The agreement is satisfactory, since the comparison requires the extrapolation of our data to the saturation pressure, which is 2 to 6 times the highest pressure at which we measured the vapor density. Better agreement might be obtained with more modern vapor pressure data, but no single set of measurements covering the temperature range from 40 to 120° is available for either alcohol. The filled circles in Fig. 3 represent volumes calculated with the aid of a vapor-pressure equation published by us²³ for ethanol, which extends only to the normal boiling point.

The unusual form of equation of state (equation 2) required for these alcohols may be made more plausible by the following argument. Woolley²⁴ has shown that an imperfect gas may be treated as a perfect gas mixture of single, double, triple, etc., molecules, the interactions being fully accounted for by considering any two interacting molecules to constitute a cluster or part of one. The equation of state is then

$$\begin{aligned} (pV)/(RT) = 1 - K_2p + (3K_2^2 - 2K_3)p^2 \\ + (12K_2K_3 - 10K_2^3 - 3K_4)p^3 + \dots \quad (11) \end{aligned}$$

where K_1 is the equilibrium constant (in terms of partial pressures) for the formation of a cluster of i molecules from single molecules. If K_3 were approximately equal to $1.5K_2^2$, which is not unlikely, then the term Cp in equation 1 would be small in comparison with Dp^2 , and the equation of state would have the form of equation 2.

On comparing equation 2 with equation 11, we find

$$-B = K_2RT \quad (12)$$

(22) E. F. Flock, D. C. Ginnings and W. B. Holton, *J. Research Natl. Bur. Standards*, **6**, 881 (1931).

(23) C. B. Kretschmer and R. Wiebe, *THIS JOURNAL*, **71**, 1793 (1949).

(24) H. W. Woolley, *J. Chem. Phys.*, **21**, 236 (1953).

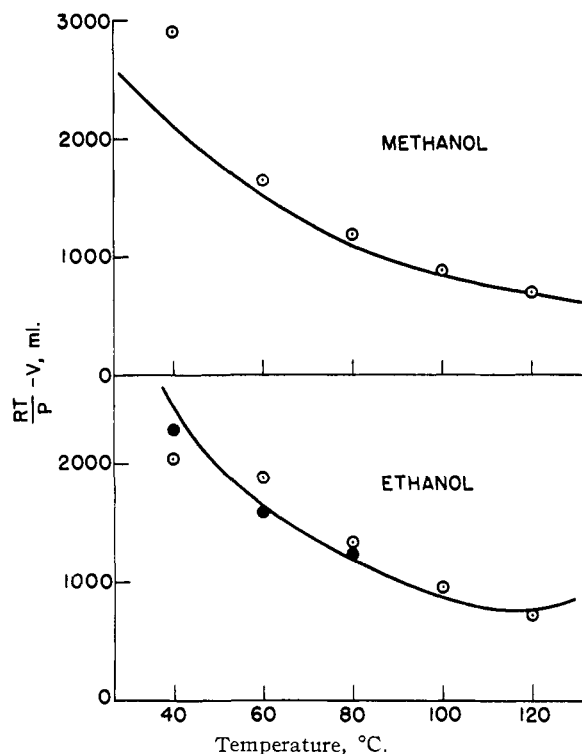


Fig. 3.—Saturated vapor volumes—calculated from our equations of state with fourth virial coefficient: \circ , calculated from heats of vaporization of Flock, Ginnings and Holton and vapor pressures of Ramsay and Young; \bullet , calculated from above heats of vaporization and our vapor pressures.

and, for the values of B and D in Table I

$$-D = 3K_4RT \quad (13)$$

to within a few per cent. By combining these equations with equations 6 to 10 one obtains equations for K_2 and K_4 which can be differentiated to give values of $-\Delta H$, the heat of formation of dimers and tetramers from single molecules. At 100°, the heats of formation of dimers of all three alcohols are very close to 4000 cal./mole, and the heats of formation of the tetramers are 22,100 cal./mole for methanol, 20,100 cal./mole for ethanol, and 22,600 cal./mole for isopropyl alcohol. These values correspond to 5030 to 5650 cal./mole for the heat of formation of a hydrogen bond, if the tetramers are assumed to contain four hydrogen bonds. This is in fairly satisfactory agreement with the value of 4000 cal./mole found for the dimers.

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