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The compressibility of gaseous ethane (C_2H_6) has been determined from 0.5 to 5.0 moles per liter and from 25° to 250°C with an estimated accuracy of 0.2 percent or better. Above 250°C ethane decomposes at an appreciable rate when confined in steel. An equation of state is fitted to the data. The average deviation of the calculated from the observed pressure is 0.13 atmosphere or 0.21 percent. The equation of state extrapolates to the critical pressure (at 7 moles/liter and 32.1°C) with an error of 10 percent and calculates the weight of a normal liter to 0.2 percent. The vapor pressures of liquid ethane at 0° and 25°C are given.

THE compressibility of the hydrocarbons is of practical as well as theoretical interest. The only hydrocarbon for which extensive modern compressibility data are available is methane, which has been investigated by Keyes and Burks.[1] We have studied the compressibility of gaseous ethane from 25° to 250°C and from 0.5 to 5.0 moles per liter.

The apparatus and the method of procedure have been described in detail elsewhere.[2] A weighed quantity of ethane (approximately 3 grams or 0.1 mole) was confined in a chrome-vanadium steel bomb (of 200 cc volume) which was placed in a thermostat regulated to ±0.001°C, the temperature being measured with a platinum resistance thermometer. The density of the gas was varied and measured by the introduction or removal of known volumes of mercury from a calibrated mercury injector thermostated at 30°C. Pressures were measured on a dead-weight piston gauge. The effect of the temperature of the bomb and of pressure on the volume measuring system was determined experimentally in a blank run in which there was no ethane in the bomb.

The pressures were measured along isometrics as well as along isotherms. At each temperature the method of procedure was to work from the smallest to the greatest gas density and then to check the pressure at the smallest density. At 275° it was found that the pressure had decreased during the course of the measurements, and the

pressure corresponding to a given density decreased slowly but steadily with time. Remeasurement of the vapor pressure at 25°C showed an increase in pressure over the previously determined value and also an increase in pressure with decreasing vapor space in the bomb, but no appreciable change with time. This indicates that at about 275° in steel, ethane cracks to give, as one product, hydrogen which rather rapidly diffuses through the walls of the bomb at this temperature. When the bomb was opened, a thin film of an oily tar was found on the inner walls.

Temperatures are given on the international platinum resistance thermometer scale. The strain-free mica-cross platinum resistance thermometer was calibrated at the ice-point (0°), the steam point (100°) and the sulfur boiling point (444.6°) at the beginning and at the end of the measurements. Special hypsometers, which permit very exact calibration at a constant pressure of one normal atmosphere, were used. The maximum difference between temperatures computed from the two calibrations was 0.001°, this maximum occurring at 250°C. Each day the ice-point of the thermometer was determined and correction made for the variation, which amounted at most to 0.002°C during the course of the investigation. The precision of the determination of temperature with one platinum resistance thermometer is about 0.002°C, but the uncertainty of the readings of a single thermometer relative to the international platinum resistance scale increases above 100°C to about 0.01° to 0.02°C at 250°C.

Pressures are given in normal atmospheres. The pressure gauge was calibrated at the vapor

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[1] F. G. Keyes and H. G. Burks, J. Am. Chem. Soc. **49**, 1403 (1927).
[2] J. A. Beattie, Proc. Am. Acad. Arts and Sci. **69**, 389 (1934).

TABLE I. *Values of the constants of the Beattie-Bridgeman equation of state for gaseous ethane (C_2H_6).*

$$p = [RT(1-\epsilon)/V^2][V+B] - A/V^2$$

$$A = A_0(1-a/V) \qquad\qquad B = B_0(1-b/V) \qquad\qquad \epsilon = c/VT^3$$

R	A_0	a	B_0	b	c	Mol.wt.
		Units: normal atmospheres, liters per mole, °K ($T°K = t°C + 273.13$).				
0.08206	5.8800	0.05861	0.09400	0.01915	90.00×10^4	30.0462
		Amagat units: normal atmospheres, $V=1$ at 0°C and 1 atm., °K				
3.69658×10^{-3}	11.9320×10^{-3}	2.6402×10^{-3}	4.2344×10^{-3}	0.8627×10^{-3}	40.543×10^3	30.0462
		Berlin units: meters of mercury, $V=1$ at 0°C and 1 meter of mercury, °K				
3.70799×10^{-3}	15.7971×10^{-3}	3.4847×10^{-3}	5.5888×10^{-3}	1.1386×10^{-3}	53.510×10^3	30.0462

TABLE II. *Comparison of the pressures calculated from the equation of state with the observed pressures for gaseous ethane.* For each temperature the first line gives the observed pressure and the second line gives the observed minus the calculated pressure. The equation used for the calculated pressures is given in Table I.

Density, moles/liter Temp., °C		0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
						Pressures, normal atmospheres					
25	obs.	11.11	20.14	27.34	32.84	36.88	39.66	41.35			
	obs.-calc.	−0.05	−0.14	−0.19	−0.25	−0.25	−0.16	±0.00			
50	obs.	12.24	22.58	31.24	38.41	44.27	49.02	52.87	55.97	58.49	60.56
	obs.-calc.	−0.02	−0.07	−0.11	−0.11	−0.08	±0.00	+0.15	+0.35	+0.57	+0.75
75	obs.	13.34	24.95	35.08	43.80	51.37	57.98	63.78	68.89	73.52	77.79
	obs.-calc.	−0.02	−0.05	−0.01	−0.02	±0.00	+0.05	+0.11	+0.10	+0.05	−0.12
100	obs.	14.43	27.28	38.79	49.03	58.29	66.68	74.36	81.50	88.25	94.73
	obs.-calc.	−0.03	−0.05	±0.00	−0.01	+0.04	+0.06	+0.05	−0.04	−0.24	−0.61
125	obs.	15.52	29.64	42.49	54.25	65.13	75.26	84.81	93.91	102.73	111.46
	obs.-calc.	−0.03	±0.00	+0.03	+0.06	+0.11	+0.12	+0.08	−0.08	−0.37	−0.80
150	obs.	16.60	31.89	46.08	59.31	71.78	83.61	94.99	106.06	117.00	127.98
	obs.-calc.	−0.03	−0.05	−0.01	+0.02	+0.07	+0.07	+0.02	−0.13	−0.40	−0.80
175	obs.	17.67	34.17	49.66	64.36	78.40	91.93	105.13	118.16	131.20	144.41
	obs.-calc.	−0.05	−0.06	−0.05	+0.02	+0.07	+0.09	+0.06	−0.05	−0.26	−0.58
200	obs.	18.71	36.44	53.25	69.38	84.97	100.19	115.20	130.18	145.30	160.77
	obs.-calc.	−0.09	−0.07	−0.05	+0.01	+0.08	+0.13	+0.14	+0.09	−0.02	−0.18
225	obs.	19.80	38.64	56.73	74.27	91.38	108.24	125.02	141.90	159.08	176.73
	obs.-calc.	−0.09	−0.15	−0.15	−0.10	−0.04	+0.02	+0.06	+0.06	+0.05	+0.01
250	obs.	20.89	40.87	60.23	79.16	97.81	116.30	134.84	153.59	172.87	192.77
	obs.-calc.	−0.08	−0.19	−0.22	−0.18	−0.09	−0.03	+0.05	+0.10	+0.26	+0.44
Average deviation (atm.)		0.049	0.083	0.082	0.078	0.083	0.073	0.072	0.111	0.247	0.477
Average % deviation		0.293	0.276	0.198	0.166	0.151	0.110	0.090	0.140	0.267	0.459

Total average deviation (atm.), 0.131; total average % deviation, 0.213

pressure of liquid carbon dioxide at 0°C for which the value 34.401 normal atmospheres[3] is used. The gauge was recalibrated after the completion of the measurements and showed the normal increase in gauge constant (normal mm of mercury per gram load) with time (0.01 percent per year), for which correction was made. The uncertainty in the determination of pressure is less than 0.05 percent.

Gas volumes at each temperature are expressed in liters per mole and are referred to the specific volume of liquid mercury at the temperature in question and 1 atmosphere. The density of mercury at 0°C was taken to be 13.5955 grams per milliliter and the effect of temperature on the volume of mercury at 1 atmosphere was obtained from the equation given in *International Critical Tables*.[4] At 0.5 mole per liter gas density, the gas

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[3] O. C. Bridgeman, J. Am. Chem. Soc. **49**, 1174 (1927).

[4] *International Critical Tables*, Vol. II, p. 457. McGraw-Hill Book Co. Inc., New York, 1927.

volume in the bomb was about 200 cc; at 5.0 moles per liter it was 20 cc. The mercury compressor can be calibrated to ±0.004 cc at one atmosphere pressure and the uncertainties of the corrections applied for the effect of pressure and temperature on the volume measuring system are about 0.02 cc. Yet the errors in the measurement of volume are larger than these figures indicate, being about 0.1 percent. At each measurement we waited from 1 to 2 hours for equilibrium and usually no change in pressure was observed after the first half hour.

The mass of ethane was determined by weighing in a stainless steel bomb against an almost identical counterpoise. Proper air-buoyancy corrections were made. The accuracy of the determination of mass was 0.01 percent.

The final tabulated pressures are believed to have an accuracy of 0.2 percent or better.

The ethane was obtained from the Linde Air Products Research Laboratory, and guaranteed to be at least 99.9 percent pure. In order to remove any non-condensible gas which might have been present, it was distilled by us three times from one bulb to another by use of liquid air, the first and last portions being discarded. After each distillation the ethane was frozen, and pumped by means of a mercury diffusion pump. It was then loaded into the weighing bottle, weighed, and transferred to the compressibility bomb. That the ethane was of extraordinary purity was indicated by the fact that at 0° the vapor pressure of the liquid remained constant within our experimental error (0.001 atmosphere for relative measurements at constant temperature) while the vapor volume was decreased from 20 to 5 cc; and at 25° the vapor pressure remained constant within the experimental error while the vapor volume was decreased from 40 to 5 cc.

The constants of the Beattie-Bridgeman equation of state[5] were determined from the data. They are given in Table I. In Table II are given the observed pressures and the deviation of the pressures calculated from the equation of state from the observed values. The average deviation is 0.13 atmosphere or 0.21 percent. Although the equation of state gives quite a satisfactory representation of our data, there is one trend in the

[5] J. A. Beattie and O. C. Bridgeman, Proc. Am. Acad. Arts and Sci. **63**, 229 (1928).

data that is not reproduced by the equation. The equation requires that the curvature of the isometrics at any temperature increase (numerically) with density. The curvature of the experimental isometrics first increase with increasing density (to about 3.5 moles per liter) and then begin to decrease. In other words the constant c of the equation of state should slowly decrease with increasing density in order that the equation represent this trend in the ethane data.

VAPOR PRESSURES

In the course of our investigation we measured the vapor pressure of liquid ethane at two temperatures. The results are given in Table III.

TABLE III. *Vapor pressure of liquid ethane.*

Temp. °C	Vapor pressure, normal atmospheres	
	Our values	I.C.T.[6]
0	23.57	23.56
25	41.37	41.5

WEIGHT OF A NORMAL LITER

In Table IV are given the value of the weight

TABLE IV. *Weight of a liter of ethane at 0°C and 1 normal atmosphere.*

Calculated from the equation of state	1.3535 grams
I.C.T.[7]	1.3566 grams

of a liter of ethane at 0°C and 1 normal atmosphere calculated from the equation of state, and the observed value. This is not a satisfactory agreement; the difference may be due to the equation which in general gives a low value for the weight of a normal liter for compressible gases (for the gases so far studied the deviation is smaller than in the case of ethane); or to the purity of the ethane used in the measured weights of a normal liter, the suspected impurity (CO_2) giving a high value.

CALCULATION OF THE CRITICAL PRESSURE

The critical data for ethane[8] are given as 48.8 atmospheres, 0.21 gram per cc (7 moles/liter), and 32.1°C, the critical density being uncertain.

[6] *International Critical Tables*, Vol. III, p. 230.
[7] *International Critical Tables*, Vol. III, p. 3.
[8] *International Critical Tables*, Vol. III, p. 248.

If we substitute the critical temperature and density into the equation of state, we calculate 44.3 atmospheres for the critical pressure, 10 percent lower than the observed value. This should not be considered a bad disagreement since it involves an extrapolation of 40 percent from our highest measured density. It should be pointed out that temperature extrapolations are in general fairly safe but density extrapolations are dangerous. This effect is one that is true of equations of state in general and it is also true of the experimental data. Since the isometrics are so nearly linear, the experimental data can safely be extrapolated over quite a temperature range; but in the region near the critical, the isotherms, no matter what variables are plotted, are too curved to permit extrapolation. That is, from the data in the range 0.5 to 5.0 moles per liter, we cannot predict the data in the region of 7 moles per liter.

The Critical Constants of Propane

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The critical constants of propane (C_3H_8) are: $t_c = 96.81 \pm 0.01°C$, $p_c = 42.01 \pm 0.02$ normal atmospheres, $v_c = 0.195$ liter per mole (4.43 cc per gram), $d_c = 5.13$ moles per liter (0.226 gram per cc). The uncertainty in the critical volume and density is 1 percent.

IN the course of our measurements of the compressibility of gaseous propane,[1] we investigated a number of isotherms in the critical region and located the critical point. The method used was the same as that employed in the measurements of the compressibility of propane and of ethane,[2] and has been described elsewhere.[3]

Pressures are given in normal atmospheres; temperatures in degrees centigrade on the international platinum resistance scale, and volumes in liters per mole. In the region of the critical point of propane the uncertainties in the measurement of pressure do not exceed 0.03 percent; those in the location of temperature do not exceed 0.005°C; and those in the measurement of volume do not exceed 0.05 percent.

In the determination of the critical data, the purity of the substance is of primary importance.

The propane was obtained from the Research Laboratories of the Linde Air Products Company at Buffalo and was stated by Doctor L. I. Dana to be 99.9 percent pure or better. That the propane was of extreme purity is indicated by the measurements of vapor pressure at 50° and 75°C given in Table I. It will be noticed that at 50°C

TABLE I. *The effect of varying the vapor volume on the vapor pressure of propane at 50° and 75°C.*

50°C		75°C	
Vapor volume cc	Vapor pressure normal atm.	Vapor volume cc	Vapor pressure normal atm.
93	16.897	50	28.112
62	16.899	35	28.113
46	16.898	26	28.113
37	16.898	15	28.113
31	16.898	11	28.113
26	16.897	9	28.113
23	16.897	7	28.112
20	16.898		
18	16.898		
0.15	16.901		

the vapor pressure remained constant within the accuracy of our measurements (± 0.001 atmos-

* Contribution No. 339.
[1] J. A. Beattie, N. Poffenberger and C. Hadlock, to be published shortly.
[2] J. A. Beattie, C. Hadlock and N. Poffenberger, J. Chem. Phys. **3**, 93 (1935).
[3] J. A. Beattie, Proc. Am. Acad. Arts and Sci. **69**, 389 (1934).