

Substitution of the critical temperature (267.01°) and volume (0.416 liter per mole) into the equation gives a calculated pressure of 28.75 atm. The observed pressure is 27.00 atm.; and the error of extrapolation from 2 to 2.40 moles per liter is 6.5%.

### Summary

Measurements are reported on the compressi-

bility of liquid normal heptane over the temperature range from 30 to 250° and to 350 atmospheres, and on the compressibility of the gas phase from 275 to 350° and from a density of 1.0 to 5.0 moles per liter.

The constants of an equation of state for the gas phase are determined from the data for densities less than the critical.

CAMBRIDGE, MASS.

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## The Compressibility of and an Equation of State for Gaseous Propane

BY JAMES A. BEATTIE, WILLIAM C. KAY AND JOSEPH KAMINSKY

The critical constants and the compressibilities of liquid and gaseous propane from 70 to 220°K. and to 200 atmospheres have been studied by Sage, Schaafsma and Lacey.<sup>1</sup> They obtain for the values of the critical constants:  $t_c = 100.1^\circ\text{C}$ .,  $p_c = 43.77$  atm.,  $v_c = 4.31$  cc. per gram. The critical constants determined in our apparatus are:<sup>2</sup>  $t_c = 96.81 \pm 0.01^\circ\text{C}$ . (Int.),  $p_c = 42.01 \pm 0.02$  normal atm.,  $v_c = 4.43$  cc. per gram (uncertainty in  $v_c$  is 1%). The agreement especially in the location of the critical temperature is not good.

regions of propane<sup>2</sup> and heptane.<sup>5</sup> The apparatus has been described elsewhere.<sup>6</sup>

The propane was obtained from the Research Laboratories of the Linde Air Products Company at Buffalo and was of exceptional purity.<sup>2</sup>

Two complete sets of runs were made. In the first run the bomb was used immediately after the study of the compressibility of ethane. The bomb was heated to 400° and evacuated for one week. When the measurements were made, decomposition of the propane began at 200°. The

TABLE I

VALUES OF THE CONSTANTS OF THE BEATTIE-BRIDGEMAN EQUATION OF STATE FOR PROPANE (C<sub>3</sub>H<sub>8</sub>)

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

R	$A = A_0(1 - a/v)$ $A_0$	$a$	$B = B_0(1 - b/v)$ $B_0$	$b$	$\epsilon = c/VT^3$ $c$	Mol. wt.
	Units: normal atmospheres, liters per mole, °K. ( $T^\circ\text{K.} = t^\circ\text{C.} + 273.13$ ).					
0.08206	11.9200	0.07321	0.18100	0.04293	$120 \times 10^4$	44.0616
	Amagat units: normal atmospheres, $V = 1$ at 0°C. and 1 atm., °K.					
$3.73059 \times 10^{-3}$	$24.6359 \times 10^{-3}$	$3.3283 \times 10^{-3}$	$8.2286 \times 10^{-3}$	$1.9517 \times 10^{-3}$	$54.554 \times 10^3$	44.0616
	Berlin units: meters of mercury, $V = 1$ at 0°C. and 1 meter of mercury, °K.					
$3.75354 \times 10^{-3}$	$32.8158 \times 10^{-3}$	$4.4062 \times 10^{-3}$	$10.8937 \times 10^{-3}$	$2.5838 \times 10^{-3}$	$72.223 \times 10^3$	44.0616

We have measured the compressibility of gaseous propane over the temperature range 96.81 to 275°C. and the density range 1 to 10 moles per liter. Our data barely overlap those of Sage, Schaafsma and Lacey. We used the same method employed in studying the compressibilities of ethane<sup>3</sup> and normal heptane,<sup>4</sup> and the critical

measurements were discontinued and the bomb taken apart and all carbon thoroughly removed by means of fine emery paper. The series of measurements reported in the present paper was then made. No perceptible decomposition took place at 250° during a period of six hours, and the decomposition at 275° during a period of six hours was sufficient to affect the pressure at the lower density (41 atm.) by 0.015 atm. The pressures of run one were lower than those of run two by 0.02% at the critical temperature and at 100°,

(1) B. H. Sage, J. G. Schaafsma, and W. N. Lacey, *Ind. Eng. Chem.*, **26**, 1218 (1934).

(2) J. A. Beattie, N. Poffenberger, and C. Hadlock, *J. Chem. Phys.*, **3**, 96 (1935).

(3) J. A. Beattie, C. Hadlock, and N. Poffenberger, *ibid.*, **3**, 93 (1935).

(4) L. B. Smith, J. A. Beattie, and W. C. Kay, *THIS JOURNAL*, **59**, 1587 (1937).

(5) J. A. Beattie and W. C. Kay, *ibid.*, **59**, 1586 (1937).

(6) J. A. Beattie, *Proc. Am. Acad. Arts Sci.*, **69**, 389 (1934).

TABLE II

COMPARISON OF THE PRESSURES CALCULATED FROM THE EQUATION OF STATE WITH THE OBSERVED PRESSURES FOR GASEOUS PROPANE ( $C_3H_8$ )

For each temperature the first line gives the observed pressure and the second line the observed minus the calculated pressure. The calculated pressures are computed from the equation given in Table I. The critical constants of propane are:  $t_c = 96.81^\circ$  (Int.);  $p_c = 42.01$  normal atmospheres;  $d_c = 5.13$  moles per liter, and  $v_c = 0.195$  liter per mole.<sup>2</sup>

Density, moles/liter	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5	6	7	8	9	10
Temp., °C. (Int.)	Pressure, normal atmospheres.													
96.81 obsd.	23.35	30.68	35.82		40.76		41.93		42.04	42.15	44.14	54.86	88.89	171.09
obsd.-calcd.	-0.38	-0.52	-0.46		-0.14		+0.97		+2.06					
100 obsd.	23.77	31.30	36.56	40.05	42.15	43.31	43.92	44.24	44.46	45.16	48.27	60.70	96.84	181.42
obsd.-calcd.	-0.28	-0.42	-0.48	-0.35	-0.07	+0.39	+0.97	+1.50	+1.72					
125 obsd.	26.42	35.64	42.79	48.30	52.59	56.01	58.87	61.49	64.11	70.72	82.73	108.04	162.47	270.12
obsd.-calcd.	-0.13	-0.19	-0.17	-0.05	+0.17	+0.42	+0.59	+0.57	+0.14					
150 obsd.	28.97	39.79	48.74	56.23	62.60	68.24	73.47	78.61	84.02	97.39	118.62	156.94	228.77	
obsd.-calcd.	-0.08	-0.10	-0.06	+0.05	+0.17	+0.26	+0.24	±0.00	-0.54					
175 obsd.	31.47	43.86	54.57	63.97	72.42	80.30	87.95	95.73	104.06	124.52	155.19	206.31	294.77	
obsd.-calcd.	-0.05	-0.05	-0.01	+0.07	+0.13	+0.15	+0.07	-0.18	-0.60					
200 obsd.	33.95	47.87	60.28	71.57	82.38	92.21	102.30	112.79	124.12	151.85	192.28	256.10		
obsd.-calcd.	-0.04	-0.05	-0.03	+0.02	+0.35	+0.07	±0.00	-0.11	-0.25					
225 obsd.	36.41	51.83	65.94	79.08	91.66	104.02	116.58	129.79	143.21	179.24	229.08	305.78		
obsd.-calcd.	-0.04	-0.07	-0.06	-0.04	±0.00	+0.02	+0.05	+0.14	-0.55					
250 obsd.	38.77	55.63	71.53	86.53	101.14	115.74	130.79	146.75	163.19	206.67	266.06			
obsd.-calcd.	-0.13	-0.23	-0.12	-0.12	-0.08	±0.00	+0.19	+0.56	+0.30					
275 obsd.	41.23	59.64	77.08	93.91	110.54	127.38	145.02	163.64	184.25	234.08	303.03			
obsd.-calcd.	-0.11	-0.17	-0.20	-0.22	-0.17	-0.01	+0.47	+1.08	+2.44					
Average deviation, atm.	0.138	0.200	0.177	0.115	0.142	0.165	0.394	0.518	0.956					
Average % deviation	0.509	0.540	0.411	0.204	0.214	0.291	0.717	0.719	1.366					
	Total average deviation, 0.313 atm.; Total average % deviation, 0.558.													

0.2% at 125°, 0.3% at 150°, and 0.4% at 175°. The differences did not depend on density but on temperature alone. Only the data of run two are reported.

### Results

The compressibility data are given in Table II. The constants of the Beattie-Bridgeman equation of state were determined from the data below the critical density and the constants for propane are given in Table I. The comparison of the pressures computed from the equation with the ob-

served pressures is given in Table II. The agreement is fair.

### Summary

Measurements are reported on the compressibility of gaseous propane over the temperature range 96.81 to 275° and from a density of 1.0 to 10.0 moles per liter.

The values of the constants of an equation of state are determined from the data for densities less than the critical.

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## The Electric Moments of Some Dioxanes and Dioxolanes

By M. M. OTTO

In a previous article<sup>1</sup> moments were determined for compounds containing two oxygen atoms attached to one carbon atom. The other valence bonds of the oxygens were satisfied with aliphatic groups, each of which was independent of the other. It should be interesting to find the effect of combining the two oxygen atoms with a carbon group to form a ring compound. Such substances as the dioxanes and dioxolanes would fulfil the

requirement and therefore moments were determined for these compounds.

**Preparation of Compounds and Apparatus.**—The 2,2-dimethyl-1,3-dioxolane was made from acetone and ethylene glycol<sup>2</sup> using *p*-toluenesulfonic acid as a catalyst. The 2-bromomethyl-1,3-dioxolane and 2-bromomethyl-1,3-dioxane were prepared<sup>3</sup> from bromoacetaldehyde and ethylene

(1) Otto, *THIS JOURNAL*, **57**, 693 (1935).

(2) R. Leutner, *Monatsh.*, **60**, 317 (1932).

(3) Hill, *THIS JOURNAL*, **50**, 2729 (1928).