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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 equa-

tions 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.

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The Critical Constants of Propane

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The critical constants of propane (C_3H_8) are: $t_c = 96.81 \pm 0.01^\circ C$, $p_c = 42.01 \pm 0.02$ 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 $0.005^\circ C$; 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 $75^\circ C$ given in Table I. It will be noticed that at $50^\circ C$

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

$50^\circ C$		$75^\circ C$	
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		

* 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).

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

TABLE II. Isotherms of propane (C_3H_8) in the critical region.

Temp., °C	Volume Density moles/liter	96.00	96.70	96.80	96.81	96.82	96.90	97.00	97.10	97.20
Pressure, normal atmospheres										
4.201	0.2380		41.9030	41.9660			42.0360	42.0995	42.1695	42.2335
4.341	.2304		41.9175							
4.490	.2227	41.3975	41.9280	41.9940			42.0675	42.1360	42.2060	42.2775
4.651	.2150		41.9300	41.9990	42.0075	42.0145	42.0730	42.1445	42.2150	42.2895
4.823	.2073		41.9295	42.0020	42.0095	42.0175	42.0765	42.1515	42.2245	42.3010
4.895	.2043			42.0030	42.0110	42.0190		42.1525	42.2280	42.3040
4.970	.2012			42.0045	42.0115	42.0195		42.1560		
5.008	.1997		41.9300				42.0800		42.2320	42.3090
5.047	.1981			42.0030	42.0120	42.0205		42.1580		
5.126	.1951			42.0040	42.0130*	42.0220		42.1595	42.2370	42.3150
5.208	.1920		41.9290	42.0045	42.0135	42.0235	42.0855	42.1620	42.2400	42.3190
5.293	.1889			42.0060	42.0155	42.0240		42.1655		
5.380	.1859			42.0075	42.0190	42.0260				
5.425	.1843		41.9305				42.0920	42.1725	42.2535	42.3345
5.471	.1828		41.9310	42.0120	42.0215	42.0295				
5.564	.1797		41.9355	42.0200	42.0290	42.0365				
5.661	.1766	41.3965	41.9425	42.0290			42.1105	42.1960	42.2810	42.3640
5.918	.1690	41.3970	41.9865	42.0785			42.1675	42.2575		

* Critical Point

phered) when the vapor volume was decreased from 93 to 18 cc; and that the vapor pressure increased 0.002 to 0.003 atmosphere when the vapor volume was further decreased to 0.15 cc. That is, during a 600-fold decrease in the vapor volume the increase in vapor pressure was practically within our experimental error. At 75°C the vapor pressure remained constant while the vapor volume was decreased from 50 to 7 cc.

In Table II are given the compressibility data on propane in the critical region, the isotherms between 96.7 and 96.9 being plotted in Fig. 1. The pressures are given to 0.0005 atmosphere since relative values are consistent to about 0.001 atmosphere. In the two phase region the densities listed are the average densities of the whole system.

From Fig. 1 it is evident that the critical temperature is $96.81 \pm 0.01^\circ\text{C}$ and the critical pressure 42.01 ± 0.02 normal atmospheres. The determination of the critical density cannot be made with so great an accuracy as those of temperature and pressure. The top of the "steam dome" and the inflection point with horizontal tangent of the 96.81°C isotherm agree quite well for a criti-

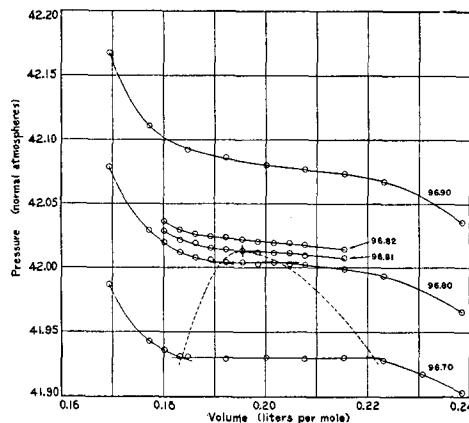


FIG. 1. Isotherms of propane in the critical region. The radius of each circle is 0.002 atmosphere.

cal volume of 0.195 liter per mole or a critical density of 5.13 moles per liter. The critical volume seems to have been located to ± 1 percent. *International Critical Tables*⁴ gives $t_c = 95.6^\circ\text{C}$, $p_c = 43$ atmospheres.

⁴ *International Critical Tables*, Vol. III, p. 248. McGraw-Hill Book Co. Inc., New York, 1928.