Pressure-Volume-Temperature Properties of Propyne

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EXPERIMENTAL pressure-volume-temperature data for propyne in the temperature range of 50° to 200° C. and pressure range of 6 to 315 atm. were measured using a Beattie-type apparatus. Critical constants were also determined. Vapor pressures and orthobaric densities from 50° C. to the critical temperature were measured, smoothed, and correlated. Because of the polymerization of propyne at higher temperatures, P-V-T properties could not be measured for temperatures higher than 200° C.

EXPERIMENTAL

Purity. The propyne was supplied by the Air Reduction Chemical Co., with the specification of 98.65% purity. The initial purification by superfractionation yielded a product of 99.9+ mole % purity. Further purification was made as suggested by Vohra and Kobe (9). From the results of mass-spectrograph and freezing point analysis, propyne so obtained was almost 100% pure (at least greater than 99.99+%).

Method and Apparatus. The apparatus used for the measurements of P-V-T properties is similar to the one designed and used by Beattie (1). A detailed description

¹Present address, Research Center, The B.F. Goodrich Co., Brecksville, Ohio. ²Deceased. of the design, construction, and calibration of the apparatus, as well as the experimental procedures and the data treatment have been given (8).

Reproducibility of Data. In selecting the sample sizes, care was taken to allow enough overlap in the volume ranges covered by different samples. The compressibility data in these regions were internally consistent and reproducible with 0.2% of uncertainty. However, at 200° C., evidence of slight polymerization was observed. Data at this temperature were estimated to have an uncertainty of 0.5%. The evidences and the estimation of this uncertainty are discussed elsewhere (8).

The maximum variation of 0.008 atm. was observed in vapor pressures obtained from the different samples at 50° C. Because of the difficulty in obtaining thermal equilibrium in the apparatus at low temperatures and the insensitivity of the dead-weight gage at low pressures, this figure was a little higher than the actual reproducibility of vapor pressure measurement, which was ± 0.003 atm.

Experimental Data. P-V-T measurements were made from 6 atm. to either the vapor pressure at the prevailing temperature or the maximum pressure of 315 atm. at 50°, 75°, 100°, 125°, 129.25°, 150°, 175°, and 200° C. Additional data included several gas-phase isotherms at 135°, 140°, and 145° C., as well as a few points near the saturation curve at 90°, 95°, 105°, 110°, and 120° C. The experimental compressibility factor data for gaseous propyne are presented in Table I and shown in Figure 1. Isotherms investigated



Figure 1. Compressibility factors of propyne

Table 1. Experimental Compressibility Data for Gaseous Propyne

t	V	р	Ζ	t	V	р	Ζ	t	V	р	Ζ
	Mass of Sam	ple = 0.4994	G.								
50	$\begin{array}{c} 84.373\\79.007\\73.444\\68.764\\64.038\\59.938\\56.195\\50.505\end{array}$	7.052 7.478 7.978 8.441 8.969 9.482 10.000 10.843	0.8990 0.9826 0.8852 0.8770 0.8677 0.8586 0.8490 0.8274	150	$\begin{array}{r} 48.798\\ 44.675\\ 41.616\\ 37.114\\ 33.214\\ 30.120\\ 27.241\\ 24.635\end{array}$	$16.157 \\ 17.498 \\ 18.649 \\ 20.628 \\ 22.716 \\ 24.683 \\ 26.859 \\ 29.174$	$\begin{array}{c} 0.9097\\ 0.9020\\ 0.8954\\ 0.8833\\ 0.8705\\ 0.8578\\ 0.8442\\ 0.8292 \end{array}$	110 115 120	11.335 11.161 11.053 10.942 9.8208 9.6725 8.395	39.218 39.416 39.554 39.609 42.927 43.107 46.886	0.5664 0.5606 0.5571 0.5523 0.5297 0.5239 0.4888
75	84.341	7.745	0.9161		22.138 20.594	$31.746 \\ 33.624$	0.8109 0.7990		Mass of San	nple = 2.36	55 G.
	74.033 69.385 65.145 61.477 56.184 42.871 39.826 37.444 35.882 22.384	8.714 9.232 9.763 10.274 11.103 13.933 14.787 15.523 16.045 16.045	$\begin{array}{c} 0.9047\\ 0.8983\\ 0.8919\\ 0.8857\\ 0.8748\\ 0.8376\\ 0.8258\\ 0.8151\\ 0.8074\\ 0.7000\end{array}$	175	18.276 15.724 13.751 12.048 10.663 9.2106 8.1019 84.413	36.782 41.070 45.006 48.976 52.679 56.923 60.578 9.725	0.7756 0.7451 0.7141 0.6808 0.6481 0.6049 0.5663 0.9471 ^a	90	$19.156 \\ 19.002 \\ 19.466 \\ 19.311 \\ 18.847 \\ 18.692 \\ 18.538 \\ 18.383 \\ 17.457$	26.600 26.696 26.399 26.514 26.798 26.863 26.915 26.956 29.003	$\begin{array}{c} 0.6850\\ 0.6820\\ 0.6909\\ 0.6883\\ 0.6790\\ 0.6751\\ 0.6708\\ 0.6662\\ 0.6714\end{array}$
100	33.384 30.833 28.664 27.545 26.923 84.424	16.939 17.969 18.928 19.454 19.740 8.413	$\begin{array}{c} 0.7930\\ 0.7770\\ 0.7608\\ 0.7515\\ 0.7453\\ 0.9293\\ \end{array}$	175	84.390 80.339 76.024 72.547 67.558 63.623 58.736	$10.356 \\ 10.854 \\ 11.440 \\ 11.965 \\ 12.790 \\ 13.528 \\ 14.578$	$\begin{array}{c} 0.9521 \\ 0.9500 \\ 0.9475 \\ 0.9456 \\ 0.9413 \\ 0.9376 \\ 0.9328 \end{array}$		$17.302 \\ 17.147 \\ 16.993 \\ 16.838 \\ 16.683 \\ 16.528$	29.140 29.271 29.391 29.498 29.579 29.644	$\begin{array}{c} 0.6714\\ 0.6686\\ 0.6652\\ 0.6623\\ 0.6587\\ 0.6544\\ 0.6498\end{array}$
	$\begin{array}{c} 79.542\\ 73.151\\ 63.161\\ 60.010\\ 54.573\\ 49.094\\ 44.764\\ 40.504\\ 36.884\\ 33.664\\ 28.512\\ 24.374\end{array}$	8.890 9.599 10.965 11.481 12.490 13.705 14.831 16.140 17.442 18.794 21.391 24.024	$\begin{array}{c} 0.9252\\ 0.9187\\ 0.9061\\ 0.9015\\ 0.8918\\ 0.8803\\ 0.8686\\ 0.8553\\ 0.8417\\ 0.8278\\ 0.7980\\ 0.7661\\ \end{array}$		52.586 48.362 44.663 36.094 31.994 28.680 26.993 24.071 21.887 19.869 18.719 18.719	16.163 17.449 18.787 22.723 25.313 27.821 29.314 32.306 34.943 37.877 39.690	0.9259 0.9193 0.9141 0.8935 0.8823 0.8692 0.8620 0.8472 0.8332 0.8199 0.8092	105	14.514 14.283 14.049 13.927 13.818 13.725 13.601 13.477 13.322 13.167 13.059	$\begin{array}{c} 34.089\\ 34.363\\ 34.643\\ 34.782\\ 34.908\\ 35.021\\ 35.162\\ 35.311\\ 35.475\\ 35.598\\ 35.719\\ 35.719\end{array}$	$\begin{array}{c} 0.6388\\ 0.6337\\ 0.6284\\ 0.6254\\ 0.6229\\ 0.6205\\ 0.6174\\ 0.6144\\ 0.6102\\ 0.6052\\ 0.6052\\ 0.6022\\ 0.6022\\ 0.6022\\ 0.6021\end{array}$
100	20.973 18.337 16.873 15.543 15.301 15.022 14.744 24.621 49.094	$\begin{array}{c} 26.662\\ 29.040\\ 30.551\\ 31.894\\ 32.160\\ 32.451\\ 32.667\\ 24.013\\ 13.696\end{array}$	0.7316 0.6967 0.6745 0.6486 0.6438 0.6378 0.6302 0.7736° 0.8798°	200	$16.540 \\ 15.204 \\ 13.793 \\ 14.131 \\ 12.667 \\ 11.237 \\ 9.7377 \\ 84.364 \\ 75.703$	$\begin{array}{r} 43.701\\ 46.584\\ 50.065\\ 49.246\\ 53.105\\ 57.211\\ 63.292\\ 11.009\\ 12.222\end{array}$	$\begin{array}{c} 0.7874\\ 0.7716\\ 0.7523\\ 0.7581\\ 0.7328\\ 0.7003\\ 0.6714\\ 0.9583\\ 0.9536\end{array}$	110 115	12.942 12.032 11.876 11.722 11.505 11.353 11.201 10.488 10.331	35.813 38.442 38.642 38.833 39.074 39.206 39.301 42.132 42.349	$\begin{array}{c} 0.5984\\ 0.5894\\ 0.5848\\ 0.5800\\ 0.5728\\ 0.5672\\ 0.5609\\ 0.5552\\ 0.5497\end{array}$
125	84.424 84.417 79.476 75.060	8.418 9.076 9.606 10.128	0.9298 ^a 0.9395 0.9361 0.9322		71.945 69.277 63.942 58.246 56.145	$12.794 \\ 13.251 \\ 14.293 \\ 15.606 \\ 16.161$	0.9498 0.9472 0.9430 0.9379	190	10.176 10.021 9.8659	42.545 42.557 42.748 42.907	0.5440 0.5382 0.5318
	$71.126 \\ 67.484 \\ 64.276 \\ 58.486$	$10.647 \\11.176 \\11.687 \\12.740$	0.9286 0.9248 0.9212 0.9137		50.145 51.722 44.470 38.875 34.614	$ \begin{array}{r} 16.161 \\ 17.439 \\ 20.069 \\ 22.705 \\ 25.249 \\ \end{array} $	0.9363 0.9307 0.9209 0.9108 0.9018	120	8.619 8.464 8.309	46.437 46.642 46.828 46.968	$\begin{array}{c} 0.3060 \\ 0.4992 \\ 0.4922 \\ 0.4846 \end{array}$
	54.517 51.298 46.527 42.494 38.869 35.585 24.946 20.539 17.199 15.036 12.613 11.164	$\begin{array}{c} 13.572 \\ 14.333 \\ 15.632 \\ 16.921 \\ 18.284 \\ 19.687 \\ 26.251 \\ 30.480 \\ 34.427 \\ 37.550 \\ 41.538 \\ 44.177 \end{array}$	$\begin{array}{c} 0.9073\\ 0.9016\\ 0.8918\\ 0.8817\\ 0.8715\\ 0.8590\\ 0.8030\\ 0.7676\\ 0.7260\\ 0.6923\\ 0.6424\\ 0.6047\\ \end{array}$		31.024 27.952 25.496 22.321 19.857 17.751 16.028 14.491 13.207 12.113 Mass of Sam	20.245 27.827 30.452 33.100 37.095 40.989 44.941 48.930 52.602 56.721 60.583 ple = 1.9760 (0.8908 0.8783 0.8783 0.8544 0.8398 0.8231 0.8092 0.7865 0.7730 0.7572 G.	129.25	$\begin{array}{c} 19.169\\ 16.992\\ 15.125\\ 13.255\\ 11.395\\ 9.5321\\ 8.2898\\ 7.6690\\ 7.3583\\ 6.7367\\ 6.2711\\ 5.8055\\ 5.4940\end{array}$	$\begin{array}{r} 32.649\\ 35.486\\ 38.273\\ 41.432\\ 44.956\\ 48.741\\ 51.244\\ 52.414\\ 52.957\\ 53.925\\ 54.257\\ 54.985\\ 55.920\end{array}$	$\begin{array}{c} 0.7593\\ 0.7316\\ 0.7023\\ 0.6663\\ 0.6215\\ 0.5637\\ 0.5154\\ 0.4877\\ 0.4728\\ 0.4407\\ 0.4149\\ 0.3873\\ 0.3252\\ 0.2522\\$
	9.0206 8.7267 8.3418	48.369 48.616 49.302	$0.5350 \\ 0.5202 \\ 0.5043 \\ 0.5043$	90 95	$18.429 \\ 18.241 \\ 16.465$	27.063 27.125 29.772	0.6705 0.6652 0.6501		5.4949 3.1657 3.0419 2.9009	55.230 56.073 56.669 58.073	0.3682 0.2154 0.2091
	7.8554 7.0821 84.420	50.043 51.059 9.078	0.4820 0.4434 0.9397°	100	16.281 16.096	29.882 29.928	0.6452 0.6388		2.7913 2.7029 2.6525		0.2035 0.2052 0.2078
150	84.411 80.845 76.582 72.802 69.376 66.147 63.251 59.246	$\begin{array}{r} 9.727\\ 10.127\\ 10.663\\ 11.178\\ 11.694\\ 12.229\\ 12.749\\ 12.527\end{array}$	0.9474 0.9446 0.9422 0.9389 0.9360 0.9333 0.9304 0.9352	105	23.609 18.496 15.013 14.828 14.643 14.458 14.273	24.469 29.274 32.270 32.471 32.665 32.822 32.911	0.7558 0.6913 0.6339 0.6300 0.6258 0.6209 0.6146		2.5999 2.5477 2.4879 2.3868 2.3000 2.2007 2.1331	67.192 70.555 75.548 87.143 102.19 128.87 154.58	$\begin{array}{c} 0.2119\\ 0.2181\\ 0.2280\\ 0.2523\\ 0.2852\\ 0.3441\\ 0.4000\\ \end{array}$
	53.565	13.537	0.9253 0.9177	105	$13.226 \\ 12.675$	35.473 36.080	0.6057 0.5904		2.0804	181.27	0.4575 (Continued)

Table I. (Continued)

t	V	р	Ζ	t	V	р	Ζ	t	V	р	Ζ
1 29.2 5	2.0362 1.9954 1.9701 1.9393 1.9122 9.5321	$\begin{array}{c} 207.59\\ 233.15\\ 259.35\\ 286.56\\ 312.33\\ 48.736\end{array}$	0.5128 0.5644 0.6199 0.6742 0.7247 0.5636°	145	$\begin{array}{c} 9.0581 \\ 8.3123 \\ 7.6673 \\ 7.0528 \\ 6.6324 \\ 6.1672 \\ 5.7191 \end{array}$	55.529 57.711 59.652 61.534 62.828 64.240 65.595	$\begin{array}{c} 0.5873 \\ 0.5601 \\ 0.5340 \\ 0.5067 \\ 0.4865 \\ 0.4626 \\ 0.4380 \end{array}$	175	3.2257 3.0482 2.9166 2.7549 2.6202 2.5210 2.4014	119.99127.87135.65148.88164.76180.76207 22	$\begin{array}{c} 0.4216\\ 0.4246\\ 0.4310\\ 0.4468\\ 0.4703\\ 0.4964\\ 0.5421 \end{array}$
135	7.9687 7.0879 6.0082 4.7265 3.4440 3.1154 2.9719	54.374 56.346 58.464 60.317 62.364 64.313 66.365	$\begin{array}{c} 0.5183 \\ 0.4777 \\ 0.4202 \\ 0.3410 \\ 0.2569 \\ 0.2397 \\ 0.2359 \end{array}$	150	9.5346 8.4230 6.9041 5.4314 4.6549 4.0167	56.003 59.425 64.942 69.964 72.996 76.219	0.6161 0.5775 0.5173 0.4384 0.3920 0.3532		$\begin{array}{c} 2.3179\\ 2.2506\\ 2.1915\\ 2.1486\\ 12.968\\ 14.955\end{array}$	$233.74 \\ 259.60 \\ 285.91 \\ 311.87 \\ 52.167 \\ 47.127$	0.5902 0.6365 0.6826 0.7300 0.7370° 0.7678°
	2.7918 2.6502 2.5530 4.0842 5.3274	70.279 76.260 82.841 61.075 59.543	0.2347 0.2417 0.2530 0.2984 0.3794		3.7315 3.5158 3.3775 3.2313 3.1368 3.0704	78.172 80.301 82.142 84.290 86.268 87.856	$\begin{array}{c} 0.3366\\ 0.3257\\ 0.3201\\ 0.3142\\ 0.3122\\ 0.3112\end{array}$	200	$\begin{array}{c} 14.962 \\ 12.797 \\ 11.090 \\ 9.6779 \\ 8.2865 \\ 7.1527 \end{array}$	51.649 58.243 64.739 71.293 79.179 87.108	$\begin{array}{c} 0.7974 \\ 0.7691 \\ 0.7408 \\ 0.7119 \\ 0.6770 \\ 0.6429 \end{array}$
140	9.4596 8.5883 7.8105 6.8681 6.0438	$52.644 \\ 54.922 \\ 56.994 \\ 59.464 \\ 61.518 \\ 6$	$\begin{array}{c} 0.5885 \\ 0.5574 \\ 0.5261 \\ 0.4826 \\ 0.4394 \end{array}$		2.9915 2.9104 2.8394 2.7477	90.183 93.057 96.236- 101.32	0.3112 0.3113 0.3125 0.3153 0.3212		6.2354 5.5938 4.9786 4.3508 3.8802	94.928 101.51 109.25 119.83 130.35	$\begin{array}{c} 0.6108 \\ 0.5859 \\ 0.5612 \\ 0.5380 \\ 0.5219 \end{array}$
	5.0248 3.9765 3.3831 3.1176 2.9646 2.7851 2.6650 2.5236 4.5450	63.825 66.267 68.880 71.560 74.279 79.795 85.810 96.234 64.876	$\begin{array}{c} 0.3790\\ 0.3114\\ 0.2754\\ 0.2636\\ 0.2602\\ 0.2626\\ 0.2702\\ 0.2870\\ 0.3484 \end{array}$		2.6700 2.5589 2.4844 2.3482 2.2573 2.1884 2.1336 2.0833 2.0525	$106.91 \\ 117.94 \\ 127.76 \\ 154.06 \\ 180.38 \\ 206.96 \\ 233.56 \\ 261.98 \\ 286.57 \\ 100.000 \\ 100$	$\begin{array}{c} 0.3293\\ 0.3482\\ 0.3662\\ 0.4174\\ 0.4698\\ 0.5234\\ 0.5750\\ 0.6297\\ 0.6786\end{array}$		3.5511 3.2780 3.0583 2.9046 2.6961 2.5537 2.4468 2.3681	140.395 154.32 167.27 180.71 207.07 233.34 260.32 285.73	$\begin{array}{c} 0.5165\\ 0.5220\\ 0.5278\\ 0.5416\\ 0.5761\\ 0.6125\\ 0.6572\\ 0.6982\\ \end{array}$
145	3.7822 5.1352	66.886 67.360	0.2989 0.4039		2.0202 9.5346	312.35 55.993	0.7280 0.6160°		2.3037 14.961 Mass of Sam	311.77 51.521	0.7411 0.7954 G
	4.3157 3.7024 3.4779 3.1370 2.9218 2.8249 2.7205 2.6471 2.5758 9.5151	70.005 72.819 74.480 78.662 82.728 87.270 92.590 97.503 103.38 54.230	$\begin{array}{c} 0.3527\\ 0.3148\\ 0.3024\\ 0.2881\\ 0.2822\\ 0.2878\\ 0.2941\\ 0.3012\\ 0.3109\\ 0.6025 \end{array}$	175	$\begin{array}{c} 12.968\\ 10.718\\ 9.0405\\ 7.7249\\ 6.5689\\ 5.5958\\ 4.8137\\ 4.2120\\ 3.8753\\ 3.4808 \end{array}$	52.180 59.480 66.074 72.485 79.046 85.628 92.150 98.835 103.79 111.99	$\begin{array}{c} 0.7372\\ 0.6945\\ 0.6508\\ 0.6100\\ 0.5657\\ 0.5220\\ 0.4833\\ 0.4535\\ 0.4382\\ 0.4247\end{array}$	125	7.9006 7.5026 7.3023 7.0029 6.8031 6.6079 7.0033 Mass of Sam	49.911 50.509 50.781 51.150 51.367 51.537 51.147 aple = 3.0284	0.4835 0.4647 0.4547 0.4392 0.4258 0.4176 0.4392 ^a G.
"Check n	oints.	04.200	0.0020		0.4000	111.33	0.4447	125	$\begin{array}{c} 12.997 \\ 6.9411 \end{array}$	40.809 51.270	0.6504 0.4364
2 P											

in the critical region were 127.00°, 128.50°, 128.80°, 129.00°, 129.10°, 129.20°, 129.22°, 129.25°, and 129.30° C. The P-V-T data in the critical region are presented in Table II and shown in Figure 2.

Vapor pressures and specific volumes of both the saturated liquid and the saturated vapor were measured from 50° C., at 5° intervals, to the critical temperature, which was $129.23 \pm 0.02^{\circ}$ C. In the liquid phase, *P-V-T* data were measured from the vapor pressure to about 315 atm. for four isotherms; 50° , 75° , 100° , and 125° C. The pressurevolume isotherms in the high-pressure region are presented in Table III and shown in Figure 3.

DERIVED QUANTITIES

Smoothed Vapor Pressures. For the experimental vapor pressure data, the constants of the Antoine equation were derived using the method of least squares. A simplified procedure of correlating, as recommended by Rossini (6), was used. In its final form, the Antoine equation for vapor pressure of propyne in the range from 50° C. to the critical temperature is as follows:

$$\log p = 4.81207 - \frac{1321.342}{t + 301.143} \tag{1}$$

Vapor pressures calculated from Equation 1 do not deviate from the experimental results by more than 0.055 atm. (0.167%) in the range 50° to 120° C. However, at 125° C. the deviation is 0.152 atm. (0.295%), which increases to 0.347 atm. (0.625%) at the critical temperature.

Smoothed vapor pressures were obtained by adding to the experimental vapor pressures the graphically smoothed residuals, which were the differences between experimental vapor pressures and the vapor pressures calculated from Equation 1. Both the experimental and smoothed vapor pressures are presented in Table IV.

Orthobaric Densities. The following equations were fitted by the method of least squares to the orthobaric densities, which were obtained by extrapolating the pressure-volume isotherms of Table I and Table III to the corresponding observed vapor pressures:

$$\mathbf{d} = (\mathbf{d}_L + \mathbf{d}_g)/2 = 0.323918 - 0.000585672 t \tag{2}$$

$$\Delta = (\mathbf{d}_L + \mathbf{d}_g)/2 = 0.067073 (t_c - t)^{1/3} - 0.0116512$$
(3)

These observed orthobaric densities were smoothed by using the same graphical residual method as employed in

Table II. Experimental Pressure-Volume Isotherms for Liquid Propyne

V	р	V	р	V	р
<i>t</i> ,	50° C.	t,	90° C.	t, 11	l5° C.
$1.7573 \\ 1.7551 \\ 1.7502 \\ 1.7418 \\ 1.7243 \\ 1$	$13.600 \\18.337 \\22.589 \\33.540 \\42.991$	2.0570 2.0522 2.0478 2.0413	$27.888 \\ 29.817 \\ 31.271 \\ 33.446$	2.4374 2.4243 2.4088 2.3915 2.2670	$\begin{array}{r} 44.025 \\ 44.890 \\ 46.138 \\ 47.384 \\ 50.046 \end{array}$
1.7343	54 726	+ 0	5º C	2.3070	50.040
1.7153 1.6995 1.6853 1.6722	73.614 101.47 128.89 157.26	$\begin{array}{c} 2.0986\\ 2.0946\\ 2.0905\\ 2.0875\end{array}$	30.886 31.929 33.305 34.362	t, 12 2.6103 2.5911	20° C. 48.091 48.825
1.6611	181.07			2.5634	50.025
1.6398	207.63	<i>t</i> , 10	ю° С.	2.0029	51.075
1.6299 1.6209 1.6118	260.52 286.36 312.42	$2.1433 \\ 2.1318 \\ 2.1110$	$35.558 \\ 38.208 \\ 43.505$	t, 12	25° C.
t.	75° C.	2.0894	50.047	2.8329	51.604
2.0590 1.9241 1.9225 1.9182 1.9094 1.8928 1.8654 1.8536 1.8226 1.8240 1.7849 1.7669 1.7491 1.7329 1.7172	$\begin{array}{c} 19.934\\ 20.383\\ 22.042\\ 23.701\\ 29.041\\ 39.045\\ 60.191\\ 75.476\\ 102.49\\ 129.24\\ 154.37\\ 180.88\\ 207.67\\ 235.88\\ 261.36\end{array}$	$\begin{array}{c} 2.0397\\ 2.0248\\ 1.9768\\ 1.9375\\ 1.9050\\ 1.8759\\ 1.8518\\ 1.8309\\ 1.8115\\ t, 10\\ 2.2397\\ 2.2328\\ 2.2092\\ 2.1969\end{array}$	5,75,8 101.49 125.77 154.05 180.39 206.71 233.02 259.36 5° C. 36.726 37.378 41.220 43.941	2.7957 2.7715 2.7151 2.6211 2.5331 2.3674 2.1845 2.1394 2.0344 2.0344 1.9970 1.9609 1.9035 1.8796	$\begin{array}{c} 52.211\\ 52.560\\ 53.615\\ 56.360\\ 60.519\\ 75.280\\ 101.64\\ 129.08\\ 154.65\\ 180.62\\ 206.85\\ 234.86\\ 260.72\\ 286.43\\ 311.80\\ \end{array}$
1.7030	287.80 313.80			t. 12	7° C.
1.0007	010.00	t, 11	0° C.	3 0180	53 479
t, 1.9982 1.9901 1.9800	25.411 28.824 33.228	$2.3325 \\ 2.3223 \\ 2.3114 \\ 2.3000$	$\begin{array}{r} 40.597 \\ 42.117 \\ 43.409 \\ 44.871 \end{array}$	2.9234 2.8799 2.8332 2.7801	54.016 54.376 54.909 55.743

Sample Mass = 2.3922 G. at 125° and 127° C.

Sample Mass = 2.3655 G. at other temperatures.

the smoothing of vapor pressures. Table IV also presents the orthobaric densities of propyne, both observed and smoothed.

Critical Constants. Critical constants of propyne were obtained from a large-scale, pressure-volume plot (Figure 2) of isotherms in the critical region. These isotherms were spaced very closely (0.02° C. apart near the critical temperature) so that the horizontal point of inflection could be determined. The critical temperature, $129.23 \pm 0.02^{\circ}$ C., was selected with the corresponding critical pressure of 55.54 ± 0.02 atm. The critical density was determined to be 0.2449 gram per c.c. from the rectilinear diameter, Equation 2, in conjunction with the smoothed residual. The critical compressibility factor, thus, is 0.27518.

DISCUSSION

A literature survey shows that practically no P-V-T measurements have been made on propyne at temperatures above the normal boiling point. Even at lower temperatures, the data are fragmentary. Thus, no comparison is made of the experimental data obtained in this work, such as compressibility factors, vapor pressures or orthobaric densities, with the data reported in literature.

No experimental values for the critical pressure or the critical volume are available. The critical pressure of propyne reported by Stull (7) represents an extrapolation of the vapor pressure curve (Cox chart) to the critical

Table III. Experimental Pressure-Volume Isotherms in the Critical Region of Propyne

(Sample Mass = 2.3922 G.)

	(•	Sample Ma	35 - 2.0022 C	.,	
V	р	V	р	V	р
t, 128	.5° C.	t, 129).1° C.		
5 4094	54 602	5 4002	55 199	1 21 24	55 517
5 31024	54 738	5 3014	55 193	4.0124	55 522
5 2122	54 778	5 1989	55 242	4 1526	55 524
5 1045	54 811	5 1110	55 278	4 0974	55 527
5 0019	54 829	5 0035	55 317	4 0513	55 527
4 8945	54.836	4.9021	55.345	3 9895	55 529
4.7754	54.838	4.8010	55.365	3.8977	55.531
4.5717	54.838	4.6964	55.384	3.8026	55.535
4.2630	54.839	4.5950	55.395	3.6060	55.547
3.8955	54.839	4.5026	55.401	3.4079	55.612
3.6802	54.838	4.4064	55.403	3.3096	55.693
3.4958	54.837	4.3124	55.405		
3.3885	54.839	4.2072	55.407		
3.2811	54.878	4.0974	55.408	+ 129	25° C
3.1748	55.027	3.9895	55.407		20 0.
3.0685	55.346	3.7073	55.409	5.4028	55.242
5.4012	54.696	3.6060	55.419	5.1989	55.348
t, 128.	8° C.	3.5078	55.431	4.8010	55.481
5.4036	54.913	3.4079	55.468	4.5950	55.515
5.2039	55.010	3.3096	00.044 55.600	4.4064	55.532
5.0043	55.063	3.2084	99.090	4.3124	00.037
4.7972	55.107			4.2072	55 544
4.6973	55.111			4.1020	55 546
4.5959	55.113	t. 129).2° C.	4.0513	55 549
4.5035	55.113	- 1000		3 9895	55 551
4.0984	55.116	5.4028	55.217	3 8977	55 553
3.7086	55.115	5.3015	55.274	3.8026	55 557
3.0072	55.115 55.117	5,1989	00.323 55.260	3.6060	55.574
3.0114	55 130	5.0035	55 202	3.4079	55.634
3 3091	55 195	4 9021	55 497	3.3096	55.713
3 2097	55 321	4.8010	55 453	5.0030	55.425°
0.2001	00.021	4 6964	55 468		
t, 125	J° C.	4.5950	55.480		
5.5864	54.962	4.5026	55.491	+ 190	20° C
5.4789	55.035	4,4064	55.498	ι, 125.	JU C.
5.3714	55.094	4.3124	55.503	5.4016	55.286
5.2640	55.146	4.2072	55.508	5.3003	55.349
5.2025	55.175	4.0974	55.507	5.1978	55.398
5.1082	55 990	3.9895	55.509	5.1098	55.442
1 9202	55 267	3.8977	55.511	5.0023	55.480
4.8036	55 287	3.8026	55.513	4.9009	55 540
4.6856	55 302	3.7073	55.515	4.1990	55 560
4.5846	55.312	3.6060	55.528	4.0502	55 573
4.4798	55.316	3.3078	55,543	4 5014	55 585
4.3880	55.322	3.4079	55 671	4 4095	55 592
4.2896	55.321	3 2084	55 836	4.3113	55.597
4.1884	55.321	0.2004	00.000	4.2037	55.602
4.0844	55.322			4.0962	55.607
3.9822	55.321			3.9884	55.614
3.8808	55.321	t 129	22° C.	3.8966	55.616
3.7736	55.322	., 120.	0.	3.8014	55.621
3.6659	55.322	5.4028	55.223	3.7062	55.626
3.5584	55.326	5.1989	55.335	3.6048	55.635
3.4009 2.2400	00.349 55 407	0.0035	55.413	3.5066	55.661
0.0400 2 9267	55.407 55.596	4.0010	00.407	3.4067	55.708
3 1286	55 785	4 4064	55 519	3.3084	00.197 55.070
5.1200	00.100	4.4004	00.012	3.2072	00.970
<u> </u>					

^e Check point.

temperature. Table V compares the critical constants obtained in this investigation with those of other investigations.

Smoothed compressibility factors from this work are compared, in Table VI, with the values obtained from the generalized charts of Nelson and Obert (5). Reduced temperatures from 0.803 to 1.176 and reduced pressures from 0.10 to 5.5 are covered in the range of this comparison. Per cent deviations observed here are no larger than those encountered by Nelson and Obert, except in the critical region, where the deviations are as high as 4 to 5%.







high-pressure region

Temn	Vapor Pressure, Atm.		Density for	r Satd. Vapor	Density of Satd. Liq.	
° C.	Observed	Smoothed	Observed	Smoothed	Observed	Smoothed
50	11.184	11.184	0.02067	0.02070	0.5784	0.5703
55	12.646	12.645	0.02300	0.02300	0.5602	0.5602
60	14.236	14.236	0.02000	0.02589		0.5501
65	15,982	15.972		0.02788		0.5413
70	17.887	17.864		0.03331		0.5279
75	19.928	19.920	0.03768	0.03780	0.5192	0.5192
80	22.149	22.149		0.04240		0.5088
85	24,554	24.556		0.04822		0.4974
90	27.144	27.145	0.05487	0.05470	0.4859	0.4861
95	29.928	29.940	0.06155	0.06214	0.4757	0.4741
100	32.916	32.947	0.06979	0.07050	0.4649	0.4603
105	36.169	36.171	0.07958	0.08018	0.4452	0.4448
110	39.624	39.623	0.09156	0.09148	0.4272	0.4275
115	43.310	43.310	0.1053	0.1058	0.4077	0.4070
120	47.275	47.255	0.1254	0.1252	0.3758	0.3812
125	51.600	51.597	0.1487	0.1560	0.3530	0.3440
127	53.405	53.410	0.1666	0.1760	0.3286	0.3204
128.5	54.838	54.843	0.2041	0.1927	0.2954	0.3011
128.8	55,115	55.127	0.2141	0.2020	0.2859	0.2912
129.0	55.322	55.352	0.2232	0.2221	0.2755	0.2709
129.1	55.407	55.426	0.2273	0.2291	0.2681	0.2637
129.2	55.508	55.528	0.2361	0.2423	0.2556	0.2503
129.23		55.540		0.2449		0.2449

Table IV. Vapor Pressure and Orthobaric Density Data for Propyne

Table V. Critical Constants for Propyne

t_c , ° C.	$P_{\rm c}$, atm.	d., g./c.c.	Reference
129.5	•••		(2)
127.9	•••	• • •	(3)
121.6	• • •		(4)
128	52.8		(7)
129.23 ± 0.02	55.54 ± 0.02	0.2449 ± 0.002	This work

Table VI. Comparison of Compressibility Factors for **Propyne with Generalized Charts**

		Z =						
Temp.,	Reduced	PV/RT,	This Work	Deviation,				
50	0.10 0.18	0.922 0.845°	0.923 0.850	-0.11 -0.59				
75	$\begin{array}{c} 0.15\\ 0.25\end{array}$	$0.907 \\ 0.842$	0.908 0.838	$-0.11 \\ 0.48$				
100	0.20 0.40	0.904 0.797	0.905 0.790	-0.11 0.89				
125	0.20 0.50 0.80	0.923 0.793° 0.607	0.925 0.796 0.603	-0.22 -0.38 0.66				
150	0.20 2.00 5.50	0.935 0.340 0.725	0.939 0.335 0.715	-0.42 1.49 1.40				
175	$0.20 \\ 2.00 \\ 5.50$	0.947 0.425 0.730	$\begin{array}{c} 0.949 \\ 0.426 \\ 0.720 \end{array}$	-0.21 -0.23 1.39				
200	$\begin{array}{c} 0.20 \\ 2.00 \\ 5.50 \end{array}$	0.955 0.540 0.750	0.957 0.557 0.731	-0.21 -3.05 -2.59				
Dbtained by extrapolation.								

NOMENCLATURE

- $d_c = critical density, g./c.c.$
- = density of saturated vapor, g./c.c. d,
- d_L = density of saturated liquid, g./c.c.
 - pressure, atm. =
- р Р = absolute pressure
- P_{c} = critical pressure, atm.
- Ŕ = gas constant
- \overline{T} = absolute temperature
- *t* = temperature, ° C.
- critical temperature, ° C. =
- $t_c V$ = volume, ml./g.
- Ζ compressibility factor, PV/RT=

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