

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

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

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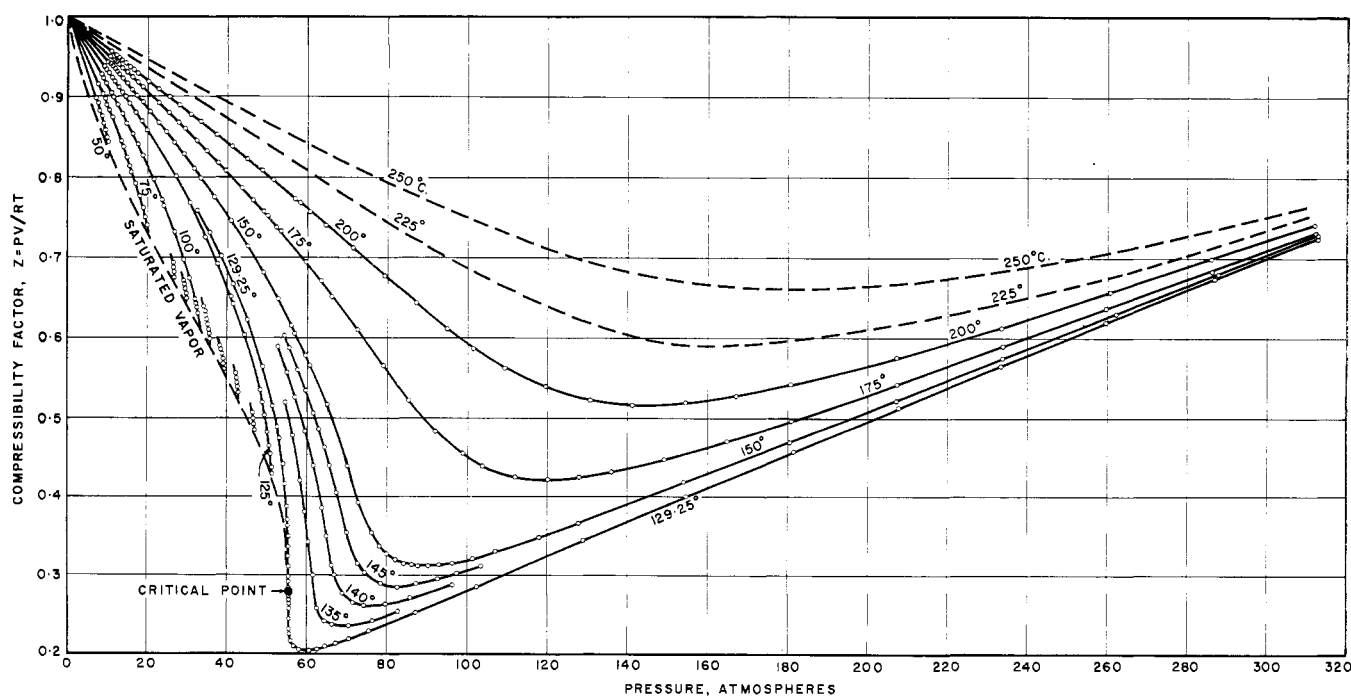


Figure 1. Compressibility factors of propyne

Table I. (Continued)

<i>t</i>	<i>V</i>	<i>p</i>	<i>Z</i>	<i>t</i>	<i>V</i>	<i>p</i>	<i>Z</i>	<i>t</i>	<i>V</i>	<i>p</i>	<i>Z</i>
129.25	2.0362	207.59	0.5128	145	9.0581	55.529	0.5873	175	3.2257	119.99	0.4216
	1.9954	233.15	0.5644		8.3123	57.711	0.5601		3.0482	127.87	0.4246
	1.9701	259.35	0.6199		7.6673	59.652	0.5340		2.9166	135.65	0.4310
	1.9393	286.56	0.6742		7.0528	61.534	0.5067		2.7549	148.88	0.4468
	1.9122	312.33	0.7247		6.6324	62.828	0.4865		2.6202	164.76	0.4703
	9.5321	48.736	0.5636 ^a		6.1672	64.240	0.4626		2.5210	180.76	0.4964
					5.7191	65.595	0.4380		2.4014	207.22	0.5421
135	7.9687	54.374	0.5183	150	9.5346	56.003	0.6161		2.3179	233.74	0.5902
	7.0879	56.346	0.4777		8.4230	59.425	0.5775		2.2506	259.60	0.6365
	6.0082	58.464	0.4202		6.9041	64.942	0.5173		2.1915	285.91	0.6826
	4.7265	60.317	0.3410		5.4314	69.964	0.4384		2.1486	311.87	0.7300
	3.4440	62.364	0.2569		4.6549	72.996	0.3920		12.968	52.167	0.7370 ^a
	3.1154	64.313	0.2397		4.0167	76.219	0.3532		14.955	47.127	0.7678 ^a
	2.9719	66.365	0.2359		3.7315	78.172	0.3366	200	14.962	51.649	0.7974
	2.7918	70.279	0.2347		3.5158	80.301	0.3257		12.797	58.243	0.7691
	2.6502	76.260	0.2417		3.3775	82.142	0.3201		11.090	64.739	0.7408
	2.5530	82.841	0.2530		3.2313	84.290	0.3142		9.6779	71.293	0.7119
	4.0842	61.075	0.2984		3.1368	86.268	0.3122		8.2865	79.179	0.6770
	5.3274	59.543	0.3794		3.0704	87.856	0.3112		7.1527	87.108	0.6429
140	9.4596	52.644	0.5885		2.9915	90.183	0.3113		6.2354	94.928	0.6108
	8.5883	54.922	0.5574		2.9104	93.057	0.3125		5.938	101.51	0.5859
	7.8105	56.994	0.5261		2.8394	96.236	0.3153		4.9786	109.25	0.5612
	6.8681	59.464	0.4826		2.7477	101.32	0.3212		4.3508	119.83	0.5380
	6.0438	61.518	0.4394		2.6700	106.91	0.3293		3.8802	130.35	0.5219
	5.0248	63.825	0.3790		2.5589	117.94	0.3482		3.5511	140.95	0.5165
	3.9765	66.267	0.3114		2.4844	127.76	0.3662		3.2780	154.32	0.5220
	3.3831	68.880	0.2754		2.3482	154.06	0.4174		3.0583	167.27	0.5278
	3.1176	71.560	0.2636		2.2573	180.38	0.4698		2.9046	180.71	0.5416
	2.9646	74.279	0.2602		2.1884	206.96	0.5234		2.6961	207.07	0.5761
	2.7851	79.795	0.2626		2.1336	233.56	0.5750		2.5537	233.34	0.6125
	2.6650	85.810	0.2702		2.0833	261.98	0.6297		2.4468	260.32	0.6572
	2.5236	96.234	0.2870		2.0525	286.57	0.6786		2.3681	285.73	0.6982
	4.5450	64.876	0.3484		2.0202	312.35	0.7280		2.3037	311.77	0.7411
	3.7822	66.886	0.2989		9.5346	55.993	0.6160 ^a		14.961	51.521	0.7954
145	5.1352	67.360	0.4039	175	12.968	52.180	0.7372		Mass of Sample = 2.3922 G.		
	4.3157	70.005	0.3527		10.718	59.480	0.6945	125	7.9006	49.911	0.4835
	3.7024	72.819	0.3148		9.0405	66.074	0.6508		7.5026	50.509	0.4647
	3.4779	74.480	0.3024		7.7249	72.485	0.6100		7.3023	50.781	0.4547
	3.1370	78.662	0.2881		6.5689	79.046	0.5657		7.0029	51.150	0.4392
	2.9218	82.728	0.2822		5.5958	85.628	0.5220		6.8031	51.367	0.4258
	2.8249	87.270	0.2878		4.8137	92.150	0.4833		6.6079	51.537	0.4176
	2.7205	92.590	0.2941		4.2120	98.835	0.4535		7.0033	51.147	0.4392 ^a
	2.6471	97.503	0.3012		3.8753	103.79	0.4382		Mass of Sample = 3.0284 G.		
	2.5758	103.38	0.3109		3.4808	111.99	0.4247	125	12.997	40.809	0.6504
	9.5151	54.230	0.6025						6.9411	51.270	0.4364

^aCheck points.

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 ± 0.02° 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 pressure-volume 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:

$$\log p = 4.81207 - \frac{1321.342}{t + 301.143} \quad (1)$$

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:

$$d = (d_L + d_g)/2 = 0.323918 - 0.000585672 t \quad (2)$$

$$\Delta = (d_L + d_g)/2 = 0.067073 (t_c - t)^{1/3} - 0.0116512 \quad (3)$$

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	p	V	p	V	p
t, 50° C.		t, 90° C.		t, 115° C.	
1.7573	13.600	2.0570	27.888	2.4374	44.025
1.7551	18.337	2.0522	29.817	2.4243	44.890
1.7502	22.589	2.0478	31.271	2.4088	46.138
1.7418	33.540	2.0413	33.446	2.3915	47.384
1.7343	43.991			2.3670	50.046
1.7268	54.726	t, 95° C.		t, 120° C.	
1.7153	73.614	2.0986	30.886		
1.6995	101.47	2.0946	31.929	2.6103	48.091
1.6853	128.89	2.0905	33.305	2.5911	48.825
1.6722	157.26	2.0875	34.362	2.5634	50.025
1.6611	181.07			2.5329	51.679
1.6504	207.83	t, 100° C.		t, 125° C.	
1.6398	235.67	2.1433	35.558		
1.6299	260.52	2.1318	38.208	2.8329	51.604
1.6209	286.36	2.1110	43.505	2.7957	52.211
1.6118	312.42	2.0894	50.047	2.7715	52.560
t, 75° C.		2.0597	60.878	2.7151	53.615
2.0590	19.934	2.0248	75.758	2.6211	56.360
1.9241	20.383	1.9768	101.49	2.5331	60.519
1.9225	22.042	1.9375	125.77	2.3674	75.280
1.9182	23.701	1.9050	154.05	2.1845	101.64
1.9094	29.041	1.8759	180.39	2.1394	129.08
1.8928	39.045	1.8518	206.71	2.0814	154.65
1.8654	60.191	1.8309	233.02	2.0344	180.62
1.8536	75.476	1.8115	259.36	1.9970	206.85
1.8226	102.49	t, 105° C.		1.9609	234.86
1.8040	129.24	2.2397	36.726	1.9310	260.72
1.7849	154.37	2.2328	37.378	1.9035	286.43
1.7669	180.88	2.2092	41.220	1.8796	311.80
1.7491	207.67	2.1969	43.941	t, 127° C.	
1.7329	235.88			3.0180	53.472
1.7172	261.36	t, 110° C.		2.9234	54.016
1.7030	287.80	2.3325	40.597	2.8799	54.376
1.6907	313.80	2.3223	42.117	2.8332	54.909
t, 85° C.		2.3114	43.409	2.7801	55.743
1.9982	25.411	2.3000	44.871		
1.9901	28.824				
1.9800	33.228				

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, $129.23 \pm 0.02^\circ \text{C.}$, was selected with the corresponding critical pressure of $55.54 \pm 0.02 \text{ atm.}$ 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.)

V	p	V	p	V	p
t, 128.5° C.		t, 129.1° C.		t, 129.25° C.	
5.4024	54.692	5.4002	55.138	4.3124	55.517
5.3102	54.738	5.3014	55.193	4.2072	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	t, 129.2° C.	
3.2811	54.878	4.0974	55.408	5.4028	55.217
3.1748	55.027	3.9895	55.407	5.3015	55.274
3.0685	55.346	3.7073	55.409	5.1989	55.323
5.4012	54.696 ^a	3.6060	55.419	5.0035	55.398
t, 128.8° C.		3.5078	55.431	4.9021	55.427
5.4036	54.913	3.4079	55.468	4.8010	55.453
5.2039	55.010	3.3096	55.544	4.6964	55.468
5.0043	55.063	3.2084	55.696	4.5950	55.480
4.7972	55.107	t, 129.2° C.		4.5026	55.491
4.6973	55.111	5.4028	55.217	4.4064	55.498
4.5959	55.113	5.3015	55.274	4.3124	55.503
4.5035	55.113	5.1989	55.323	4.2072	55.508
4.0984	55.116	5.0035	55.362	4.0974	55.507
3.7086	55.116	4.9021	55.398	3.9895	55.509
3.6072	55.115	4.8010	55.427	3.8977	55.511
3.5114	55.117	4.6964	55.468	3.8026	55.513
3.4074	55.130	4.5950	55.480	3.7073	55.515
3.3091	55.195	4.5026	55.491	3.6060	55.528
3.2097	55.321	4.4064	55.498	3.5078	55.543
t, 129° C.		4.3124	55.503	3.4079	55.590
5.5864	54.962	4.2072	55.508	3.3096	55.671
5.4789	55.035	4.0974	55.507	3.2084	55.836
5.3714	55.094	3.9895	55.509		
5.2640	55.146	3.8977	55.511	t, 129.22° C.	
5.2025	55.175	3.8026	55.513	5.4028	55.223
5.1082	55.211	3.7073	55.515	5.1989	55.335
5.0154	55.239	3.6060	55.528	5.0035	55.413
4.9202	55.267	3.5078	55.543	4.8010	55.467
4.8036	55.287	3.4079	55.590	4.5950	55.497
4.6856	55.302	3.3096	55.671	4.4064	55.512
4.5846	55.312				
4.4798	55.316				
4.3880	55.322				
4.2896	55.321				
4.1884	55.321				
4.0844	55.322				
3.9822	55.321				
3.8808	55.321				
3.7736	55.322				
3.6659	55.322				
3.5584	55.326				
3.4509	55.349				
3.3436	55.407				
3.2367	55.536				
3.1286	55.785				

^a 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%.

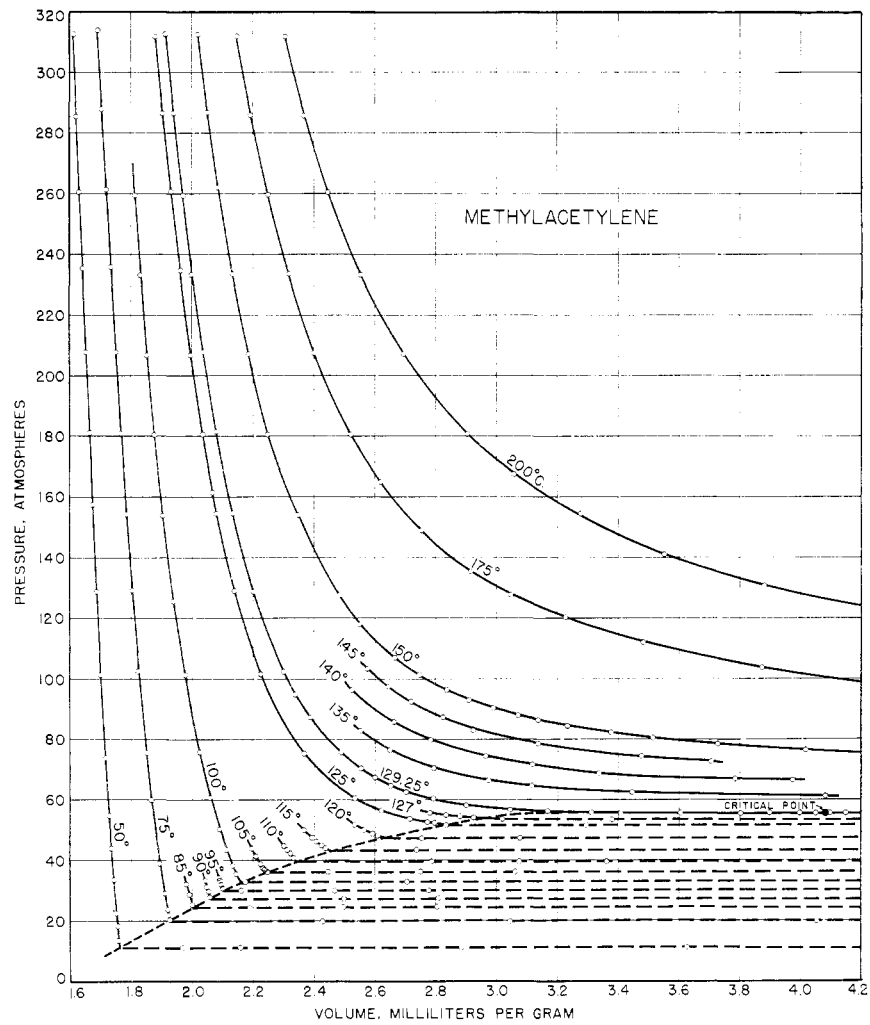


Figure 2. Pressure-volume isotherms in the critical region of propyne

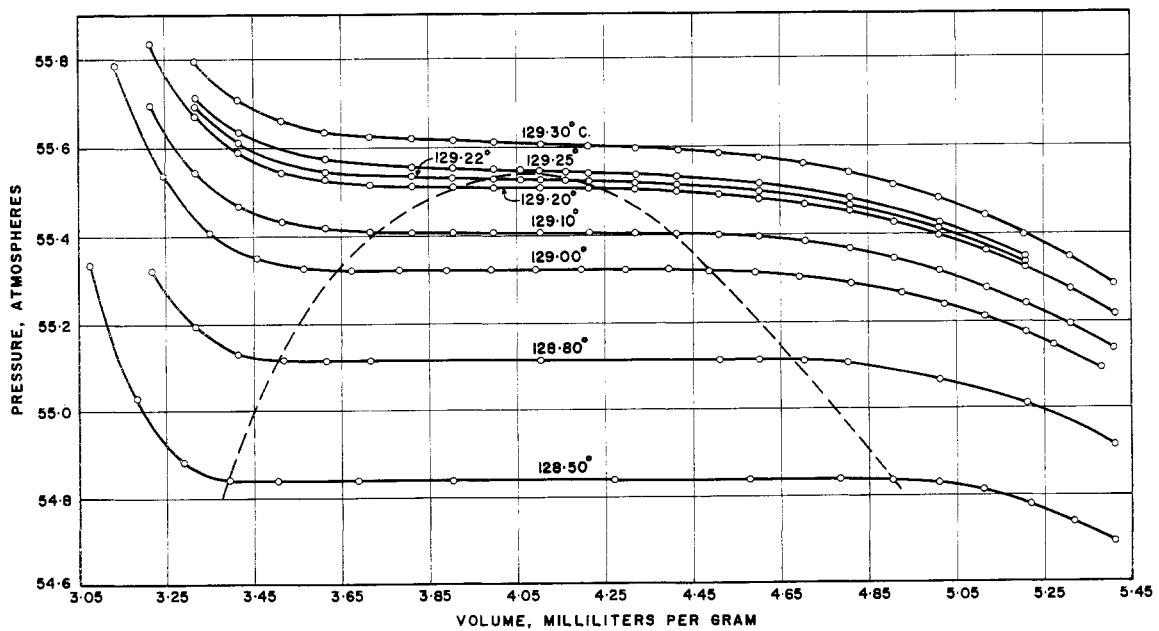


Figure 3. Pressure-volume isotherms for propyne in the high-pressure region

Table IV. Vapor Pressure and Orthobaric Density Data for Propyne

Temp., ° C.	Vapor Pressure, Atm.		Density for Satd. Vapor		Density of Satd. Liq.	
	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	...	0.02589	...	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 V. Critical Constants for Propyne

t_c , ° C.	P_c , atm.	d_c , 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

Temp., ° C.	Reduced Pressure	$Z = PV/RT$, (5)	This Work	Deviation, %
50	0.10	0.922	0.923	-0.11
	0.18	0.845 ^a	0.850	-0.59
75	0.15	0.907	0.908	-0.11
	0.25	0.842	0.838	0.48
100	0.20	0.904	0.905	-0.11
	0.40	0.797	0.790	0.89
125	0.20	0.923	0.925	-0.22
	0.50	0.793 ^a	0.796	-0.38
	0.80	0.607	0.603	0.66
150	0.20	0.935	0.939	-0.42
	2.00	0.340	0.335	1.49
	5.50	0.725	0.715	1.40
175	0.20	0.947	0.949	-0.21
	2.00	0.425	0.426	-0.23
	5.50	0.730	0.720	1.39
200	0.20	0.955	0.957	-0.21
	2.00	0.540	0.557	-3.05
	5.50	0.750	0.731	-2.59

^a Obtained by extrapolation.

NOMENCLATURE

d_c = critical density, g./c.c.
 d_v = density of saturated vapor, g./c.c.
 d_L = density of saturated liquid, g./c.c.
 p = pressure, atm.
 P = absolute pressure
 P_c = critical pressure, atm.
 R = gas constant
 T = absolute temperature
 t = temperature, ° C.
 t_c = critical temperature, ° C.
 V = volume, ml./g.
 Z = compressibility factor, PV/RT

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LITERATURE CITED

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