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Volumetric Behavior, Vapor Pressures, and Critical Properties of Cyclopropane

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Pressure-volume-temperature relations of cyclopropane (trimethylene) over the temperature range of 20° to 200° C. and up to a pressure of 310 atm. were measured using the Beattie method. Vapor pressures were determined from 20° C. to the critical temperature at 5° increments. These data were used to derive the critical constants, the orthobaric densities, the heats and entropies of vaporization, the fugacity coefficients, the volume residuals, and the compressibility factors.

The equipment used in this investigation follows, in general, the basic design of that described by Keyes (*10*) and Beattie (*1*). The method involves the direct measurement of pressure as a function of volume, which is continuously variable, for a known mass of material maintained at a controlled temperature. An Amagat dead-weight gage was used for the pressure measurements. Samples were confined over mercury in the *P-V-T* cell. The sample volumes were calculated from the difference between the amount of mercury originally in the system and the amount withdrawn into the thermostated volumetric pump. Four different samples (0.5, 1.5, 3.5, and 8.5 grams) were used for the present work. Sample masses were determined by direct weighing of the samples, contained in specially designed, light-weight weighing bombs, on an analytical balance. A platinum resistance thermometer associated with a Mueller bridge was used for the temperature measurements. Detailed descriptions of the apparatus, the calibrations, and the experimental procedures have been given by Couch (*4*), Hellwig (*8*), Hsu (*9*), and Lin (*11*).

MATERIAL

The purity of the original cyclopropane sample was 99.91% as stated by the Phillips Petroleum Co. The sample was further purified by passage through a molecular sieve column, followed by vacuum distillation with condensation by means of liquid nitrogen. The sample used in the measurements was approximately the 35% center cut, which had a minimum purity of 99.95% as shown by chromatographic analysis. The final impurity consisted chiefly of equal portions of propane and propylene.

PHYSICAL CONSTANTS

The fundamental constants and conversion factors used throughout this work were given by Abramowitz and Stegun (*7*) and Weast (*6*). The molecular weight of cyclopropane, 42.0813, is based on the newest atomic weight scale (*3*). The international temperature scale of 1948 (ITS-48) was used because the platinum resistance thermometer was calibrated by the National Bureau of Standards in 1951.

EXPERIMENTAL RESULTS

Vapor Phase. In the vapor phase, the pressure-volume-temperature behavior of cyclopropane was measured from 20° to 200° C. The major isotherms were spaced at 20° C. intervals, and the pressures were measured from 6 atm. up to the vapor pressure for each isotherm below the critical temperature and up to the maximum pressure allowed by the equipment, 310 atm., for each isotherm at and above the critical temperature. For the isotherms at 130°, 135°, 145°, and 150° C., the pressures were measured from 37 to 127 atm. The results are shown as compressibility factors, $Z = PV/RT$, in Figure 1. For the saturated states, the specific volumes were obtained along isotherms spaced at 5° C. intervals from 20° C. to the critical temperature, and the data are presented in Table I (Tables I to IV deposited with ASIS).

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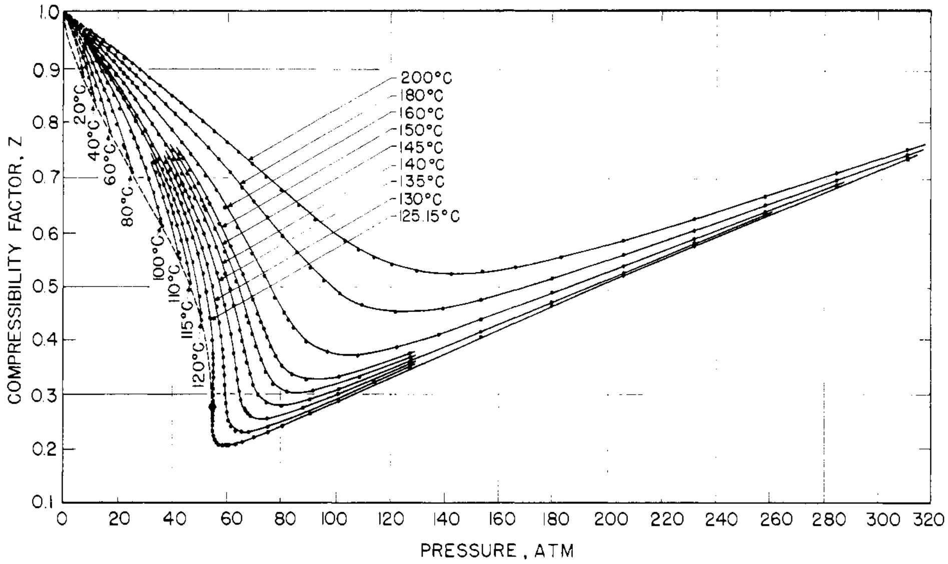

Figure 1. Compressibility factors of cyclopropane

Liquid Phase. In the liquid phase, the specific volumes were measured from 20° to 120° C. The major isotherms were spaced at 20° C. intervals, and the pressures were measured from vapor pressures up to 310 atm. Supplementary isotherms were at 5° C. intervals, and the pressures were measured to 20 atm. above each vapor pressure. The liquid *P-V-T* data are presented in Table II. Figure 2 shows the pressure-volume isotherms for high density states, including the critical region.

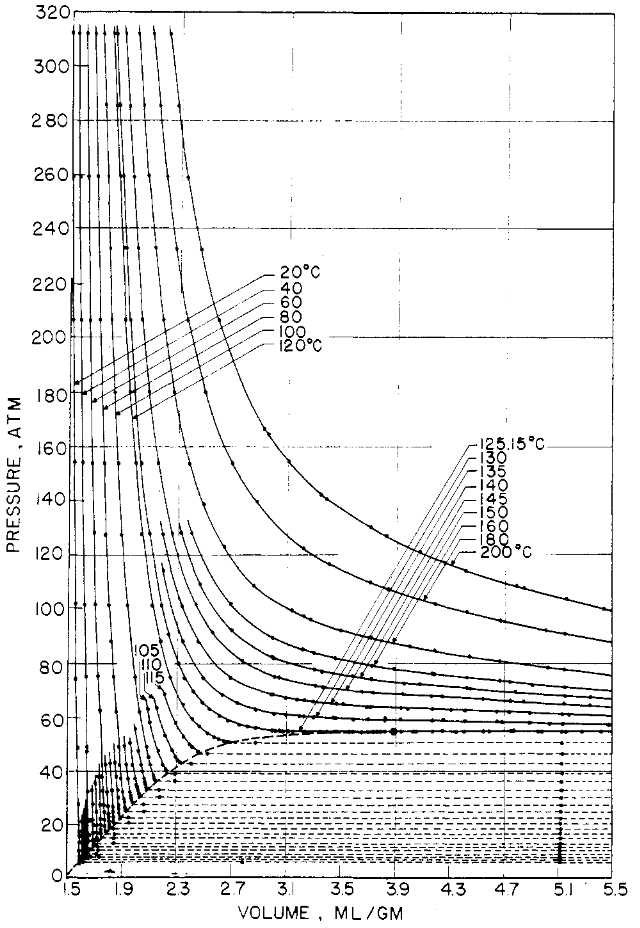

Figure 2. Specific volumes of cyclopropane in the high pressure region

Two-Phase and Critical Region. In the two-phase region, the specific volumes were measured isothermally at 5° C. intervals from 20° C. to the critical temperature (Table III). In the critical region, 13 isotherms between 124.0° and 125.25° C. were measured at small pressure increments in order to determine the critical constants. The data are presented in Table IV, and seven of the isotherms are shown in Figure 3.

Analysis of Errors. The sources of experimental error in sample mass measurement are the precision of the analytical balance (±0.07 mg.) and the weight calibration (±0.005 mg.). Errors in pressure measurement are attributed to the precision of each measurement (±0.0013 atm.), the dead-weight gage calibration (±0.002%), the weight calibrations (±0.001%), the determination of the mercury and oil hydraulic heads (±0.01%), and the variation of the gage constant with pressure (±0.02% up to 300 atm.) and room temperature (±0.005% up to 30° C.). The sources of error in volume measurement are the precision of each measurement (±0.001 ml.), the volumetric pump calibration (±0.001 ml.), the blank run measurement (±0.001 ml.), and the determination of bench volume (±0.001 ml.). The error in temperature measurement consists of errors in the precision of each measurement (±0.001° C.), the calibrations of the Mueller bridge and the platinum resistance thermometer (±0.002° C.), and the fluctuation of the temperature controller (±0.002° C.). In summary, the maximum experimental uncertainties in measurement are estimated to be 0.015% in sample mass, 0.04% in pressure, 0.06% in volume, and 0.01° C. in temperature.

Four different sizes of sample—0.47444, 1.49991, 3.52671, and 8.58354 grams—were used in this investigation. The series of measurements with each sample overlapped in both pressure and volume ranges. One measure of the internal consistency of the experimental data can be obtained from the overlapped regions. A detailed comparison of experimental compressibility factors with graphically smoothed values in these regions was made. Generally, the deviations did not exceed 0.0002, with the exception of the critical region, where deviations were as large as 0.0004. Intercomparison at two temperatures, 125.15° and 200° C., is made in Table V. In addition, the consistency of the vapor pressure measurements among four samples was ±0.005 atm. (Table III).

It is inherent in the experimental method that random errors will be most serious in the low density region. Hence, isothermal data below the critical pressure were used to fit a second-order virial equation of state ($Z = 1 + Bd + Cd^2$) for an error analysis. By minimizing the sum of squares of the residuals of $(Z - 1)/d$, the two coefficients were determined for each isotherm. These values of B and C were used to evaluate compressibility factors of the corresponding isotherms at the experimental densities, and the standard deviations and average absolute percentage deviations between the experimental and calculated values were computed (Table VI). In general, the standard deviation of each isotherm was less than 0.0005, except in the saturated and moderate density regions, where a higher order equation may be expected to be required.

SMOOTHED QUANTITIES

Smoothed Volume Residuals. The volume residuals were calculated from the experimental P-V-T data by the relation

$$\gamma = RT/P - V \tag{1}$$

The zero-pressure volume residual was evaluated from the second virial coefficients reported by Lin (*11*). Vapor state volume residuals were analytically smoothed and interpolated at fixed intervals of pressure for each isotherm. The technique consisted of least-squares fitting second (or third)-order polynomials in pressure to the four (or five) experimental volume residuals nearest to a desired interpolating pressure. Then the fitted polynomial was used to evaluate the volume residual at that pressure. The same order of polynomial was used throughout the whole isotherm, and the choice was dictated by the curvature of each isotherm as it appeared in the diagram of volume residual *vs.* pressure.

Volume residuals were interpolated at intervals of 0.25 atm. for each isotherm. The values so obtained were considered as smoothed volume residuals. The agreement of the interpolated values with experimental volume residual data was excellent, within ±0.01%. As an example of the interpolated results, a section of the critical isotherm represented by third-order polynomials is shown in Figure 4.

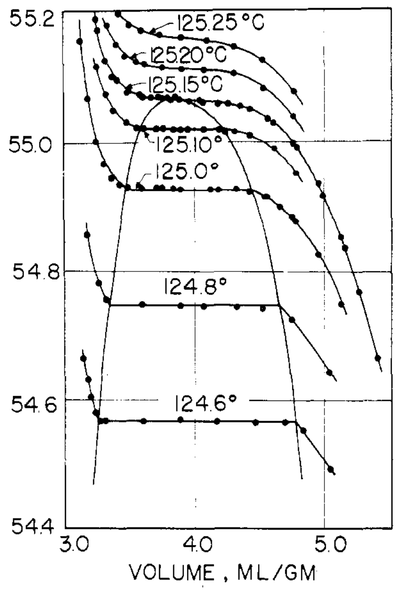

Figure 3. Specific volumes of cyclopropane in the critical region

Smoothed Compressibility Factors. The smoothed compressibility factors were calculated from the smoothed volume residuals by the relation

$$Z = 1 - P\gamma/RT \tag{2}$$

Table V. Intercomparison of Samples of Cyclopropane

125.15° C.

Sample[a] No.	P, atm.	Z, exptl.	Z, smoothed	Dev.
11	22.270	0.8433	0.8433	0.0000
9	23.492	0.8335	0.8335	0.0000
11	23.589	0.8327	0.8327	0.0000
11	24.916	0.8219	0.8219	0.0000
9	24.997	0.8213	0.8212	0.0001
11	26.285	0.8105	0.8105	0.0000
9	26.399	0.8097	0.8097	0.0000
9	27.895	0.7971	0.7971	0.0000
9	41.724	0.6585	0.6586	−0.0001
6	42.575	0.6485	0.6483	0.0002
9	43.124	0.6411	0.6412	−0.0001
6	44.027	0.6297	0.6296	0.0001
9	44.509	0.6228	0.6229	−0.0001
6	45.227	0.6133	0.6132	0.0001
9	45.791	0.6048	0.6049	−0.0001
6	46.143	0.6000	0.5999	0.0001
6	54.835	0.3645	0.3645	0.0000
7	54.852	0.3627	0.3626	0.0001
6	54.918	0.3528	0.3529	−0.0001
7	54.935	0.3506	0.3506	0.0000
7	54.992	0.3384	0.3384	0.0000
6	54.996	0.3369	0.3369	0.0000
7	55.030	0.3260	0.3262	−0.0002
6	55.036	0.3228	0.3227	0.0001
7	55.050	0.3135	0.3139	−0.0004

200° C.

Sample No.	P, atm.	Z, exptl.	Z, smoothed	Dev.
11	29.124	0.8885	0.8885	0.0000
9	29.329	0.8877	0.8877	0.0000
11	30.671	0.8824	0.8824	0.0000
9	31.021	0.8810	0.8810	0.0000
11	32.313	0.8757	0.8857	0.0000
9	32.916	0.8735	0.8734	0.0001
11	34.037	0.8689	0.8690	−0.0001
9	35.056	0.8650	0.8649	0.0001
9	55.288	0.7817	0.7817	0.0000
6	56.853	0.7751	0.7751	0.0000
9	57.251	0.7733	0.7733	0.0000
9	59.361	0.7643	0.7643	0.0000
6	60.031	0.7614	0.7614	0.0000
9	61.349	0.7557	0.7557	0.0000
6	64.211	0.7432	0.7432	0.0000
6	69.006	0.7222	0.7222	0.0000
6	107.968	0.5666	0.5666	0.0000
7	108.689	0.5645	0.5645	0.0000
7	114.397	0.5495	0.5495	0.0000
7	121.347	0.5356	0.5356	0.0000
6	127.232	0.5276	0.5275	0.0001
7	130.284	0.5243	0.5243	0.0000
6	141.278	0.5196	0.5195	0.0001
7	142.791	0.5191	0.5292	−0.0001

[a] Sample weights. No. 6 = 3.52671 g.
No. 7 = 8.58354 g.
No. 9 = 1.49991 g.
No. 11 = 0.47444 g.

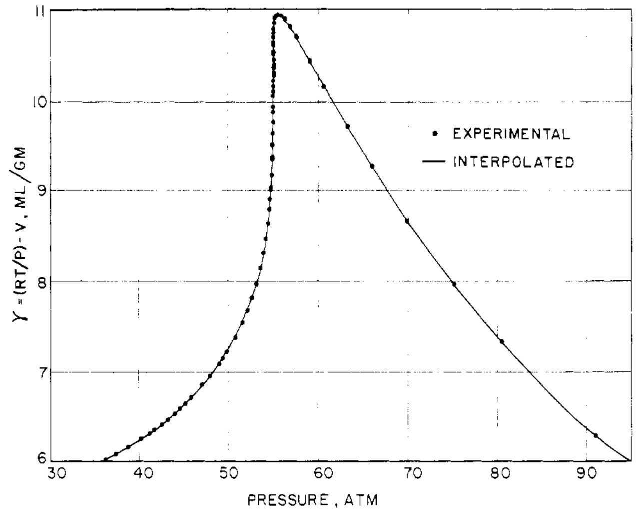

Figure 4. Comparison of experimental volume residuals with numerically interpolated results for the critical isotherm

The smoothed compressibility factors are presented along with the smoothed volume residuals and the fugacity coefficients in Table VII.

FUGACITY COEFFICIENTS

The fugacity coefficients of cyclopropane were calculated from the smoothed volume residuals by the equation

$$\nu = f/P = \exp\left(\frac{-1}{RT}\int_0^P \gamma\, dP\right) \qquad (3)$$

The integration was carried out numerically, applying the Newton-Cotes seven-point formula (5) with an integration interval of 0.25 atm. The saturated-state fugacity coefficients were obtained graphically by extrapolating the data of each isotherm to the corresponding vapor pressure. The fugacity coefficients so obtained are plotted in Figure 5 and presented in Table VII. The maximum error of values calculated from Equation 3 was estimated to be less than 0.1%.

Table VI. Random Error Analysis in Low Density Region with Equation, $Z = 1 + Bd + Cd^2$

Deviation = $Z_{\text{exptl}} - Z_{\text{calcd}}$

Temp., ° C.	Maximum Density, G. Mole/Liter	No. of Observations	B, Liters/G. Mole	C, (Liters/G. Mole)^2	Standard Deviation	Av. Absolute % Deviation
20	0.2912	4	−0.3744	−0.1005	0.0001	0.027
40	0.4665	9	−0.3337	−0.0126	0.0001	0.014
60	0.7537	14	−0.2992	+0.0137	0.0001	0.009
80	0.9312	21	−0.2684	0.0198	0.0002	0.025
	1.221	27	−0.2684	0.0198	0.0008	0.062
100	1.158	20	−0.2381	0.0178	0.0005	0.035
	1.939	28	−0.2381	0.0178	0.0024	0.204
120	1.654	31	−0.2130	0.0164	0.0002	0.019
	2.387	40	−0.2130	0.0164	0.0009	0.105
125.15	1.823	31	−0.2067	0.0158	0.0002	0.020
	2.353	37	−0.2067	0.0158	0.0011	0.092
140	2.008	36	−0.1913	0.0150	0.0002	0.022
	2.459	40	−0.1913	0.0150	0.0006	0.046
160	1.764	31	−0.1733	0.0144	0.0003	0.022
	2.143	37	−0.1733	0.0144	0.0009	0.079
180	1.671	30	−0.1570	0.0133	0.0002	0.015
	2.321	38	−0.1570	0.0133	0.0011	0.075
200	1.731	32	−0.1426	0.0124	0.0001	0.013
	2.461	40	−0.1426	0.0124	0.0007	0.042

Table VII. Smoothed Compressibility Factors, Volume Residuals, and Fugacity Coefficients of Cyclopropane

Volume residual, Ml./G.

	20° C.			40° C.			60° C.		
P, Atm.	Z	γ	f/P	Z	γ	f/P	Z	γ	f/P
1.5	0.9762	9.070	0.9768	0.9800	8.127	0.9805	0.9834	7.195	0.9836
3.0	0.9503	9.462	0.9534	0.9591	8.325	0.9608	0.9663	7.302	0.9673
4.5	0.9209	10.044	0.9293	0.9366	8.597	0.9411	0.9487	7.412	0.9510
6.0	0.8865	10.816	0.9043	0.9138	8.771	0.9212	0.9302	7.554	0.9347
6.233	0.8824	10.965	0.9001						
7.5				0.8891	9.028	0.9013	0.9111	7.701	0.9184
9.0				0.8626	9.321	0.8813	0.8913	7.844	0.9021
10.5				0.8308	9.837	0.8609	0.8708	7.996	0.8857
12.0							0.8491	8.171	0.8693
13.5							0.8261	8.366	0.8529
15.0							0.8016	8.591	0.8364
16.5							0.7743	8.885	0.8197
16.603							0.7704	8.975	0.8186
	80° C.			100° C.			120° C.		
1.5	0.9860	6.431	0.9862	0.9882	5.747	0.9883	0.9900	5.099	0.9901
3.0	0.9716	6.512	0.9724	0.9760	5.809	0.9766	0.9799	5.134	0.9802
4.5	0.9572	6.553	0.9586	0.9637	5.863	0.9649	0.9696	5.171	0.9704

(*continued*)

Table VII. (*Continued*)

	80° C.			100° C.			120° C.		
P, Atm.	Z	γ	f/P	Z	γ	f/P	Z	γ	f/P
6.0	0.9419	6.668	0.9449	0.9511	5.936	0.9532	0.9596	5.168	0.9607
7.5	0.9264	6.762	0.9312	0.9387	5.946	0.9416	0.9487	5.247	0.9509
9.0	0.9107	6.830	0.9175	0.9260	5.979	0.9301	0.9378	5.301	0.9412
10.5	0.8945	6.917	0.9038	0.9129	6.037	0.9187	0.9270	5.330	0.9314
12.0	0.8778	7.012	0.8902	0.8994	6.097	0.9073	0.9162	5.355	0.9217
13.5	0.8606	7.110	0.8766	0.8859	6.151	0.8959	0.9050	5.393	0.9121
15.0	0.8428	7.214	0.8631	0.8720	6.211	0.8846	0.8936	5.439	0.9025
16.5	0.8242	7.336	0.8495	0.8575	6.282	0.8732	0.8822	5.475	0.8929
18.0	0.8051	7.457	0.8359	0.8427	6.359	0.8619	0.8704	5.520	0.8834
19.5	0.7847	7.602	0.8223	0.8274	6.441	0.8506	0.8583	5.571	0.8738
21.0	0.7628	7.777	0.8087	0.8155	6.392	0.8395	0.8460	5.622	0.8643
22.5	0.7390	7.985	0.7949	0.7970	6.563	0.8283	0.8333	5.679	0.8548
24.0	0.7154	8.164	0.7811	0.7788	6.706	0.8170	0.8206	5.729	0.8453
24.954	0.6886	8.585	0.7717						
27.0				0.7432	6.921	0.7944	0.7942	5.842	0.8264
30.0				0.7032	7.199	0.7716	0.7662	5.975	0.8075
33.0				0.6569	7.565	0.7485	0.7362	6.128	0.7886
36.0				0.5998	8.089	0.7248	0.7038	6.306	0.7697
36.048				0.5982	8.109	0.7244			
39.0							0.6684	6.517	0.7506
42.0							0.6280	6.790	0.7313
45.0							0.5814	7.131	0.7117
48.0							0.5217	7.639	0.6915
50.583							0.4270	8.684	0.6729

	125.15° C.			140° C.			160° C.		
6	0.9609	5.057	0.9622	0.9660	4.558	0.9664	0.9700	4.224	0.9708
12	0.9200	5.179	0.9249	0.9293	4.747	0.9333	0.9394	4.266	0.9420
18	0.8765	5.327	0.8881	0.8915	4.857	0.9005	0.9078	4.326	0.9137
24	0.8294	5.519	0.8516	0.8513	4.992	0.8681	0.8749	4.402	0.8858
30	0.7787	5.729	0.8154	0.8091	5.128	0.8360	0.8408	4.482	0.8583
36	0.7217	6.005	0.7793	0.7635	5.292	0.8042	0.8053	4.568	0.8312
42	0.6553	6.374	0.7430	0.7134	5.498	0.7725	0.7677	4.672	0.8043
48	0.5708	6.945	0.7059	0.6571	5.756	0.7408	0.7277	4.791	0.7778
54	0.4222	8.309	0.6663	0.5910	6.102	0.7089	0.6848	4.929	0.7514
60	0.2042	10.301	0.6151	0.5079	6.608	0.6762	0.6383	5.092	0.7251
66	0.2116	9.277	0.5703	0.3913	7.430	0.6419	0.5877	5.276	0.6989
72	0.2227	8.385	0.5328	0.2945	7.894	0.6058	0.5332	5.476	0.6727
78	0.2352	7.615	0.5009	0.2748	7.490	0.5720	0.4766	5.667	0.6466
84	0.2486	6.947	0.4735	0.2763	6.941	0.5421	0.4263	5.769	0.6208
90	0.2613	6.374	0.4498	0.2865	6.387	0.5159	0.3918	5.707	0.5959
96	0.2752	5.864	0.4290	0.2958	5.909	0.4928	0.3746	5.502	0.5726
102	0.2892	5.412	0.4107	0.3083	5.463	0.4724	0.3670	5.241	0.5512
108	0.3053	4.996	0.3946	0.3208	5.066	0.4542	0.3687	4.937	0.5316
114	0.3203	4.631	0.3802	0.3335	4.710	0.4380	0.3717	4.655	0.5138
120	0.3269	4.356	0.3672	0.3422	4.416	0.4234	0.3798	4.365	0.4976
126	0.3430	4.049	0.3555	0.3566	4.114	0.4101	0.3887	4.098	0.4829
132	0.3587	3.773	0.3449	0.3708	3.840	0.3982	0.3977	3.854	0.4694
138	0.3663	3.566	0.3353	0.3787	3.627	0.3873	0.4076	3.626	0.4571
144	0.3826	3.330	0.3265	0.3938	3.391	0.3773	0.4179	3.414	0.4459
150	0.3985	3.114	0.3184	0.4087	3.176	0.3682	0.4282	3.219	0.4355
156	0.4037	2.969	0.3111	0.4140	3.026	0.3598	0.4397	3.034	0.4259
162	0.4184	2.788	0.3042	0.4279	2.845	0.3520	0.4512	2.861	0.4171
168	0.4332	2.620	0.2980	0.4420	2.676	0.3449	0.4602	2.714	0.4089
174	0.4479	2.464	0.2922	0.4560	2.519	0.3383	0.4722	2.562	0.4013
180	0.4622	2.320	0.2868	0.4697	2.374	0.3321	0.4843	2.420	0.3943
186	0.4701	2.213	0.2818	0.4773	2.264	0.3264	0.4932	2.301	0.3878
192	0.4840	2.087	0.2772	0.4907	2.137	0.3211	0.5055	2.175	0.3816
198	0.4980	1.969	0.2729	0.5041	2.018	0.3162	0.5178	2.057	0.3759
204	0.5117	1.859	0.2689	0.5173	1.906	0.3116	0.5300	1.946	0.3706
210	0.5212	1.771	0.2651	0.5265	1.817	0.3073	0.5388	1.855	0.3657
216	0.5346	1.673	0.2616	0.5393	1.718	0.3033	0.5508	1.757	0.3610
222	0.5480	1.581	0.2583	0.5523	1.625	0.2996	0.5629	1.663	0.3566
228	0.5613	1.494	0.2553	0.5651	1.537	0.2961	0.5749	1.575	0.3526
234	0.5717	1.421	0.2524	0.5752	1.462	0.2928	0.5845	1.500	0.3487
240	0.5847	1.344	0.2498	0.5878	1.384	0.2897	0.5963	1.421	0.3452
246	0.5977	1.270	0.2472	0.6003	1.309	0.2868	0.6082	1.345	0.3418
252	0.6106	1.200	0.2449	0.6129	1.238	0.2841	0.6200	1.273	0.3386
258	0.6235	1.133	0.2427	0.6253	1.170	0.2816	0.6318	1.205	0.3356
264	0.6343	1.076	0.2406	0.6357	1.112	0.2792	0.6417	1.146	0.3329
270	0.6469	1.016	0.2387	0.6480	1.050	0.2769	0.6534	1.084	0.3302

(continued on page 488)

Table VII. (*Continued*)

	125.15° C.			140° C.			160° C.		
P, Atm.	Z	γ	f/P	Z	γ	f/P	Z	γ	f/P
276	0.6596	0.9578	0.2369	0.6603	0.9915	0.2748	0.6651	1.025	0.3278
282	0.6722	0.9027	0.2352	0.6725	0.9355	0.2729	0.6767	0.9684	0.3254
288	0.6847	0.8503	0.2336	0.6846	0.8822	0.2710	0.6882	0.9145	0.3233
294	0.6970	0.8005	0.2321	0.6965	0.8316	0.2693	0.6995	0.8633	0.3212
300	0.7090	0.7535	0.2307	0.7081	0.7838	0.2677	0.7106	0.8148	0.3193
306	0.7206	0.7090	0.2294	0.7195	0.7386	0.2662	0.7214	0.7690	0.3175
312	0.7319	0.6673	0.2282	0.7304	0.6961	0.2648	0.7318	0.7259	0.3159

	180° C.			200° C.		
P, Atm.	Z	γ	f/P	Z	γ	f/P
6	0.9743	3.791	0.9748	0.9778	3.427	0.9781
12	0.9480	3.829	0.9498	0.9550	3.462	0.9564
18	0.9210	3.878	0.9253	0.9323	3.471	0.9351
24	0.8937	3.913	0.9011	0.9087	3.509	0.9141
30	0.8655	3.961	0.8773	0.8850	3.537	0.8934
36	0.8366	4.010	0.8539	0.8612	3.558	0.8730
42	0.8068	4.064	0.8308	0.8370	3.580	0.8530
48	0.7760	4.124	0.8080	0.8123	3.608	0.8333
54	0.7441	4.187	0.7856	0.7872	3.636	0.8139
60	0.7109	4.257	0.7634	0.7615	3.667	0.7948
66	0.6765	4.332	0.7414	0.7354	3.699	0.7760
72	0.6410	4.405	0.7198	0.7090	3.728	0.7574
78	0.6051	4.473	0.6984	0.6827	3.753	0.7392
84	0.5696	4.528	0.6774	0.6566	3.771	0.7214
90	0.5358	4.557	0.6568	0.6315	3.778	0.7039
96	0.5063	4.544	0.6368	0.6076	3.771	0.6868
102	0.4825	4.483	0.6175	0.5858	3.747	0.6702
108	0.4656	4.372	0.5992	0.5665	3.703	0.6542
114	0.4554	4.221	0.5820	0.5504	3.638	0.6387
120	0.4498	4.051	0.5659	0.5380	3.552	0.6239
126	0.4478	3.872	0.5508	0.5289	3.449	0.6099
132	0.4508	3.676	0.5369	0.5230	3.334	0.5966
138	0.4540	3.496	0.5240	0.5198	3.210	0.5840
144	0.4591	3.319	0.5120	0.5192	3.080	0.5722
150	0.4661	3.145	0.5009	0.5205	2.949	0.5611
156	0.4733	2.983	0.4906	0.5231	2.820	0.5507
162	0.4813	2.829	0.4810	0.5271	2.693	0.5409
168	0.4903	2.681	0.4721	0.5321	2.569	0.5317
174	0.4996	2.541	0.4638	0.5380	2.450	0.5231
180	0.5093	2.409	0.4560	0.5449	2.333	0.5150
186	0.5192	2.284	0.4488	0.5520	2.222	0.5075
192	0.5283	2.171	0.4421	0.5597	2.116	0.5004
198	0.5388	2.058	0.4358	0.5677	2.014	0.4937
204	0.5495	1.951	0.4299	0.5762	1.917	0.4874
210	0.5579	1.860	0.4244	0.5849	1.824	0.4815
216	0.5687	1.764	0.4192	0.5933	1.737	0.4760
222	0.5795	1.673	0.4143	0.6025	1.652	0.4708
228	0.5905	1.587	0.4098	0.6119	1.570	0.4659
234	0.5995	1.512	0.4055	0.6214	1.493	0.4612
240	0.6103	1.435	0.4014	0.6299	1.423	0.4569
246	0.6213	1.360	0.3976	0.6397	1.351	0.4528
252	0.6323	1.289	0.3941	0.6495	1.283	0.4489
258	0.6432	1.222	0.3907	0.6594	1.218	0.4453
264	0.6526	1.163	0.3876	0.6682	1.159	0.4419
270	0.6635	1.101	0.3846	0.6782	1.100	0.4386
276	0.6744	1.042	0.3818	0.6882	1.042	0.4356
282	0.6853	0.9861	0.3792	0.6982	0.9872	0.4327
288	0.6961	0.9324	0.3767	0.7082	0.9346	0.4300
294	0.7068	0.8813	0.3744	0.7182	0.8845	0.4275
300	0.7173	0.8328	0.3723	0.7279	0.8367	0.4251
306	0.7275	0.7869	0.3702	0.7375	0.7913	0.4229
312	0.7374	0.7435	0.3683	0.7469	0.7484	0.4207

	130° C.		135° C.		145° C.		150° C.	
P, Atm.	Z	γ	Z	γ	Z	γ	Z	γ
39	0.7077	5.891	0.7243	5.627	. . .	. . .		
45	0.6431	6.235	0.6660	5.907	0.7040	5.363	0.7200	5.133
51	0.5607	6.771	0.5967	6.293	0.6498	5.598	0.6709	5.324
57	0.4300	7.861	0.5058	6.900	0.5874	5.902	0.6162	5.555
63	0.2316	9.588	0.3512	8.195	0.5121	6.315	0.5533	5.850
69	0.2299	8.773	0.2594	8.542	0.4183	6.874	0.4802	6.216
75	0.2387	7.980	0.2538	7.918	0.3345	7.235	0.4020	6.579

(*continued*)

Table VII. (*Continued*)

P, Atm.	130° C. Z	130° C. γ	135° C. Z	135° C. γ	145° C. Z	145° C. γ	150° C. Z	150° C. γ
81	0.2494	7.285	0.2557	7.313	0.3043	7.003	0.3480	6.642
87	0.2614	6.674	0.2693	6.684	0.2977	6.582	0.3271	6.382
93	0.2769	6.112	0.2805	6.157	0.3032	6.109	0.3213	6.021
99	0.2922	5.620	0.2942	5.674	0.3087	5.693	0.3255	5.621
105	0.3059	5.196	0.3088	5.239	0.3223	5.263	0.3321	5.248
111	0.3165	4.840	0.3232	4.853	0.3328	4.901	0.3393	4.911
117	...	...	0.3362	4.515	0.3442	4.570	0.3492	4.590
123	...	...	0.3467	4.227	0.3560	4.269	0.3614	4.284
129	...	...	0.3537	3.987	0.3674	3.998	0.3758	3.993

Table VIII. Orthobaric Densities of Cyclopropane

Temp., ° C.	Vapor Density, G./Ml. Exptl.	Vapor Density, G./Ml. Calcd.	Vapor Density, G./Ml. Exptl.-calcd.	Liquid Density, G./Ml. Exptl.	Liquid Density, G./Ml. Calcd.	Liquid Density, G./Ml. Exptl.-calcd.
20	0.01240	0.01320	−0.00080	0.6268	0.6256	0.0012
25	0.01413	0.01457	−0.00044	0.6191	0.6184	0.0007
30	0.01607	0.01621	−0.00014	0.6112	0.6110	0.0002
35	0.01826	0.01814	+0.00012	0.6030	0.6033	−0.0003
40	0.02070	0.02035	0.00035	0.5948	0.5953	−0.0005
45	0.02336	0.02289	0.00047	0.5864	0.5870	−0.0006
50	0.02636	0.02576	0.00060	0.5776	0.5784	−0.0008
55	0.02957	0.02899	0.00058	0.5687	0.5694	−0.0007
60	0.03309	0.03263	0.00046	0.5592	0.5600	−0.0008
65	0.03714	0.03669	0.00045	0.5495	0.5501	−0.0006
70	0.04146	0.04124	0.00022	0.5395	0.5398	−0.0003
75	0.04648	0.04633	0.00015	0.5287	0.5289	−0.0002
80	0.05195	0.05203	−0.00008	0.5175	0.5174	+0.0001
85	0.05820	0.05844	−0.00024	0.5055	0.5052	0.0003
90	0.06527	0.06570	−0.00043	0.4927	0.4922	0.0005
95	0.07337	0.07398	−0.00061	0.4787	0.4781	0.0006
100	0.08290	0.08357	−0.00067	0.4636	0.4627	0.0009
105	0.09394	0.09489	−0.00095	0.4469	0.4456	0.0013
110	0.1078	0.1087	−0.0009	0.4283	0.4260	0.0023
115	0.1259	0.1265	−0.0006	0.4033	0.4024	0.0009
120	0.1524	0.1524	+0.0000	0.3707	0.3707	0.0000
124.00	0.1959	0.1936	0.0023	0.3225	0.3248	−0.0023
124.20	0.1993	0.1976	0.0017	0.3181	0.3206	0.0025
124.40	0.2033	0.2022	0.0011	0.3134	0.3158	−0.0024
125.10	0.2373	0.2356	0.0017	0.2805	0.2815	−0.0010
125.15	0.2585	0.2586	−0.0001	0.2585	0.2586	−0.0001

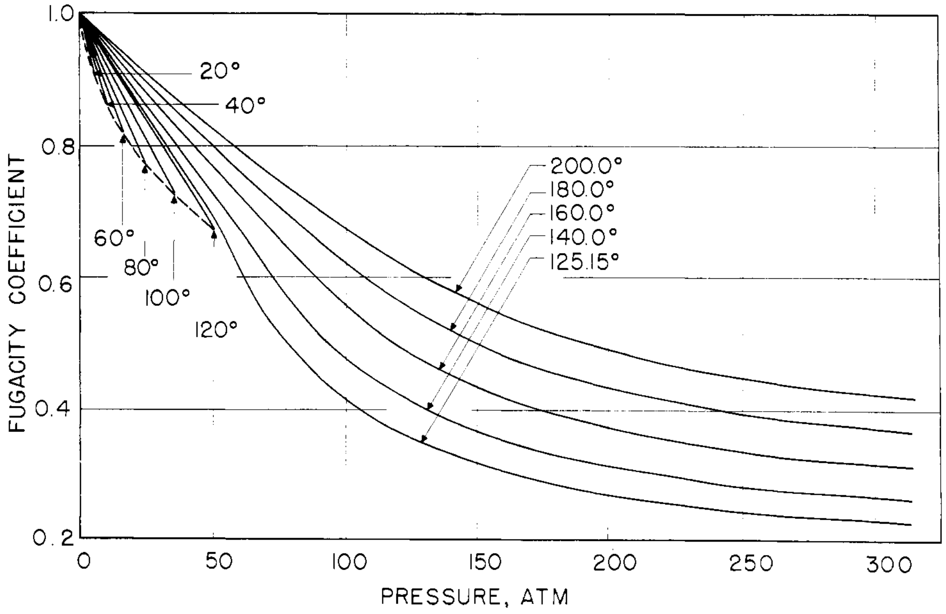

Figure 5. Fugacity coefficients of cyclopropane

Table IX. Critical Properties of Cyclopropane

	This work	Booth and Morris (2)	Matheson Co. (*12*)
T_c, °C.	125.15 ± 0.02	124.65	124.4
P_c, atm.	55.065 ± 0.02	54.23	54.2
V_c, ml./g.	3.868 ± 0.01		

Table X. Vapor Pressure of Cyclopropane

Pressure Units, Atm.

Temp., °C.	Exptl.	Nernst Eq. Calcd.	Nernst Eq. Dev.	Antoine Eq. Calcd.	Antoine Eq. Dev.
20	6.233	6.229	0.004	6.262	–0.029
25	7.151	7.150	0.001	7.164	–0.013
30	8.165	8.166	–0.001	8.163	0.002
35	9.281	9.284	–0.003	9.265	0.016
40	10.503	10.508	–0.005	10.478	0.025
45	11.837	11.846	–0.009	11.808	0.029
50	13.297	13.302	–0.005	13.262	0.035
55	14.884	14.885	–0.001	14.847	0.037
60	16.603	16.601	0.002	16.570	0.033
65	18.462	18.456	0.006	18.438	0.024
70	20.470	20.459	0.010	20.459	0.011
75	22.629	22.617	0.012	22.638	–0.009
80	24.954	24.940	0.014	24.984	–0.030
85	27.453	27.434	0.019	27.503	–0.050
90	30.127	30.111	0.016	30.202	–0.075
95	32.988	32.980	0.008	33.089	–0.101
100	36.048	36.052	–0.004	36.170	–0.122
105	39.292	39.339	–0.047	39.452	–0.160
110	42.784	42.852	–0.068	42.941	–0.157
115	46.567	46.606	–0.039	46.645	–0.078
120	50.583	50.614	–0.031	50.569	0.014
125	54.927	54.891	0.036	54.721	0.206
125.10	55.020	54.979	0.041	54.806	0.214
125.15	55.065	55.024	0.041	54.849	0.216
Av. deviation, %			0.053		0.23

Table XI. Heat and Entropy of Vaporization for Cyclopropane

Temp., °C.	ΔH_v, Cal./G. Exptl.	ΔH_v, Cal./G. Calcd.	ΔH_v, Cal./G. Dev.	ΔS_v, Cal./G.-° C.
20	98.255	98.314	–0.059	0.33537
25	96.673	96.485	0.188	0.32361
30	94.857	94.603	0.254	0.31207
35	92.749	92.663	0.086	0.30071
40	90.504	90.658	–0.154	0.28950
45	88.437	88.582	–0.145	0.27843
50	86.057	86.427	–0.370	0.26745
55	83.966	84.183	–0.217	0.25654
60	81.856	81.841	0.015	0.24566
65	79.269	79.384	–0.115	0.23476
70	76.942	76.798	0.144	0.22380
75	74.089	74.062	0.027	0.21273
80	71.300	71.151	0.149	0.20148
85	68.159	68.031	0.128	0.18995
90	64.792	64.656	0.136	0.17804
95	61.093	60.964	0.129	0.16560
100	56.886	56.865	0.021	0.15239
105	52.322	52.215	0.107	0.13808
110	46.785	46.770	0.015	0.12207
115	39.849	40.043	–0.194	0.10316
120	30.479	30.739	–0.260	0.07819
124	16.812	17.063	–0.251	0.04296
124.2	15.760	15.826	–0.066	0.03983
124.4	14.577	14.418	0.159	0.03627
125.1	5.538	4.944	0.594	0.01242

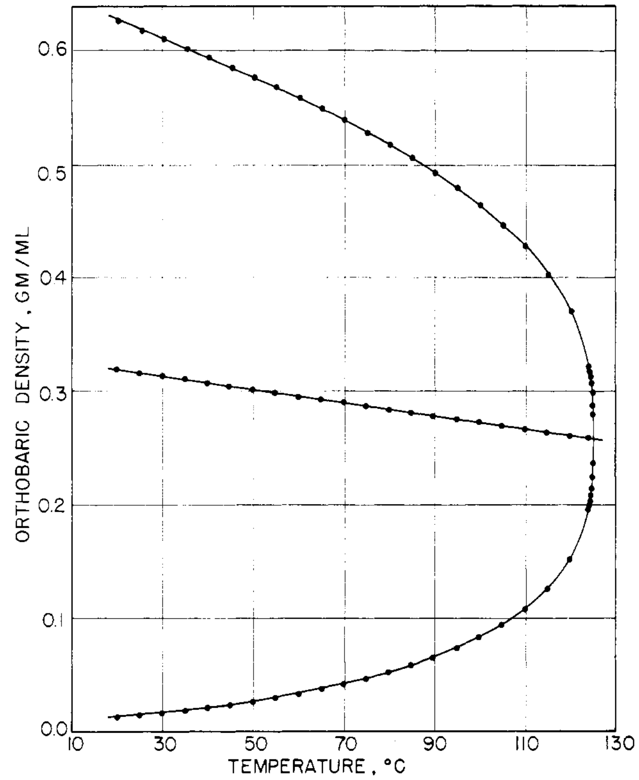

Figure 6. Orthobaric densities of cyclopropane

ORTHOBARIC DENSITIES

The orthobaric densities of cyclopropane at each temperature were found by extrapolating each pressure-volume isotherm to its vapor pressure. The densities were determined from 20° to 120° C. at 5° C. increments and from 124.0° to 125.1° C. with fine increments of temperature. The results were correlated by the least-squares method to the following two equations.

$$\tfrac{1}{2}(d_l + d_g) = 2.58558 \times 10^{-1} + 5.80779 \times 10^{-4}(t_c - t) - 2.23584 \times 10^{-8}(t_c - t)^2 \quad (4)$$

and

$$\tfrac{1}{2}(d_l - d_g) = 6.22176 \times 10^{-2}(t_c - t)^{1/3} + 3.43601 \times 10^{-4}(t_c - t) - 2.13549 \times 10^{-6}(t_c - t)^2 \quad (5)$$

The standard errors of the regressions were 0.00024 gram per ml. for Equation 4 and 0.00097 gram per ml. for Equation 5. The smoothed orthobaric densities of cyclopropane were then calculated from these two equations. The calculated orthobaric densities, the observed densities, and their deviations are presented in Table VIII and plotted in Figure 6. The average absolute deviation for vapor densities was less then 0.001 gram per ml., or 0.5%, and for liquid densities was also less than 0.001 gram per ml., or 0.2%.

CRITICAL CONSTANTS

The critical temperature and pressure were determined graphically from Figure 3. With the aid of the orthobaric density plot (Figure 6), the critical volume was determined. The critical constants reported in the literature (*2, 12*) are compared with those obtained in this investigation in Table IX.

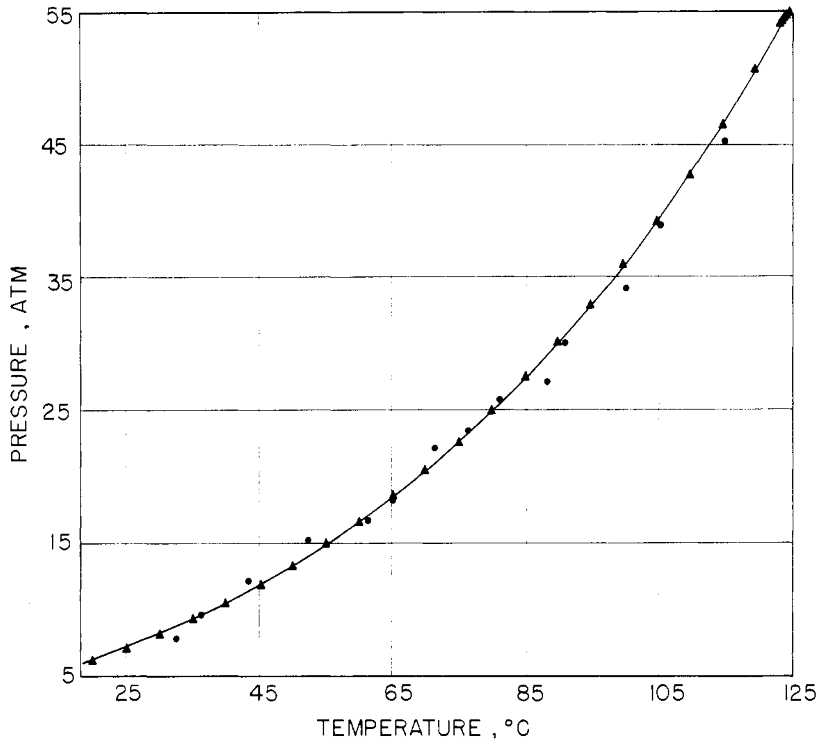

Figure 7. Vapor pressures of cyclopropane

▲ This work

● Booth and Morris (2)

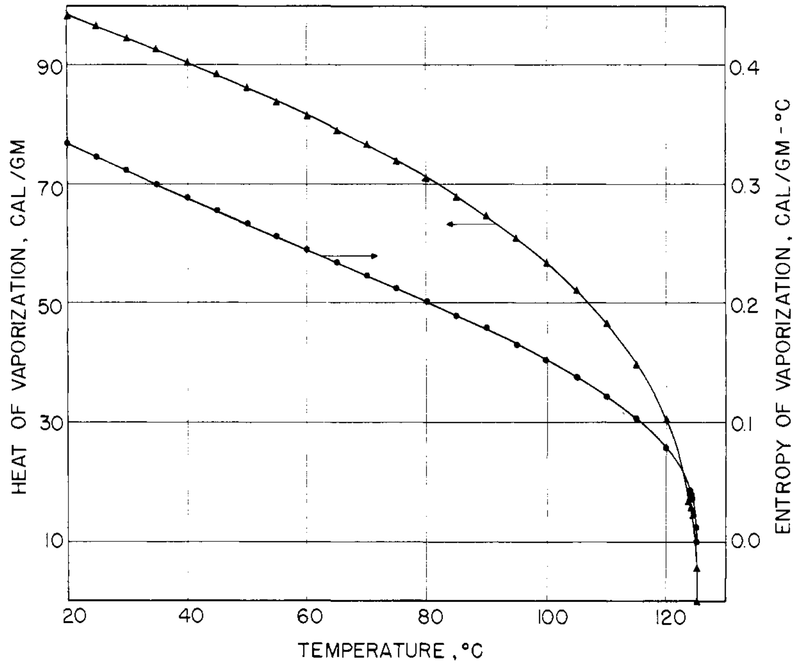

Figure 8. Heats and entropies of vaporization for cyclopropane

VAPOR PRESSURES

The experimental vapor pressure at each temperature was determined from the graph of pressure *vs.* specific volume from the data of Tables III and IV. These values then were correlated by the least-squares method to the Antoine equation,

$$\log_{10}P = 7.52692 - 1248.45/(304.330 + t) \qquad (6)$$

and the Nernst equation,

$$\log_{10}P = 30.7012 - 1.94638 \times 10^{3}/T - 9.66071 \log_{10}T + 6.59279 \times 10^{-6}T^{2} \qquad (7)$$

The standard errors of the regression were 0.00114 for Equation 6 and 0.00027 for Equation 7. The experimental vapor pressures are compared with the calculated values in Table X and plotted in Figure 7 along with the data reported by Booth and Morris (*2*).

HEATS AND ENTROPIES OF VAPORIZATION

The heat of vaporization for cyclopropane was calculated from the Nernst equation and the experimental orthobaric density data using the Clapeyron equation,

$$\Delta H_v = JT(V_g - V_l)\, dP/dT \qquad (8)$$

The entropy of vaporization was calculated from the relation

$$\Delta S_v = H_v/T = J(V_g - V_l)\, dP/dT \qquad (9)$$

The results are shown in Table XI and plotted in Figure 8. The maximum possible error in the values obtained from Equation 8 or 9 is believed less than 0.5%.

The heats of vaporization so evaluated were correlated by the least squares methods to the equation

$$\Delta H_v = -5.23241 \times 10^{-2}(t_c - t) + 1.30462 \times 10^{-4}(t_c - t)^2 + 16.2013(t_c - t)^{0.386} \qquad (10)$$

Deviations between experimental values and those calculated from Equation 10 are shown in Table XI. The average absolute deviation is 0.71%, while the standard error of the regressions was found to be 0.90 cal per gram.

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The Phillips Petroleum Co. supplied the high-purity cyclopropane. The Gulf Oil Corp. contributed to the research equipment used in this study, and the Gulf Research and Development Co. provided fellowship support. The authors are grateful for their contributions.

NOMENCLATURE

d = molal density, g.-mole/liter
f = fugacity, atm.
ΔH_v = heat of vaporization, cal./g.
J = dimensional constant, 0.0242179 cal./ml. atm.
R = gas constant of cyclopropane, 1.9498804 atm. ml./° K.-g.
P = pressure, atm.
ΔS_v = entropy of vaporization, cal./g.° C.
T = absolute temperature, ° K.
t = temperature, ° C.
V = specific volume, ml./g.
Z = compressibility factor, PV/RT
γ = volume residual, ml./g.
ν = fugacity coefficient, f/P

Subscripts

c = critical state
g = saturated vapor state
l = saturated liquid state

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Liquid-Vapor Equilibria in the Sodium-Lead System

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Total vapor pressure measurements were made on liquid Na-Pb alloys of compositions from 0.15 to 0.90 atom fraction sodium, and at temperatures from 480 to 998° C. Transpiration experiments were done at 853° C on liquids containing 0.1, 0.2, and 0.3 atom fraction sodium. Activities for sodium were calculated directly from the data, and activity coefficients for lead were obtained by a graphical Gibbs-Duhem integration.

Thermodynamic information for the sodium-lead system as determined from measurements on liquid-vapor equilibria is reported in a sequel to our earlier study of the sodium-bismuth system (*4*). An "interpretation" of the data in terms of a quasi-ideal solution model is possible, and has been applied successfully. However, the unsupported assumption of the treatment, that of a pseudo-compound in a liquid metal, becomes very tenuous in the case of the sodium-lead system, and the treatment is omitted here, in order not to lend apparent credence to the assumption. Our position is one of suspended judgment; if and when independent measurements confirm the existence and nature of the particular intermetallic species involved in a system, a meaningful quasi-ideal solution treatment may be possible.

EXPERIMENTAL

Vapor-liquid equilibrium data were obtained from total vapor pressure measurements made by the quasi-static method (*3*) and from transpiration experiments performed in equipment described earlier (*4*). The total pressure measurements provided vapor pressures as a function of