Pressure-Volume-Temperature Properties of Methyl Chloride

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P-V-T properties of methyl chloride were determined using a Beattie apparatus. The temperature range was 35° to 225° C. and the pressure range was from six to 310 atm. Vapor pressures were measured from 30° C. to the critical temperature at 5° increments. These data were used to derive the orthobaric densities, the latent heats of vaporization, and the fugacity coefficients. The constants for three empirical equations of state, as well as the critical constants, are also presented.

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EXPERIMENTAL

Method. The compressibility equipment used in this investigation is essentially the same as Beattie's (*1*). A description of the apparatus, the calibration, and the operation has been given (*6, 7, 9*). The estimated over-all error in the compressibility measurements varied from 0.1% to 0.3%. The error in the vapor pressure measurements was estimated at 0.01 atm.

Material. The purity of the original methyl chloride sample was 99.7%. Further purification of the sample was accomplished by bubbling it through a 95 to 98% H_2SO_4 scrubbing tower, then through a scrubber packed with alternating layers of glass wool and anhydride phosphorus pentoxide, and condensing it in a receiver. The sample used in the measurements was a center cut which had a purity of at least 99.9% as shown by mass-spectroscopic analysis.

PHYSICAL CONSTANTS

The fundamental constants and conversion factors used throughout this work were given by Rossini (*13*). The molecular weight of methyl chloride, 50.48806, is based on the newest atomic weight scale (*5*). The new absolute temperature scale, 0° C. = 273.15° K., was not used because the platinum resistance thermometer was calibrated by the National Bureau of Standards in terms of the International Temperature Scale, for which the ice point is 273.16° K.

COMPRESSIBILITY FACTORS

The compressibility factors of methyl chloride in the gaseous state were measured from 35° to 225° C. Below the critical isotherm, the compressibilities were measured at pressures up to the corresponding vapor pressure at 5° increments, and above the critical isotherm, the measurements were extended to 310 atm. at 25° increments with the exception of the four isotherms, 155°, 160°, 165°, and 170° C., where the pressure range was from 50 to 140 atm. These experimental results are shown in Figure 1.

The compressibility data were smoothed using the smoothed volume residuals:

$$Z = 1 - \frac{\gamma P}{RT} \qquad (1)$$

The smoothed volume residuals were obtained graphically from plotting the volume residuals, calculated from experimental *P-V-T* data, *vs.* pressure on a large scale graph. The smoothed compressibility factors are given in Table I.

LIQUID *P-V-T* DATA

In the liquid phase, the specific volumes for four isotherms, 50°, 75°, 100°, and 125° C. were measured from the saturated liquid pressure to 310 atm. Figure 2 is the *P-V* diagram showing both the liquid and gas specific volumes from 1.1 to 3.0 $cm.^3$ per gram. The experimental data are given in Table II.

ISOTHERMS IN THE CRITICAL REGION

In order to determine the critical constants of methyl chloride, eight isotherms, (142.2°, 142.4°, 142.6°, 142.8°, 142.9°, 143.00°, 143.05°, and 143.10° C.) were measured at small pressure intervals. Figure 3 is the plot of the *P-V* isotherms from the data in Table III. With this plot and with the aid of the orthobaric density plot (Figure 4), the critical constants of methyl chloride were determined and given in Table V.

VAPOR PRESSURES

The vapor pressures of methyl chloride were measured over a temperature range from 30° C. to the critical temperature, 143.10° C., at 5° intervals. At each temperature, the pressure was measured with different fractions of vapor condensed, and the results were averaged to give the observed vapor pressure at that temperature.

The observed vapor pressure data were correlated using the following equation:

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$$\log P = -6.27772154 - 650.828951/T$$
$$+ 3.76725649 \log T - 0.0000119952882\, T^2 \quad (2)$$

The maximum difference between the observed vapor pressure and the value calculated from Equation 2 was 0.018 atm., with an average deviation of 0.006 atm. (see Table IV). The vapor pressures given in the International Critical Tables (*10*) are persistently lower, varying from 0.3 to 2.65% as the temperature decreases. The Methyl Chloride Manual (*12*) gives lower vapor pressures at lower temperatures with a deviation of about 1%, while at higher temperatures the values agree with the calculated values from Equation 2.

DERIVED QUANTITIES

Orthobaric Densities. The observed orthobaric densities of methyl chloride, given in Table V, were obtained by extrapolating each P-V isotherm to its vapor pressure in

Table I. Smoothed Compressibility Factors of Methyl Chloride

Press., Atm.	Z 35° C.	40° C.	45° C.	50° C.	55° C.
1	0.9840	0.9848	0.9855	0.9863	0.9872
2	0.9676	0.9693	0.9707	0.9725	0.9742
3	0.9509	0.9535	0.9560	0.9585	0.9611
4	0.9338	0.9374	0.9409	0.9442	0.9478
5	0.9160	0.9209	0.9256	0.9298	0.9343
6	0.8974	0.9039	0.9099	0.9152	0.9206
7.452	0.8680				
7			0.8939	0.9002	0.9066
8			0.8772	0.8849	0.8921
8.483		0.8610			
9				0.8690	0.8771
9.624			0.8499		
10					0.8616
10.881				0.8374	
11					0.8456
12					0.8269
12.262					0.8226
	60° C.	65° C.	75° C.	100° C.	125° C.
2.	0.9759	0.9773	0.9795	0.9837	0.9871
4	0.9511	0.9539	0.9587	0.9671	0.9740
6	0.9257	0.9299	0.9365	0.9502	0.9606
8	0.8989	0.9048	0.9152	0.9329	0.9471
10	0.8705	0.8784	0.8919	0.9152	0.9333
12	0.8408	0.8505	0.8673	0.8971	0.9194
13.776	0.8119				
14		0.8205	0.8416	0.8785	0.9051
15.429		0.7960			
16			0.8147	0.8593	0.8907
18			0.7852	0.8395	0.8760
19.190			0.7651		
20				0.8191	0.8610
22				0.7980	0.8458
24				0.7759	0.8801
26				0.7528	0.8184
28				0.7285	0.7975
30				0.7017	0.7799
31.633				0.6775	
32					0.7617
34					0.7426
36					0.7226
38					0.7015
40					0.6789
42					0.6549
44					0.6285
46					0.5993
48					0.5653
49.273					0.5382
		160° C.	165° C.	170° C.	
50	0.6975	0.7138	0.7289	0.7424	
55	0.6569	0.6766	0.6945	0.7104	
60	0.6110	0.6364	0.6576	0.6769	
65	0.5582	0.5914	0.6180	0.6414	
70	0.4951	0.5394	0.5741	0.6030	
75	0.4089	0.4783	0.5249	0.5614	
80	0.3025	0.4045	0.4693	0.5156	
85	0.2632	0.3288	0.4070	0.4653	
90	0.2566	0.2915	0.3507	0.4143	
95	0.2577	0.2797	0.3179	0.3708	
100	0.2671	0.2781	0.3055	0.3431	
105	0.2742	0.2841	0.3011	0.3285	
110	0.2770	0.2881	0.3027	0.3248	
115	0.2819	0.2919	0.3054	0.3238	
120	0.2871	0.2964	0.3100	0.3246	
125	0.2932	0.3017	0.3158	0.3275	
130	0.3017	0.3085	0.3222	0.3322	
135	0.3115	0.3173	0.3295	0.3380	
140	0.3220	0.3270	0.3361	0.3461	

Press., Atm.	Z 143.1° C.	150° C.	175° C.	200° C.	225° C.
1	0.9944	0.9950	0.9955	0.9964	0.9971
3	0.9831	0.9849	0.9866	0.9891	0.9912
5	0.9718	0.9747	0.9777	0.9818	0.9853
10	0.9428	0.9481	0.9552	0.9634	0.9704
15	0.9130	0.9204	0.9325	0.9447	0.9552
20	0.8824	0.8914	0.9094	0.9257	0.9399
25	0.8506	0.8607	0.8858	0.9065	0.9242
30	0.8175	0.8284	0.8614	0.8869	0.9082
35	0.7821	0.7944	0.8361	0.8670	0.8918
40	0.7439	0.7586	0.8100	0.8467	0.8747
45	0.7025	0.7208	0.7830	0.8260	0.8572
50	0.6567	0.6794	0.7548	0.8084	0.8408
55	0.6025	0.6347	0.7252	0.7832	0.8236
60	0.5371	0.5821	0.6941	0.7613	0.8067
65	0.4142	0.5158	0.6617	0.7388	0.7897
70	0.2008	0.4252	0.6273	0.7160	0.7727
75	0.1977	0.2644	0.5908	0.6926	0.7555
80	0.2026	0.2334	0.5517	0.6686	0.7384
85	0.2126	0.2342	0.5095	0.6441	0.7212
90	0.2228	0.2313	0.4665	0.6195	0.7040
95	0.2294	0.2455	0.4246	0.5949	0.6868
100	0.2392	0.2502	0.3896	0.5704	0.6699
105	0.2451	0.2550	0.3657	0.5464	0.6532
110	0.2527	0.2604	0.3521	0.5240	0.6371
115	0.2612	0.2678	0.3460	0.5038	0.6213
120	0.2705	0.2773	0.2438	0.4858	0.6065
125	0.2805	0.2884	0.3444	0.4709	0.5927
130	0.2909	0.3033	0.3473	0.4601	0.5780
135	0.2996	0.3104	0.3502	0.4511	0.5671
140	0.3078	0.3193	0.3544	0.4458	0.5570
145	0.3142	0.3270	0.3598	0.4421	0.5480
150	0.3184	0.3341	0.3661	0.4402	0.5409
155	0.3239	0.3417	0.3731	0.4401	0.5352
160	0.3312	0.3498	0.3812	0.4412	0.5307
165	0.3398	0.3594	0.3886	0.4430	0.5272
170	0.3494	0.3687	0.3955	0.4460	0.5253
175	0.3595	0.3781	0.4027	0.4495	0.5238
180	0.3705	0.3876	0.4091	0.4544	0.5233
185	0.3815	0.3969	0.4156	0.4592	0.5238
190	0.3923	0.4060	0.4222	0.4651	0.5248
195	0.4034	0.4145	0.4295	0.4705	0.5267
200	0.4141	0.4228	0.4371	0.4765	0.5292
205	0.4240	0.4298	0.4456	0.4826	0.5323
210	0.4335	0.4366	0.4551	0.4891	0.5355
215	0.4413	0.4448	0.4634	0.4954	0.5387
220	0.4495	0.4530	0.4708	0.5014	0.5427
225	0.4576	0.4618	0.4783	0.5076	0.5470
230	0.4656	0.4709	0.4856	0.5134	0.5520
235	0.4738	0.4799	0.4931	0.5193	0.5568
240	0.4824	0.4888	0.5008	0.5256	0.5622
245	0.4912	0.4977	0.5086	0.5323	0.5676
250	0.4997	0.5060	0.5167	0.5387	0.5730
255	0.5092	0.5135	0.5246	0.5457	0.5786
260	0.5211	0.5210	0.5324	0.5527	0.5841
265	0.5280	0.5284	0.5398	0.5593	0.5899
270	0.5355	0.5371	0.5470	0.5664	0.5955
275	0.5431	0.5458	0.5545	0.5737	0.6012
280	0.5509	0.5542	0.5622	0.5806	0.6068
285	0.5589	0.5628	0.5700	0.5875	0.6131
290	0.5675	0.5716	0.5776	0.5942	0.6193
295	0.5753	0.5801	0.5853	0.6010	0.6254
300	0.5845	0.5882	0.5935	0.6068	0.6313
305	0.5843	0.5964	0.6018	0.6125	0.6380
310	0.6024	0.6024	0.6101	0.6178	0.6443

both the vapor and liquid region. The results were correlated using the following two equations:

$$\frac{1}{2}(d_l + d_g) = 0.362597537 + 9.00397351 \times 10^{-4}(t_c - t) - 5.57140526 \times 10^{-7}(t_c - t)^2 \quad (3)$$

and

$$\frac{1}{2}(d_l - d_g) = 0.0925242495\,(t_c - t)^{0.312133666} + 6.54182852\,(t_c - t) - 2.86746013 \times 10^{-6}(t_c - t)^2 \quad (4)$$

The smoothed orthobaric densities of methyl chloride were calculated from these two equations. The values are listed in Table V and plotted in Figure 4 along with other sources of data (*10, 12, 14*). The saturated liquid densities given in the International Critical Tables agree with the smoothed values of this work. The agreement is not as good for the saturated vapor densities.

Latent Heats of Vaporization. The Clapeyron equation was used to evaluate the latent heats of vaporization of methyl chloride.

$$H_v = T(V_g - V_l)\left(\frac{dP}{dT}\right)J \quad (5)$$

from the vapor pressure and orthobaric density correlations. The calculated values from Equation 5 were correlated by the equation,

$$H_v = 14.91210102\,(t_c - t)^{0.350} + 0.1808199665\,(t_c - t) - 0.001011614467\,(t_c - t)^2 \quad (6)$$

The average deviation is ● 0.23% (see Table VI).

Fugacity Coefficients. The fugacity coefficients of methyl chloride were calculated from the following equation

Table II. Experimental Pressure-Volume Isotherms for Liquid Methyl Chloride

(Mass of Sample = 7.9152 gm.)

Volume, Cc./Gram	Pressure, Atm.	Volume, Cc./Gram	Pressure, Atm.	Volume, Cc./Gram	Pressure, Atm.
35° C.		75° C.		115° C.	
1.1221	8.013	1.2448	29.244	1.4967	42.105
1.1212	10.727	1.2314	48.899	1.4921	43.725
1.1196	15.979	1.2158	75.243	1.4869	45.038
1.1182	21.240	1.2030	101.50	1.4826	46.353
1.1169	26.503	1.1910	127.78	1.4782	47.669
40° C.		1.1816	154.07	1.4730	50.211
1.1367	8.894	1.1708	180.40	1.4585	55.474
1.1358	10.737	1.1620	206.70	1.4458	60.743
1.1338	16.001	1.1539	233.04	1.4236	71.247
1.1324	21.256	1.1463	259.37	1.4052	81.770
1.1304	26.504	1.1385	285.68	120° C.	
45° C.		1.1314	311.82	1.5501	45.964
1.1500	10.738			1.5461	46.755
1.1490	13.372	80° C.		1.5417	47.542
1.1480	16.000	1.2725	22.681	1.5298	50.180
1.1471	18.634	1.2716	24.003	1.5192	52.807
1.1460	21.254	1.2695	26.608	1.5076	56.792
50° C.		1.2675	29.242	1.4946	60.742
1.1654	11.263	1.2652	31.877	1.4723	68.641
1.1647	13.371	85° C.		1.4471	79.145
1.1635	15.997	1.2959	22.420	125° C.	
1.1625	18.631	1.2945	26.626	1.6131	49.859
1.1615	21.252	1.2919	29.254	1.6064	50.698
1.1594	26.501	1.2895	31.875	1.6007	51.490
1.1488	48.896	1.2872	34.509	1.5919	52.806
1.1404	75.241	90° C.		1.5764	55.446
1.1318	101.50	1.3263	26.636	1.5019	75.239
1.1247	127.78	1.3190	29.274	1.4403	101.50
1.1181	154.07	1.3158	31.895	1.3987	127.77
1.1111	180.39	1.3134	34.509	1.3677	154.06
1.1045	206.70	1.3105	37.141	1.3411	180.39
1.0988	233.03	95° C.		1.3189	206.70
1.0929	259.37	1.3528	29.507	1.2989	235.66
1.0879	285.68	1.3468	31.879	1.2943	259.36
1.0826	311.82	1.3428	34.513	1.2696	285.67
55° C.		1.3389	37.143	1.2562	311.81
1.1807	13.370	100° C.		130° C.	
1.1796	15.994	1.3829	32.400	1.6938	54.110
1.1784	18.630	1.3772	34.511	1.6873	54.686
1.1771	21.250	1.3725	37.141	1.6780	55.477
1.1750	26.499	1.3680	39.769	1.6639	56.797
60° C.		1.3559	48.895	1.6409	59.427
1.1966	15.210	1.3230	77.390	1.6511	59.432
1.1962	15.999	1.2984	101.50	1.6126	64.680
1.1950	18.633	1.2779	127.77	1.5836	69.934
1.1937	21.254	1.2604	154.06	1.5383	80.457
1.1911	26.503	1.2419	180.38	1.4918	96.133
65° C.		1.2318	206.70	135° C.	
1.2139	15.997	1.2199	233.03	1.8065	58.638
1.2125	18.631	1.2084	259.37	1.7937	59.163
1.2109	21.252	1.1984	285.67	1.7666	60.476
1.2079	26.499	1.1890	311.81	1.7265	63.109
70° C.				1.6967	65.740
1.2316	17.944	105° C.		1.6322	75.240
1.2313	18.740	1.4167	35.828	1.5775	85.772
1.2299	21.360	1.4092	38.458	1.5415	96.275
1.2282	23.994	1.4033	41.092	140° C.	
1.2264	26.609	1.3982	43.720	1.9957	63.380
75° C.		110° C.		1.9575	64.112
1.2508	20.579	1.4558	38.719	1.9038	65.213
1.2506	21.362	1.4515	39.769	1.8408	67.324
1.2485	23.996	1.4443	42.409	1.7897	69.954
1.2466	26.610	1.4371	45.037	1.7359	75.195
				1.6498	85.597
				1.6076	93.496
				1.5702	102.71

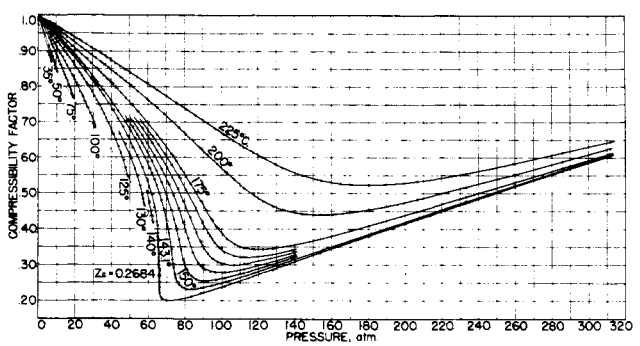

Figure 1. Compressibility factors of methyl chloride

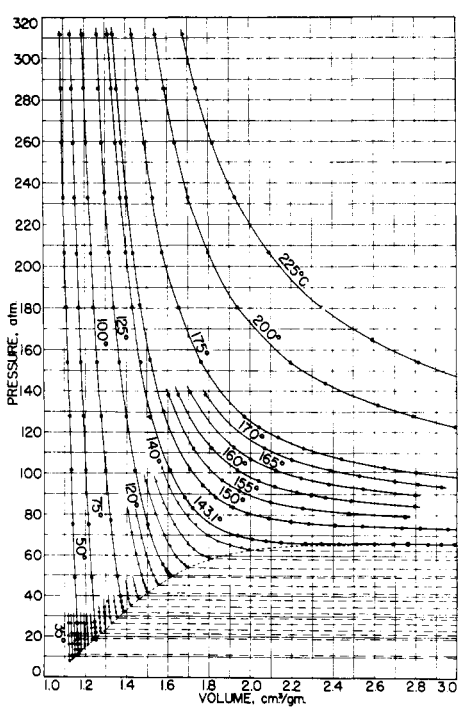

Figure 2. *P-V* isotherms for liquid methyl chloride

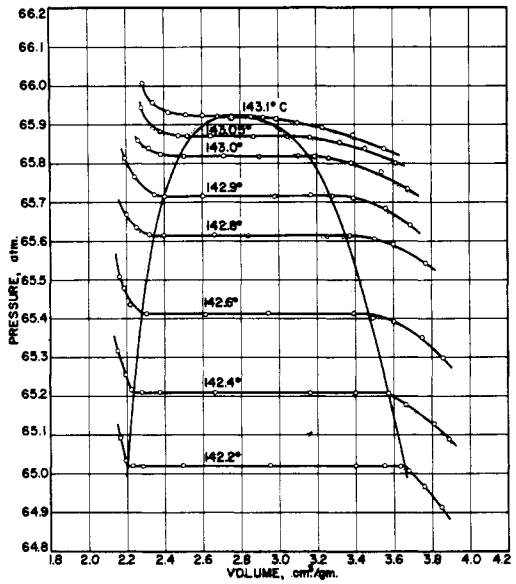

Figure 3. *P-V* isotherms in the critical region

$$\nu = \frac{f}{P} = e^{\left[-\frac{1}{RT} \int_0^P \gamma \, dP \right]} \quad (7)$$

using the smoothed volume residuals.

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

(Mass of Sample = 2.3716 gram)

Volume, Cc./Gram	Pressure, Atm.	Volume, Cc./Gram	Pressure, Atm.	Volume, Cc./Gram	Pressure, Atm.
142.2° C.		142.8° C.		143.05° C.	
3.850	64.913	3.771	65.543	3.616	65.799
3.761	64.967	3.600	65.592	3.457	65.838
3.681	65.006	3.506	65.605	3.323	65.854
3.635	65.019	3.373	65.613	3.165	65.867
3.550	65.020	3.235	65.612	3.049	65.869
3.399	65.020	2.840	65.614	2.869	65.869
2.951	65.022	2.666	65.616	2.646	65.870
2.495	65.021	2.398	65.614	2.525	65.870
2.284	65.019	2.322	65.616	2.477	65.871
2.229	65.020	2.254	65.635	2.379	65.882
2.196	65.035	2.201	65.668	2.282	65.943
2.169	65.092	142.9° C.		143.10° C.	
142.4° C.		3.692	65.641	3.579	65.834
3.890	65.089	3.566	65.683	3.558	65.838
3.813	65.128	3.394	65.710	3.489	65.855
3.664	65.187	3.284	65.715	3.402	65.869
3.576	65.207	3.170	65.718	3.394	65.872
3.401	65.208	2.980	65.715	3.230	65.891
3.162	65.208	2.606	65.715	3.100	65.904
2.665	65.209	2.404	65.715	2.991	65.914
2.375	65.210	2.329	65.720	2.924	65.918
2.280	65.210	2.244	65.765	2.859	65.920
2.227	65.217	2.192	65.814	2.774	65.919
2.193	65.255	143.00° C.		2.685	65.921
2.154	65.317	3.678	65.734	2.605	65.923
142.6° C.		3.540	65.778	2.517	65.925
3.860	65.298	3.385	65.801	2.422	65.931
3.749	65.749	3.264	65.813	2.345	65.957
3.602	65.392	3.190	65.817	2.288	66.060
3.493	65.401	3.105	65.818		
3.396	65.413	2.904	65.817		
2.944	65.414	2.716	65.819		
2.617	65.410	2.505	65.818		
2.308	65.413	2.382	65.823		
2.220	65.435	2.321	65.840		
2.189	65.478	2.267	65.869		
2.166	65.509	2.210	65.945		

The integration involved in Equation 7 was carried out numerically, applying Newton-Cotes' seven-point formula (*8*). The integration interval was 0.5 atm. The fugacity coefficients so obtained are plotted in Figure 5 (see Table VII). The saturation line of Figure 5 was obtained by extrapolating the calculated fugacity coefficient data of each isotherm to the corresponding vapor pressure.

EQUATIONS OF STATE

Three empirical equations of state—namely, the Benedict-Webb-Rubin (B-W-R) equation (*3*), the Beattie-Bridgeman (B-B) equation (*2*), and Martin-Hou (M-H) equation (*11*),—were selected to represent *P-V-T* relationships of gaseous methyl chloride. The equations and their specific constants for methyl chloride are presented in Table VIII.

The general procedure for the determination of the specific constants in the B-W-R equation followed the method of Brough, Schlinger, and Sage (*4*). A total of 672 unsmoothed experimental data points of *P-V-T* measurements for methyl chloride were used to fit the B-W-R equation. In the evaluation of the constants in the B-B equation, the constant C was adjusted while the rest of the constants were obtained by means of the least-square method. The correct value of C was that where the sum of the square of the residuals was at a minimum. The compressibility data measured in this work at pressures beyond 150 atm. were excluded in order to have a better fit at the low and moderate pressure range. The numerical constants in the M-H equation were evaluated according to the general procedure described by Martin and Hou (*11*).

The comparison of the representation of the *P-V-T* relationships for methyl chloride between these three equations of state and the experimental data are given in Table IX. In the light of the deviations of the calculated pressure from the observed value, the B-W-R equation represents the system over nearly the entire range of experimental *P-V-T* data with a maximum deviation of 3.89% and an average deviation of 0.53%. The M-H equation of state gives about the same precision as the B-W-R equation at low pressures. The M-H equation is

Table IV. Smoothed Vapor Pressure for Methyl Chloride

Temp., ° C.	Obsd. *P*, Atm.	Smoothed *P*, Atm.	Obsd.–Smoothed, ΔP	Dev., %[a]
30	6.529	6.521	0.008	0.123
35	7.445	7.452	−0.007	−0.087
40	8.475	8.483	−0.008	−0.099
45	9.623	9.624	−0.001	−0.011
50	10.885	10.881	0.004	0.035
55	12.266	12.262	0.004	0.029
60	13.773	13.776	−0.005	−0.020
65	15.430	15.429	0.001	0.005
70	17.232	17.231	0.001	0.005
75	19.190	19.190	0.000	0.000
80	21.317	21.314	0.003	0.015
85	23.606	23.611	−0.005	−0.023
90	26.105	26.091	0.014	0.052
95	28.769	28.762	0.007	0.024
100	31.633	31.633	0.000	0.000
105	34.707	34.711	−0.004	−0.011
110	38.001	38.006	−0.005	−0.012
115	41.528	41.525	0.003	0.007
120	45.275	45.278	−0.003	−0.007
125	49.263	49.273	−0.010	−0.020
130	53.499	53.517	−0.018	−0.034
135	58.005	58.019	−0.014	−0.024
140	62.777	62.786	−0.011	−0.014
143.10	65.919	65.877	...	...

[a] Devation, % = $\Delta P \times 100$/observed *P*.

Table V. Critical Constants and Orthobaric Densities for Methyl Chloride

Temp.,	Obsd. Den., Gram/Cc.		Smoothed Den., Gram/Cc.		Deviation, %[a]	
° C.	Vapor	Liquid	Vapor	Liquid	Vapor	Liquid
35	0.01715	0.8910	0.01711	0.8897	0.22	0.14
40	0.01941	0.8796	0.01930	0.8797	0.59	−0.01
45	0.02211	0.8692	0.02180	0.8693	1.42	−0.02
50	0.02466	0.8579	0.02463	0.8586	0.13	−0.08
55	0.02793	0.8466	0.02781	0.8474	0.43	−0.09
60	0.03124	0.8352	0.03137	0.8358	−0.41	−0.07
65	0.03531	0.8236	0.03533	0.8237	−0.05	−0.01
70	0.03979	0.8115	0.03972	0.8112	0.18	0.04
75	0.04430	0.7988	0.04458	0.7981	−0.64	0.09
80	0.04957	0.7853	0.04996	0.7844	−0.79	0.11
85	0.05562	0.7707	0.05591	0.7701	−0.53	0.07
90	0.06242	0.7537	0.06251	0.7552	−0.14	−0.20
95	0.06978	0.7374	0.06982	0.7394	−0.06	−0.27
100	0.07753	0.7226	0.07798	0.7228	−0.58	−0.02
105	0.08714	0.7049	0.08712	0.7051	0.03	−0.02
110	0.09764	0.6866	0.09745	0.6861	0.20	0.07
115	0.1097	0.6674	0.1093	0.6657	0.41	0.26
120	0.1238	0.6442	0.1230	0.6432	0.66	0.15
125	0.1403	0.6192	0.1394	0.6181	0.68	0.18
130	0.1609	0.5889	0.1597	0.5889	0.76	0.00
135	0.1861	0.5518	0.1870	0.5527	−0.48	−0.17
140	0.2303	0.4981	0.2317	0.4991	−0.60	−0.20

[a] Deviation % = (observed value − smoothed value) × 100/observed value.

critical constsnts { t_c, ° C. = 143.10 ± 0.02; P_c, atm. = 65.919 ± 0.02; V_c, cm.^{3}/gram = 2.755 ± 0.001

Table VI. Latent Heats of Vaporization for Methyl Chloride

Temp., ° C.	Calcd., H_v, B.t.u./lb.	Smoothed H_v, B.t.u./lb.	Dev., %
35	83.85	84.52	−0.81
40	83.84	83.43	−0.03
45	82.53	82.24	0.35
50	81.34	80.96	0.48
55	79.92	79.57	0.44
60	78.33	78.09	0.30
65	76.60	76.50	0.14
70	74.77	74.79	−0.02
75	72.85	72.96	−0.14
80	70.83	71.00	−0.24
85	68.69	68.69	−0.29
90	66.43	66.63	−0.31
95	64.04	64.21	−0.25
100	61.47	61.58	−0.18
105	58.69	58.74	−0.08
110	55.65	55.63	0.03
115	52.29	52.21	0.15
120	48.50	48.40	0.23
125	44.14	44.03	0.25
130	38.96	38.89	0.19
135	32.41	32.41	0.00
140	22.67	22.71	−0.09

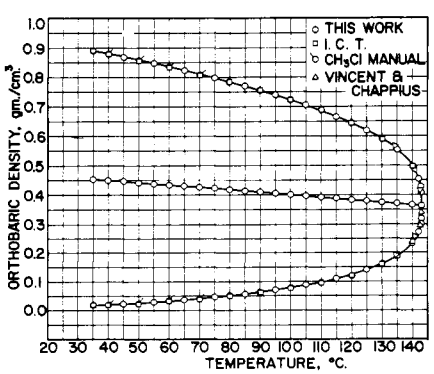

Figure 4. Orthobaric densities for methyl chloride

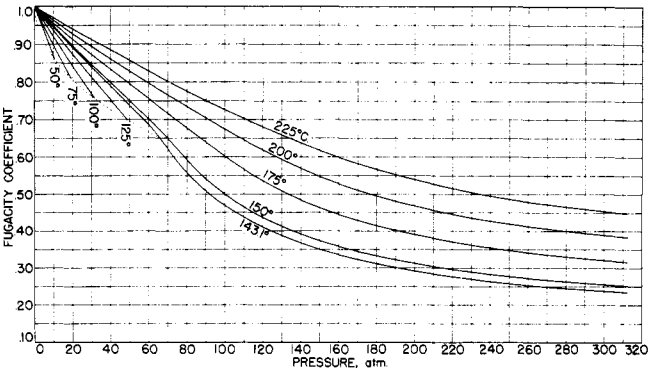

Figure 5. Fugacity coefficients for methyl chloride

Table VII. Fugacity Coefficients of Methyl Chloride

P, Atm.	Fugacity Coefficient, f/P				
	35° C.	40° C.	45° C.	50° C.	55° C.
3	0.9528	0.9564	0.9568	0.9596	0.9621
6	0.9063	0.9127	0.9149	0.9202	0.9250
7.452	0.8848				
8.483		0.8772			
9			0.8740	0.8815	0.8885
9.624			0.8644		
10.881				0.8583	
12					0.8521
12.262					0.8488
	60° C.	65° C.	75° C.	100° C.	125° C.
3	0.9645	0.9666	0.9698	0.9758	0.9797
6	0.9297	0.9336	0.9363	0.9520	0.9607
9	0.8953	0.9010	0.9071	0.9284	0.9418
12	0.8610	0.8685	0.8780	0.9050	0.9232
13.776	0.8406				
15		0.8360	0.8488	0.8818	0.9046
15.429		0.8304			
18			0.8196	0.8588	0.8862
19.190			0.8078		
21				0.8359	0.8680
24				0.8131	0.8498
27				0.7903	0.8318
30				0.7675	0.8139
31.633				0.7551	
33					0.7960
36					0.7780
39					0.7600
42					0.7418
45					0.7234
48					0.7045
49.273					0.6961
	143.1° C	150° C.	175° C.	200° C.	225° C.
3	0.9833	0.9851	0.9867	0.9892	0.9912
6	0.9669	0.9703	0.9736	0.9784	0.9825
9	0.9505	0.9555	0.9609	0.9677	0.9738
12	0.9343	0.9407	0.9478	0.9571	0.9656
15	0.9183	0.9229	0.9351	0.9466	0.9566
18	0.9024	0.9051	0.9226	0.9362	0.9481
21	0.8866	0.8905	0.9101	0.9258	0.9396
24	0.8710	0.8760	0.8978	0.9155	0.9311
27	0.8555	0.8614	0.8856	0.9053	0.9226
30	0.8401	0.8469	0.8734	0.8952	0.9142
33	0.8248	0.8324	0.8614	0.8851	0.9059
36	0.8096	0.8179	0.8494	0.8750	0.8975
39	0.7944	0.8034	0.8374	0.8651	0.8892
42	0.7793	0.7889	0.8256	0.8552	0.8808
45	0.7641	0.7745	0.8138	0.8453	0.8725
48	0.7490	0.7601	0.8020	0.8356	0.8642
51	0.7338	0.7456	0.7903	0.8258	0.8529
54	0.7184	0.7312	0.7787	0.8162	0.8448
57	0.7030	0.7167	0.7671	0.8066	0.8367
60	0.6872	0.7021	0.7555	0.7970	0.8286
63	0.6709	0.6873	0.7440	0.7875	0.8207
66	0.6530	0.6723	0.7325	0.7781	0.8127
69	0.6303	0.6568	0.7210	0.7687	0.8049
72	0.6092	0.6405	0.7095	0.7594	0.7971
75	0.5896	0.6228	0.6981	0.7502	0.7893
78	0.5714	0.6047	0.6867	0.7410	0.7816
81	0.5544	0.5875	0.6753	0.7318	0.7740

(Continued on page 50)

Table VII. Fugacity Coefficients of Methyl Chloride *(Continued)*

P, Atm.	Fugacity Coefficient, f/P 35° C.	40° C.	45° C.	50° C.	55° C.
84	0.5387	0.5713	0.6639	0.7228	0.7664
87	0.5240	0.5561	0.6524	0.7137	0.7589
90	0.5104	0.5419	0.6411	0.7048	0.7515
93	0.4976	0.5286	0.6297	0.6958	0.7441
96	0.4856	0.5160	0.6184	0.6870	0.7368
99	0.4744	0.5042	0.6072	0.6782	0.7295
102	0.4638	0.4931	0.5962	0.6696	0.7223
105	0.4537	0.4825	0.5854	0.6609	0.7152
108	0.4442	0.4725	0.5750	0.6524	0.7081
111	0.4352	0.4630	0.5649	0.6440	0.7012
114	0.4266	0.4540	0.5551	0.6357	0.6943
117	0.4185	0.4455	0.5458	0.6275	0.6875
120	0.4108	0.4374	0.5368	0.6195	0.6807
123	0.4055	0.4297	0.5282	0.6116	0.6741
126	0.3966	0.4224	0.5199	0.6039	0.6675
129	0.3900	0.4154	0.5143	0.5963	0.6610
132	0.3837	0.4088	0.5043	0.5890	0.6546
135	0.3777	0.4025	0.4970	0.5818	0.6484
138	0.3719	0.3965	0.4900	0.5748	0.6422
141	0.3664	0.3907	0.4832	0.5680	0.6361
144	0.3612	0.3852	0.4767	0.5613	0.6301
147	0.3561	0.3799	0.4705	0.5549	0.6243
150	0.3512	0.3748	0.4645	0.5487	0.6185
153	0.3465	0.3699	0.4587	0.5427	0.6129
156	0.3420	0.3652	0.4531	0.5368	0.6074
159	0.3376	0.3607	0.4478	0.5311	0.6020
162	0.3334	0.3563	0.4426	0.5256	0.5986
165	0.3294	0.3521	0.4377	0.5202	0.5916
168	0.3255	0.3481	0.4329	0.5150	0.5866
171	0.3218	0.3442	0.4283	0.5100	0.5817
174	0.3182	0.3405	0.4238	0.5051	0.5769
177	0.3148	0.3369	0.4195	0.5004	0.5722
180	0.3114	0.3334	0.4154	0.4954	0.5677
183	0.3082	0.3301	0.4113	0.4914	0.5632
186	0.3051	0.3269	0.4074	0.4871	0.5589
189	0.3022	0.3238	0.4037	0.4829	0.5546
192	0.2993	0.3207	0.4000	0.4788	0.5505
195	0.2965	0.3178	0.3965	0.4749	0.5465
198	0.2938	0.3150	0.3931	0.4711	0.5426
201	0.2913	0.3123	0.3897	0.4674	0.5387
204	0.2888	0.3097	0.3865	0.4638	0.5350
207	0.2863	0.3071	0.3834	0.4603	0.5314
210	0.2840	0.3046	0.3804	0.4569	0.5278
213	0.2817	0.3022	0.3775	0.4537	0.5243
216	0.2795	0.2998	0.3747	0.4505	0.5210
219	0.2775	0.2976	0.3719	0.4474	0.5177
222	0.2754	0.2954	0.3693	0.4443	0.5145
225	0.2734	0.2932	0.3667	0.4414	0.5113
228	0.2715	0.2912	0.3642	0.4385	0.5083
231	0.2696	0.2892	0.3617	0.4358	0.5053
234	0.2678	0.2872	0.3593	0.4330	0.5024
237	0.2660	0.2853	0.3570	0.4304	0.4996
240	0.2642	0.2835	0.3548	0.4278	0.4968
243	0.2626	0.2817	0.3526	0.4235	0.4942
246	0.2609	0.2800	0.3505	0.4229	0.4915
249	0.2593	0.2783	0.3484	0.4205	0.4890
252	0.2578	0.2766	0.3464	0.4182	0.4865
255	0.2563	0.2750	0.3444	0.4160	0.4841
258	0.2548	0.2735	0.3425	0.4138	0.4817
261	0.2534	0.2720	0.3407	0.4116	0.4794
264	0.2520	0.2705	0.3389	0.4095	0.4771
267	0.2507	0.2691	0.3371	0.4075	0.4749
270	0.2494	0.2677	0.3354	0.4055	0.4728
273	0.2481	0.2663	0.3338	0.4036	0.4707
276	0.2469	0.2650	0.3321	0.4017	0.4686
279	0.2457	0.2637	0.3306	0.3999	0.4666
282	0.2445	0.2624	0.3290	0.3981	0.4647
285	0.2434	0.2612	0.3275	0.3964	0.4628
288	0.2422	0.2600	0.3260	0.3947	0.4609
291	0.2412	0.2589	0.3246	0.3930	0.4591
294	0.2401	0.2578	0.3232	0.3914	0.4573
297	0.2391	0.2567	0.3219	0.3898	0.4556
300	0.2381	0.2556	0.3203	0.3883	0.4539
303	0.2371	0.2546	0.3191	0.3868	0.4522
306	0.2361	0.2535	0.3178	0.3853	0.4506
309	0.2352	0.2526	0.3166	0.3838	0.4490
312	0.2343	0.2516	0.3154	0.3824	0.4475

Table VIII. Equations of State and their Specific Constants for Methyl Chloride[a]

(Benedict-Webb-Rubin Equation)

$$P = RT/V + (B_0RT - A_0 - C_0/T^2)/V^2 + (bRT - a)/V^3 + a\alpha/V^6 + (x/V^3T^2)[1 + (\gamma/V^2)e^{-\gamma/V^2}$$

B_0 = 0.0096762547	a = 0.521422468
b = 0.0108436448	α = 0.000168666593
A_0 = 2.20450849	c = 92198.4450
C_0 = 739067.438	γ = 0.0093

(Beattie-Bridgeman Equation)

$$P = (RT/V^2)(1 - C/VT^3)[V + B_0(1 - b/V)] - (A/RTV)(1 - a/V)$$

C = 50000	B_0 = 0.28310593
b = 0.07268835	A = 15.6783255
a = 0.066511	

(Martin-Hou Equation)

$$P = RT/(V - b) + (A_2 + B_2T + C_2\, e^{-5.475T/T_c})/(V - b)^2 + (A_3 + B_3T + C_3\, e^{-5.475T/T_c})/(V - b)^3 + A_4/(V - b)^4 + B_5T/(V - b)^5$$

b = 0.0487575	B_3 = 0.00074168283
A_2 = −10.2233898	C_3 = 21.7717907
B_2 = 0.0081804454	A_4 = −0.068940713
C_2 = −153.061055	B_5 = 5.0385878 × 10^{-6}
A_3 = 1.219453756	

[a] Units: atm., liter/mole, ° K.

exceedingly good at the critical region where the B-W-R equation shows much less accuracy and the B-B equation gives really poor results at increasing pressure. The precision of the M-H equation declines rapidly, particularly along the critical isotherm. The B-B equation has the least precision and the most limited range of use. At the critical region, an error as high as 10% is shown for the B-B equation.

ACKNOWLEDGMENT

E. I. du Pont Co. supplied the high purity methyl chloride. The National Science Foundation sponsored this project. The authors are grateful for this assistance.

NOMENCLATURE

- d_g = saturated vapor density, gm./cc.
- d_l = saturated liquid density, gm./cc.
- e = base of nature logarithm
- f = fugacity
- H_v = latent heat of vaporization, cal./gm.
- J = dimensional constant, 0.024217394 cal./cc. atm.
- P = normal pressure, atm.
- R = gas constant = 82.0567 cc. atm./° K. mole
- T = absolute temperature, ° K.
- t = temperature, ° C.
- t_c = critical temperature of methyl chloride, ° C.
- V = volume, cc./g., or liter/mole
- V_g = saturated specific volume of vapor, cc./gm.
- V_l = saturated specific volume of liquid, cc./gm.
- Z = compressibility factor, PV/RT
- γ = volume residual, cc./gm.
- ν = fugacity coefficient

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Table IX. Comparison of Observed *P-V-T* Data of CH_3Cl with those Calculated from Equation of State

Temp., °C.	Spec. Vol., L./Mole	Press., Atm. Obs.	B-W-R Obs.-calc.	B-W-R dev.	M-H Obs.-calc.	M-H dev.	B-B Obs.-calc.	B-B dev.
50	3.9999	6.061	−0.014	−0.23	−0.029	−0.48	−0.063	−1.04
	2.8755	8.141	−0.017	−0.21	−0.043	−0.53	−0.108	−1.32
	2.5890	8.962	0.029	0.32	−0.003	−0.03	−0.083	−0.92
	2.245	10.236	0.158	0.58	0.118	1.15	0.011	0.11
75	4.3316	6.173	−0.001	−0.02	−0.008	−0.03	−0.021	−0.34
	2.5256	10.084	−0.003	−0.03	−0.021	−0.21	−0.060	−0.60
	1.5332	15.347	−0.025	−0.16	−0.064	−0.42	−0.166	−1.08
	1.1396	19.190	−0.070	−0.37	−0.128	−0.67	−0.309	−1.61
100	4.7331	6.179	0.028	0.45	0.026	0.42	0.020	0.32
	2.7032	10.398	0.035	0.34	0.030	0.29	0.014	0.13
	1.6399	16.130	0.035	0.22	0.026	0.16	−0.016	−0.10
	1.2575	20.063	0.039	0.19	0.028	0.14	−0.038	−0.19
	0.8923	25.942	0.024	0.09	0.015	0.06	−0.102	−0.39
	0.6727	31.146	0.021	0.07	0.026	0.08	−0.147	−0.47
125	4.4564	6.975	−0.031	−0.44	−0.029	−0.41	−0.035	−0.50
	1.4023	20.049	−0.068	−0.34	−0.050	−0.25	−0.098	−0.49
	0.8246	30.664	−0.061	−0.20	−0.013	−0.04	−0.111	−0.36
	0.5589	39.817	−0.044	−0.11	0.048	0.12	−0.060	−0.15
	0.3637	49.015	0.080	0.16	0.240	0.49	0.404	0.82
143.1	3.3862	9.567	0.006	0.06	0.012	0.12	−0.002	−0.02
	1.4696	20.440	−0.078	−0.28	−0.049	−0.24	−0.114	−0.56
	0.9138	30.398	−0.128	−0.42	−0.062	−0.20	−0.194	−0.64
	0.6096	41.029	−0.165	−0.40	−0.054	−0.13	−0.244	−0.59
	0.4201	51.077	−0.584	−1.14	−0.457	−0.89	−0.555	−1.09
	0.2731	62.135	0.648	1.04	0.594	0.95	1.499	2.42
	0.0979	69.954	−0.699	−1.00	2.392	3.41	−9.908	14.30
	0.0869	83.157	0.912	1.09	5.119	6.13		
	0.0813	101.510	3.262	3.21	2.373	2.33		
	0.0743	154.090	5.99	3.89	−33.327	−21.8		
	0.0707	206.85	4.12	1.99				
	0.0682	259.46	−0.190	−0.07				
	0.0664	311.81	−7.23	−2.32				
175	3.6692	9.580	−0.038	−0.40	−0.030	−0.31	−0.055	−0.57
	1.5327	21.617	−0.115	−0.53	−0.074	−0.34	−0.202	−0.93
	0.9801	31.960	−0.162	−0.50	−0.081	−0.25	−0.354	−1.11
	0.7478	39.870	−0.226	−0.56	−0.117	−0.29	−0.523	−1.31
	0.5411	50.924	−0.279	−0.55	−0.164	−0.32	−0.749	−1.47
	0.3298	69.975	−0.100	−0.14	−0.298	−0.42	−0.757	−1.08
	0.2504	80.447	0.275	0.34	−0.591	−0.72	−0.027	−0.03
	0.1415	100.47	−0.069	−0.07	−3.195	−3.18	4.734	4.71
	0.080	206.69	0.585	0.26	−7.208	−3.48		
	0.0722	311.84	−2.775	−0.89				
200	3.9159	9.558	−0.027	−0.28	−0.019	−0.20	−0.054	−0.56
	1.6741	21.330	−0.097	−0.45	−0.059	−0.28	−0.233	−1.09
	1.0722	31.866	−0.135	−0.42	−0.065	−0.20	−0.446	−1.40
	0.8265	39.810	−0.208	−0.52	−0.119	−0.30	−0.702	−1.76
	0.6199	50.321	−0.267	−0.53	−0.181	−0.36	−1.068	−2.12
	0.4986	59.452	−0.292	−0.49	−0.266	−0.45	−1.417	−2.38
	0.3753	72.748	−0.189	−0.26	−0.433	−0.59	−1.833	−2.52
	0.3215	80.455	−0.077	−0.10	−0.646	−0.80	−2.001	−2.49
	0.2138	101.89	0.509	0.50	−2.073	−2.07	−1.363	−1.34
200	0.0908	206.81	−0.297	−0.14	−0.929	−0.45		
	0.0779	311.79	1.340					
225	4.1651	9.537	−0.005	−0.05	0.002	−0.02	−0.042	−0.04
	1.7901	21.345	−0.047	−0.22	−0.018	−0.09	−0.237	−0.11
	1.1591	31.827	−0.063	−0.20	−0.013	−0.04	−0.496	−0.15
	0.6822	50.297	−0.258	−0.51	−0.222	−0.44	−1.383	−2.75
	0.5559	59.467	−0.282	−0.47	−0.315	−0.53	−1.873	−3.15
	0.4506	70.085	−0.264	−0.38	−0.473	−0.67	−2.485	−3.54
	0.3740	80.503	−0.191	−0.24	−0.727	−0.90	−3.100	−3.85
	0.2678	101.49	0.247	0.25	−1.668	−1.67	−3.976	−3.91
	0.1056	206.67	0.502	0.24	−8.55	−4.14		
	0.0847	311.77	3.165	1.01				

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