Volumetric Behavior, Vapor Pressures, and Critical Properties of Neopentane

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The *PVT* relations of 2,2-dimethylpropane (neopentane) over the temperature range of 70–225°C and to a pressure of 310 atm were measured for both liquid and vapor phase using the Beattie method. Vapor pressures and saturated phase densities were determined at intervals of 5°C up to the critical temperature. These data were used to evaluate compressibility factors, fugacity coefficients, heats of vaporization, critical properties, and second and third virial coefficients.

The technique used for the *PVT* measurements in this work was essentially the same as that first described by Keyes (*10*) and Beattie (*1*). In this method, a known mass of a pure sample is confined by a mercury column in a high-pressure cell, which is surrounded by a thermostated oil bath. The volume occupied by the sample is varied by means of a calibrated piston and cylinder which controls the amount of mercury in the cell. The resulting pressure is measured by an Amagat type of dead-weight gage.

Four different samples of the following masses were charged using two different weighing techniques:

Sample 1	0.56085 gram
Sample 2	1.28865 gram
Sample 3	3.9961 gram
Sample 4	8.7208 gram

The weighing bomb method described by Couch (*5*) was used in loading the largest sample. The other three samples were weighed in a sealed glass bulb by the procedure originally reported by Beattie (*1*) and used more recently by Hellwig (*9*). The temperature was measured with a platinum resistance thermometer used in conjunction with a Mueller bridge and a ballistic galvanometer. The apparatus has been described by Couch (*5*), Hellwig (*9*), and most recently by Lin (*11, 12*) and Dawson (*6*).

Material

Research grade neopentane was furnished by Phillips Petroleum Co., who specified a minimum purity of 99.96%. The samples were further purified by drying in a molecular sieve column and by multiple batchwise distillation. Analysis of the finished material by glc showed no other pentanes. The most likely impurity, *n*-butane, could not be detected at levels below 0.1%. However, the small pressure variation in the two-phase region, less than 0.04% for the largest sample, is taken as the best indication of the purity of the material.

Physical Constants

Fundamental constants and dimensional equivalents used for this work were taken from the U.S. Bureau of Standards (*15*). The molecular weight of neopentane is 72.151 (*4*). The international temperature scale of 1948 (ITS-48) was used because the experimental work was largely completed prior to the establishment of the 1968 scale (IPTS-1968).

Experimental Results

The volumetric behavior of neopentane was measured over the entire pressure range possible with this apparatus, 5–310 atm, for major isotherms from 70–225°C at 25° intervals, and for the critical temperature, 160.60°C. Additional abbreviated isotherms were studied above the critical temperature at 5° intervals to 175°C. Other short isotherms were covered from 70–155°C in the proximity of the saturated vapor and liquid states. The results of these measurements are presented in Table I and Figure 1 as compressibility factors, $Z = PV/RT$, for the vapor phase. Liquid phase data are reported as specific volumes in Table II and Figure 2, which also includes the high-density isotherms above the critical temperature.

Specific volumes in the two-phase region were measured for the evaluation of vapor pressures and to establish the purity of the samples as previously mentioned (Table III). In addition, five short isotherms were measured from 160.0–160.65°C to determine the critical properties (Table IV). (Tables I, II, and III presented here are condensations. The complete tables are available from the ACS Microfilm Depository Service.)

Accuracy

Analysis of accuracy with the Beattie method is somewhat complicated. The relative error in measurement of sample size is inversely proportional to its mass. For the smallest one, the uncertainty in weighing was ±0.07 mg or ±0.015%. Relative errors are smaller in the larger samples. The repeatability of the temperature control and measurement was ±0.002°C. However, a somewhat larger error, ±0.04° at 200°C, results from the use of the Callender equation for the thermometer calibration. The total uncertainty is therefore ±0.01% in absolute temperature. Errors in pressure measurement come from several sources. The readability of the dead-weight gage was ±0.0013 atm. Gage calibration uncertainty was ±0.002 atm. Additional errors result from measurement of hydraulic heads, ±0.1 mm Hg, and weight calibration, ±0.01%. However, the largest error is attributable to the variation in gage calibration with pressure, ±0.02% at 300 atm. The overall maximum error in pressure measurement is estimated from these observations to be ±0.04%. The largest source of error is in the measurement of volume. Including the volumetric pump calibrations, six readings are involved in the determination of each sample volume, with a precision of ±0.001 ml each. The maximum relative error, which corresponds to the smallest sample volume (10 ml) is ±0.06%. The overall maximum error is believed to be ±0.10% in compressibility factors and ±0.05% in specific volumes.

An analysis of at least two sources of error, volume and mass, is available from inspection of results where data from the different samples overlap. Table V shows

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Table I. Experimental Gas Compressibility Data for Neopentane (Sample 1)

Press., atm	Vol, ml/gram	$Z = PV/RT$	Press., atm	Vol, ml/gram	$Z = PV/RT$
	70°C			90°C	
5.638	58.890	0.8508	7.900	42.995	0.8225
5.693	58.171	0.8486	8.456	39.389	0.8065
5.749	57.453	0.8464	8.761	37.585	0.7973
			8.984	36.285	0.7893
	75°C				
5.698	59.597	0.8577		95°C	
5.877	57.438	0.8525	8.644	39.362	0.8127
6.032	55.639	0.8476	9.301	35.751	0.7942
6.298	52.761	0.8392	9.701	33.765	0.7824
6.469	50.961	0.8326	9.957	32.501	0.7730
	80°C			100°C	
6.503	52.035	0.8426	5.814	64.844	0.8885
6.891	48.433	0.8310	6.162	60.683	0.8811
7.185	45.912	0.8214	6.550	56.527	0.8725
7.240	45.372	0.8179	6.989	52.370	0.8625
7.255	45.192	0.8164	7.467	48.393	0.8515
			8.015	44.417	0.8389
	85°C		8.639	40.440	0.8233
6.831	50.218	0.8422	9.364	36.463	0.8046
7.487	44.816	0.8238	10.126	32.846	0.7838
7.967	41.356	0.8089	10.952	29.413	0.7591
8.076	40.581	0.8046	11.011	29.142	0.7561
				105°C	
			11.938	26.850	0.7454
			12.095	26.304	0.7398

Table II. Experimental Liquid Volumes of Neopentane (Sample 4)

Press., atm	Vol, ml/gram	Press., atm	Vol, ml/gram	Press., atm	Vol, ml/gram
70°C		85°C		100°C	
5.834	1.8901	8.217	1.9688	75.220	1.9468
6.112	1.8895	8.480	1.9684	101.468	1.9158
8.218	1.8867	9.531	1.9665	127.731	1.8892
		12.170	1.9619	154.007	1.8666
75°C				206.620	1.8286
6.663	1.9141	90°C		259.263	1.7976
7.165	1.9133	9.066	1.9988	311.687	1.7712
8.216	1.9121	9.328	1.9980		
10.854	1.9081	9.805	1.9973	105°C	
16.101	1.9014	10.855	1.9948	12.309	2.1015
26.611	1.8892			12.483	2.1009
48.892	1.8648	95°C		12.690	2.1000
101.472	1.8200	10.145	2.0302		
154.011	1.7854	10.405	2.0298	110°C	
206.624	1.7567	10.854	2.0285	13.561	2.1417
259.266	1.7328	12.168	2.0254	14.004	2.1397
311.691	1.7117			14.796	2.1364
		100°C		17.434	2.1268
80°C		11.168	2.0656		
7.424	1.9411	11.170	2.0661	115°C	
7.687	1.9406	11.377	2.0649	14.850	2.1858
8.215	1.9399	11.456	2.0637	15.320	2.1829
10.854	1.9357	12.168	2.0619	17.958	2.1715
		13.493	2.0585		
		16.101	2.0507	120°C	
		21.352	2.0391	16.233	2.2339
		31.870	2.0168	16.624	2.2315
		48.889	1.9858	18.729	2.2202

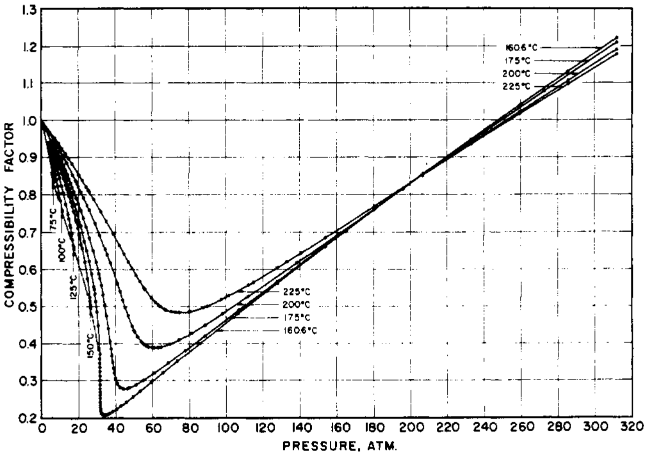

Figure 1. Compressibility factors of neopentane

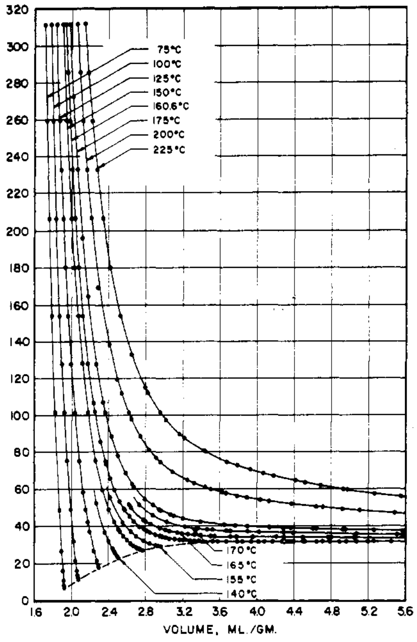

Figure 2. Specific volumes of neopentane in the high-pressure region

the comparison of results for all four samples for two isotherms, 200° and 225°C. Maximum deviations between individual sample results and the smoothed compressibility factors is seen to be 0.00022, which is smaller than the estimated maximum error, ±0.10%. It is also noted from Table III that maximum deviation in vapor pressure for the four samples is 0.01 atm and the average deviation is 0.003 atm.

Smoothed Quantities

Smoothed volume residuals. Volume residuals were calculated for all vapor phase data according to the relationship

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

The zero pressure volume residual was evaluated from the second virial coefficient (Table XIII).

These results were smoothed according to the least-squares method described by Lin (*11*, *12*). The interpolation and smoothing were accomplished by fitting second- (or third-) order polynomials in pressure. The four (or five) data points nearest to the desired interpolating pressure were used to evaluate the constants by the method of least squares. The value of the smoothed volume residual was then calculated from the polynomial. The

Table III. Experimental Vapor Pressures

Press., atm	Vol, ml/gram	Press., atm	Vol, ml/gram	Press., atm	Vol, ml/gram
70°C (Sample 1)		75°C (Sample 3)		85°C (Sample 1)	
5.780	56.64	6.491	7.117	8.095	39.94
5.780	55.65	6.489	6.359	8.097	39.40
5.782	52.05	6.489	4.970	8.097	34.00
5.784	43.06	6.489	3.075		
5.786	28.67	6.489	1.938	85°C (Sample 3)	
5.789	16.08			8.097	7.118
5.789	2.592	75°C (Sample 4)		8.096	6.358
		6.489	5.550	8.096	5.599
70°C (Sample 3)		6.490	3.597	8.097	4.840
5.784	7.121	6.492	1.924	8.097	2.309
5.782	5.498			8.096	2.006
5.783	4.344	80°C (Sample 1)			
5.783	3.081	7.260	44.92	85°C (Sample 4)	
5.782	2.073	7.261	39.42	8.097	5.612
				8.097	3.656
70°C (Sample 4)		80°C (Sample 3)		8.098	1.970
5.783	5.489	7.261	7.119		
5.783	4.757	7.259	6.107	90°C (Sample 1)	
5.783	3.293	7.261	5.096	8.999	36.10
5.783	2.561	7.261	4.084	8.999	35.78
5.783	1.927	7.260	3.326	9.002	28.56
5.784	1.891	7.259	2.188		
		7.261	1.948	90°C (Sample 3)	
75°C (Sample 1)				9.002	7.117
6.488	50.60	80°C (Sample 4)		8.999	4.584
6.489	30.03	7.261	5.575	8.999	2.025
		7.262	1.946		
75°C (Sample 2)				90°C (Sample 4)	
6.494	25.41			9.002	5.613
6.495	21.49			9.002	3.777
6.493	2.688			9.002	2.000

Table IV. Experimental Data in the Critical Region

Press., atm	Vol, ml/gram	Press., atm	Vol, ml/gram	Press., atm	Vol, ml/gram
160.0°C (Sample 4)		160.3°C (Sample 2)		160.6°C (Sample 4)	
31.188	5.6890	31.433	3.6093	31.545	4.3263
31.194	5.6528	31.503	3.4900	31.545	4.2643
31.221	5.5038	31.729	3.3308	31.547	4.2022
31.231	5.4295			31.549	4.0783
31.238	5.3799	160.5°C (Sample 4)		31.552	3.9295
31.242	5.1940	31.404	5.6279	31.563	3.7809
31.240	4.7602	31.441	5.4419	31.590	3.6631
31.243	4.2644	31.466	5.2559	31.631	3.5702
31.244	3.6444	31.489	4.8841	31.664	3.5206
31.263	3.5640	31.496	4.6360		
31.283	3.5205	31.495	4.3261	160.65°C (Sample 4)	
31.397	3.3967	31.495	4.1402	31.552	4.0082
		31.495	4.0167	31.563	4.7107
160.3°C (Sample 2)		31.500	3.8307	31.569	4.5124
31.289	5.7953	31.528	3.6634	31.570	4.3636
31.345	5.5567	31.560	3.5828	31.571	4.2644
31.385	5.2390	31.6101	3.5084	31.572	4.1653
31.390	5.1592			31.575	4.0041
31.394	5.0818	160.6°C (Sample 4)		31.583	4.8616
31.398	4.5244	31.446	5.6276	31.604	3.7189
31.400	4.3660	31.483	5.4421		
31.401	4.1272	31.509	5.2563		
31.402	3.8884	31.526	5.0704		
31.407	3.7288	31.535	4.8844		
		31.541	4.6985		
		31.543	4.5126		
		31.544	4.3883		

Table V. Intercomparison of Samples

Sample	Press., atm	Z_{expt}	ΔZ^a
		200°C	
1	18.353	0.8372	−0.00013
2	19.340	0.8278	0.00018
1	19.943	0.8213	−0.00007
2	21.115	0.8095	0.00011
1	21.360	0.8067	−0.00010
1	22.813	0.7915	0.00004
2	23.238	0.7872	0.00008
1	24.660	0.7714	−0.00007
2	25.807	0.7591	0.00003
2	34.435	0.6545	0
3	35.532	0.6399	0.00001
3	37.218	0.6167	−0.00001
3	48.199	0.4576	0.00005
4	49.009	0.4475	−0.00003
3	49.951	0.4371	0.00005
4	50.284	0.4335	−0.00003
3	51.860	0.4190	0
4	53.288	0.4088	0
3	53.945	0.4049	0.00001
4	55.178	0.3990	0.00001
3	56.228	0.3951	0
3	57.983	0.3908	0.00001
4	60.676	0.3882	0.00002
3	62.996	0.3885	0
4	64.723	0.3901	0.00004
		225°C	
1	22.158	0.8375	0.00003
1	24.220	0.8210	−0.00012
2	25.292	0.8126	0.00022
1	26.026	0.8060	−0.00018
2	28.263	0.7876	0.00009
2	38.758	0.6955	0.00000
3	39.978	0.6844	0.00001
2	42.051	0.6653	−0.00004
3	42.179	0.6642	0.00004
3	53.030	0.5682	0.00004
4	55.277	0.5506	−0.00010
3	59.495	0.5232	0.00007
4	59.866	0.5208	−0.00007
4	61.748	0.5113	0.00003
3	63.308	0.5046	0.00005
4	66.859	0.4930	−0.00004
4	87.577	0.4972	0.00000
3	89.709	0.5011	−0.00002
4	97.292	0.5182	0.00003
3	101.49	0.5288	−0.00004
3	127.67	0.6035	−0.00012
4	133.01	0.6203	0.00015
4	153.97	0.6855	0.00018
3	153.97	0.6850	−0.00018
4	180.30	0.7686	0.00000

[a] $\Delta Z = Z_{expt} - Z_{smooth}$.

Table VI. Smoothed Compressibilities, Residual Volumes, and Fugacity Coefficients

		75°C			100°C	
Press., atm	Z	γ, ml/gram	ν	Z	γ, ml/gram	ν
1.5	0.9663	8.888	0.9676	0.9734	7.510	0.9741
3.0	0.9298	9.265	0.9349	0.9455	7.702	0.9483
4.5	0.8904	9.642	0.9020	0.9155	7.970	0.9223
6.0	0.8482	10.020	0.8690	0.8845	8.167	0.8964
7.5				0.8508	8.441	0.8704
9.0				0.8142	8.761	0.8444
10.5				0.7721	9.210	0.8181
		125°C			150°C	
1.5	0.9785	6.475	0.9790	0.9825	5.603	0.9828
3.0	0.9563	6.597	0.9590	0.9645	5.691	0.9657
4.5	0.9332	6.720	0.9371	0.9459	5.782	0.9485
6.0	0.9090	6.868	0.9162	0.9269	5.865	0.9315
7.5	0.8836	7.024	0.8954	0.9071	5.959	0.9145
9.0	0.8569	7.201	0.8746	0.8866	6.023	0.8975
10.5	0.8286	7.393	0.8537	0.8655	6.166	0.8806
12.0	0.7980	7.620	0.8327	0.8433	6.284	0.8636
13.5	0.7653	7.873	0.8116	0.8198	6.422	0.8467
15.0	0.7292	8.175	0.7904	0.7957	6.555	0.8297
16.5	0.6879	8.566	0.7688	0.7700	6.707	0.8128
18.0				0.7428	6.877	0.7958
19.5				0.7131	7.080	0.7786
21.0				0.6806	7.320	0.7614
22.5				0.6444	7.606	0.7439
24.0				0.6027	7.967	0.7261
25.5				0.5511	7.471	0.7077
		160.6°C			175°C	
6	0.9331	5.503	0.9378	0.9406	5.049	0.9434
12	0.8577	5.849	0.8753	0.8746	5.327	0.8876
18	0.7705	6.289	0.8131	0.8010	5.633	0.8322
24	0.6608	6.973	0.7504	0.7153	6.046	0.7770
30	0.4838	8.487	0.6843	0.6081	6.658	0.7212
31.5	0.3408	10.323	0.6655			
33	0.2071	11.853	0.6417	0.5388	7.123	0.6926
34.5	0.2064	11.346	0.6195			
36	0.2090	10.838	0.5989	0.4471	7.827	0.6629
42	0.2281	9.065	0.5309	0.2824	8.707	0.5993
48	0.2509	7.698	0.4796	0.2808	7.636	0.5442
54	0.2745	6.628	0.4397	0.2966	6.639	0.5005
60	0.2986	5.766	0.4079	0.3164	5.806	0.4652
66	0.3223	5.065	0.3819	0.3378	5.113	0.4363
72	0.3464	4.478	0.3604	0.3599	4.531	0.4122
78	0.3694	3.988	0.3424	0.3818	4.039	0.3920
84	0.3940	3.559	0.3239	0.4048	3.611	0.3747
90	0.4160	3.201	0.3139	0.4264	3.248	0.3600
96	0.4425	2.864	0.3025	0.4505	2.917	0.3471
102	0.4650	2.588	0.2927	0.4725	2.636	0.3360
108	0.4865	2.345	0.2840	0.4937	2.389	0.3262
114	0.5125	2.109	0.2764	0.5148	2.169	0.3175
120	0.5343	1.914	0.2698	0.5399	1.954	0.3099
126	0.5554	1.741	0.2638	0.5606	1.777	0.3032
132	0.5813	1.565	0.2586	0.5806	1.619	0.2972
138	0.6035	1.417	0.2540	0.6085	1.446	0.2919
144	0.6250	1.285	0.2498	0.6302	1.309	0.2872
150	0.6479	1.158	0.2461	0.6511	1.185	0.2830
156	0.6703	1.043	0.2429	0.6714	1.074	0.2793
162	0.6922	0.9371	0.2400	0.6947	0.9603	0.2759
168	0.7138	0.8405	0.2374	0.7162	0.8609	0.2730
174	0.7360	0.7483	0.2351	0.7372	0.7699	0.2704
180	0.7581	0.6629	0.2331	0.7576	0.6863	0.2681
186	0.7799	0.5839	0.2313	0.7776	0.6093	0.2660
192	0.8014	0.5104	0.2298	0.8007	0.5290	0.2643
198	0.8229	0.4411	0.2285	0.8220	0.4581	0.2627
204	0.8447	0.3755	0.2274	0.8430	0.3923	0.2614
210	0.8662	0.3142	0.2264	0.8636	0.3310	0.2603
216	0.8876	0.2567	0.2256	0.8839	0.2739	0.2594
222	0.9089	0.2024	0.2250	0.9046	0.2189	0.2586
228	0.9303	0.1507	0.2245	0.9257	0.1661	0.2580

Table VI. *Continued*

		160.6°C			175°C	
Press., atm	Z	γ, ml/gram	ν	Z	γ, ml/gram	ν
234	0.9516	0.1019	0.2242	0.9465	0.1165	0.2576
240	0.9728	0.0559	0.2240	0.0672	0.0697	0.2583
246	0.9938	0.0124	0.2239	0.9876	0.0257	0.2572
252	1.0149	−0.0293	0.2239	1.0078	−0.0159	0.2572
258	1.0360	−0.0689	0.2240	1.0280	−0.0552	0.2573
264	1.0569	−0.1065	0.2243	1.0479	−0.0925	0.2575
270	1.0778	−0.1422	0.2246	1.0678	−0.1279	0.2579
276	1.0986	−0.1763	0.2250	1.0876	−0.1617	0.2583
282	1.1193	−0.2087	0.2257	1.1074	−0.1942	0.2588
288	1.1400	−0.2397	0.2262	1.1274	−0.2254	0.2595
294	1.1606	−0.2694	0.2269	1.1475	−0.2557	0.2602
300	1.1812	−0.2979	0.2277	1.1679	−0.2852	0.2610
306	1.2019	−0.3255	0.2286	1.1887	−0.3143	0.2620
312	1.2227	−0.3521	0.2295	1.2100	−0.3430	0.2630
		200°C			225°C	
6	0.9507	4.423	0.9525	0.9590	3.871	0.9602
12	0.8978	4.582	0.9059	0.9157	3.980	0.9211
18	0.8407	4.761	0.8599	0.8703	4.081	0.8826
24	0.7787	4.961	0.8146	0.8229	4.180	0.8448
30	0.7105	5.192	0.7698	0.7727	4.292	0.8078
33	0.6732	5.328	0.7476			
36	0.6335	5.478	0.7254	0.7204	4.400	0.7714
42	0.5470	5.804	0.6812	0.6658	4.508	0.7359
48	0.4601	6.052	0.6374	0.6111	4.590	0.7013
54	0.4046	5.933	0.5960	0.5604	4.612	0.6678
60	0.3885	5.484	0.5592	0.5202	4.530	0.6362
66	0.3918	4.958	0.5275	0.4953	4.332	0.6070
72	0.4032	4.460	0.5006	0.4849	4.053	0.5806
78	0.4185	4.011	0.4775	0.4848	3.742	0.5571
84	0.4360	3.613	0.4577	0.4913	3.431	0.5364
90	0.4578	3.260	0.4405	0.5017	3.137	0.5181
96	0.4741	2.947	0.4255	0.5151	2.862	0.5019
102	0.4936	2.670	0.4124	0.5302	2.609	0.4875
108	0.5142	2.420	0.4009	0.5464	2.379	0.4748
114	0.5341	2.199	0.3907	0.5632	2.171	0.4635
120	0.5540	2.000	0.3816	0.5805	1.981	0.4535
126	0.5740	1.819	0.3736	0.5984	1.805	0.4445
132	0.5945	1.653	0.3665	0.6171	1.643	0.4364
138	0.6162	1.497	0.3600	0.6352	1.498	0.4292
144	0.6347	1.365	0.3544	0.6529	1.365	0.4228
150	0.6525	1.247	0.3493	0.6716	1.240	0.4170
156	0.6697	1.139	0.3447	0.6918	1.119	0.4118
162	0.7051	0.9794	0.3405	0.7114	1.009	0.4072
168	0.7256	0.8787	0.3371	0.7307	0.9081	0.4031
174	0.7457	0.7868	0.3340	0.7488	0.8178	0.3994
180	0.7658	0.7002	0.3312	0.7676	0.7313	0.3962
186	0.7858	0.6196	0.3288	0.7864	0.6505	0.3933
192	0.8054	0.5454	0.3266	0.8057	0.5732	0.3907
198	0.8245	0.4770	0.3248	0.8247	0.5017	0.3885
204	0.8389	0.4250	0.3231	0.8435	0.4346	0.3866
210	0.8595	0.3601	0.3217	0.8628	0.2700	0.3850
216	0.8798	0.2994	0.3206	0.8816	0.3106	0.3836
222	0.9000	0.2525	0.3196	0.9003	0.2545	0.3825
228	0.1916	0.3188	0.9191	0.9191	0.2009	0.3815
234	0.9387	0.1410	0.3182	0.9379	0.1503	0.3808
240	0.9585	0.9030	0.3178	0.9566	0.1024	0.3803
246	0.9783	0.0475	0.3176	0.9752	0.0571	0.3800
252	0.9980	0.0043	0.3175	0.9939	0.0138	0.3798
258	1.0176	−0.0366	0.3175	1.0125	−0.0274	0.3799
264	1.0371	−0.0756	0.3177	1.0311	−0.0667	0.3800
270	1.0565	−0.1126	0.3181	1.0495	−0.1040	0.3804
276	1.0758	−0.1478	0.3185	1.0680	−0.1395	0.3809
282	1.0951	−0.1814	0.3191	1.0863	−0.1734	0.3815
288	1.1143	−0.2135	0.3198	1.1047	−0.2059	0.3823
294	1.1335	−0.2443	0.3206	1.1230	−0.2370	0.3832
300	1.1526	−0.2738	0.3216	1.1414	−0.2669	0.3842
306	1.1719	−0.3023	0.3226	1.1598	−0.2958	0.3854
312	1.1912	−0.3297	0.3237	1.1783	−0.3238	0.3866

Table VII. Comparison of Smoothed Compressibilities with Experimental Results of Beattie et al. (3)

Press., atm	Z, Beattie	ΔZ[a]	Press., atm	Z, Beattie	ΔZ[a]
	160.6°C			200°C	
23.75	0.6671	−0.0003	28.35	0.7306	−0.0003
28.73	0.5384	−0.0010	36.51	0.6273	−0.0004
30.84	0.4335	−0.0001	42.25	0.5444	−0.0006
31.48	0.3540	−0.0001	46.59	0.4803	−0.0005
31.56	0.2957	−0.0001	50.43	0.4332	−0.0004
31.58	0.2536	−0.0001	54.63	0.4023	−0.0003
31.73	0.2230	0.0000	60.38	0.3890	−0.0002
33.12	0.2069	−0.0002	69.68	0.3991	−0.0003
38.56	0.2168	0.0000	85.87	0.4426	−0.0002
85.36	0.3999	−0.0009	165.35	0.7102	−0.0023
258.30	1.0373	0.0007		225°C	
			31.21	0.7640	−0.0011
	175°C		41.29	0.6738	−0.0009
25.46	0.6927	−0.0007	49.18	0.6019	−0.0007
31.62	0.5735	−0.0004	55.92	0.5475	−0.0007
35.13	0.4780	−0.0003	62.44	0.5094	−0.0006
37.12	0.4040	−0.0002	69.85	0.4885	−0.0006
38.46	0.3488	−0.0005	79.60	0.4871	−0.0006
39.70	0.3086	+0.0003	94.10	0.5118	−0.0005
41.77	0.2841	−0.0002	117.24	0.5739	−0.0005
46.03	0.2783	−0.0003	217.08	0.8856	−0.0006
55.45	0.3017	0.0000			
114.62	0.5197	0.0023			
297.92	1.1586	0.0018			

[a] Smoothed − Beattie.

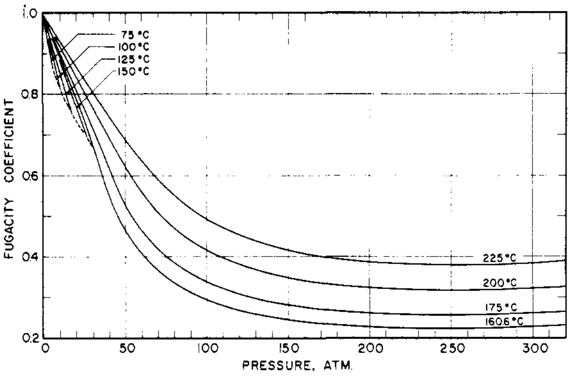

Figure 3. Fugacity coefficients of neopentane

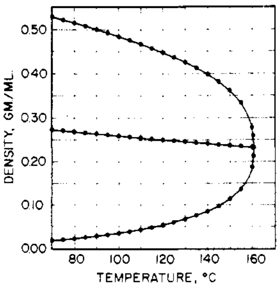

Figure 4. Orthobaric densities of neopentane

Table VIII. Comparison of Smoothed Compressibilities with the Experimental Results of Heichelheim (8, 14)

Press., atm	Z, Heichel-heim	ΔZ[a]	Press., atm	Z, Heichel-heim	ΔZ[a]
75°C (Run 8)			175°C (Run 18)		
4.700	0.8840	0.0004	36.068	0.4388	0.0025
5.198	0.8699	0.0015	38.673	0.3323	0.0023
5.734	0.8539	0.0023	45.274	0.2748	0.0005
100°C (Run 10)			200°C (Run 21)		
4.320	0.9178	0.0007	7.694	0.9354	0.0015
5.897	0.8846	0.0019	10.450	0.9098	0.0019
7.916	0.8385	0.0021	14.216	0.8749	0.0021
10.343	0.7735	0.0031	19.029	0.8194	0.0093
			24.897	0.7654	0.0028
125°C (Run 12)			27.012	0.7417	0.0028
4.108	0.9373	0.0019	29.195	0.7160	0.0030
5.662	0.9123	0.0021	31.437	0.6889	0.0030
7.713	0.8774	0.0022	33.705	0.6597	0.0029
10.326	0.8293	0.0022	35.984	0.6290	0.0030
13.459	0.7632	0.0024	38.247	0.5970	0.0031
150°C (Run 14)			200°C (Run 19)		
5.280	0.9339	0.0023	40.376	0.5751	−0.0022
7.268	0.9075	0.0025	42.629	0.5423	−0.0026
9.883	0.8712	0.0027	44.864	0.5097	−0.0028
13.198	0.8214	0.0026	47.126	0.4781	−0.0030
17.167	0.7543	0.0029	49.531	0.4488	−0.0032
25.267	0.5536	0.0036	52.346	0.4237	−0.0035
26.090	0.5087	0.0080	56.134	0.4057	−0.0041
			62.114	0.4008	−0.0050
175°C (Run 18)			73.157	0.4216	−0.0065
6.694	0.9319	0.0012			
9.205	0.9048	0.0013			
12.502	0.8676	0.0010			
16.666	0.8165	0.0013			
21.642	0.7487	0.0018			
27.081	0.6614	0.0016			
32.209	0.5551	0.0019			

[a] Smoothed − Heichelheim.

order of the polynomial used depended on the curvature of the graph of volume residual vs. pressure. The same order of polynomial was used throughout an isotherm. The interpolating interval was 0.25 atm. This scheme was tested at the lowest and highest pressures and at points of maximum curvature by comparison with graphical interpolation and was found to be of suitable precision. The fit was also tested by recalculating the original data. Maximum deviations were found to be ±0.02% except near the critical point, where deviations were as large as ±0.04%.

Smoothed compressibility factors. Smoothed compressibility factors were calculated from the interpolated volume residuals by the relationship

$$Z = 1 - P\gamma / RT \qquad (2)$$

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

Experimental gas compressibility data for neopentane have been published by Beattie et al. (*3*) and Heichelheim (*8*). Smoothed compressibility factors from the current work are compared to the results of Beattie in Table VII. Minor corrections have been applied to the Beattie data to compensate for the use of a different molecular weight (72.0924) and absolute temperature scale (K = °C + 273.13). A third correction was applied because Beattie et al. reported using a value of CO_2 vapor pressure for their dead-weight gage calibration different from the more recently reported value used by the current investigators (*6*, *11*). The agreement is excellent, with maximum deviations less than ±0.001 except at 175°C.

Table IX. Orthobaric Densities of Neopentane

Temp, °C	Vapor density, gram/ml Exptl	Calcd	Dev[a]
70	0.01753	0.01795	−0.00042
75	0.01970	0.01988	−0.00018
80	0.02214	0.02208	0.00006
85	0.02472	0.02458	0.00014
90	0.02763	0.02740	0.00023
95	0.03085	0.03056	0.00029
100	0.03434	0.03411	0.00023
105	0.03833	0.03808	0.00025
110	0.04272	0.04253	0.00019
115	0.04753	0.04751	0.00002
120	0.05306	0.05312	−0.00006
125	0.05930	0.05946	−0.00016
130	0.06644	0.06671	−0.00027
135	0.07484	0.07509	−0.00025
140	0.08464	0.08497	−0.00033
145	0.09652	0.09698	−0.00046
150	0.11215	0.11238	−0.00023
155	0.13490	0.13449	0.00041
160	0.18678	0.18513	0.00165
		Liquid density	
70	0.52904	0.52842	0.00062
75	0.52192	0.52185	0.00007
80	0.51499	0.51501	−0.00002
85	0.50787	0.50788	−0.00001
90	0.50022	0.50045	−0.00023
95	0.49246	0.49267	−0.00021
100	0.48368	0.48453	−0.00085
105	0.47569	0.47598	−0.00028
110	0.46672	0.46696	−0.00024
115	0.45723	0.45741	−0.00018
120	0.44743	0.44725	0.00018
125	0.43655	0.43636	0.00019
130	0.42503	0.42458	0.00045
135	0.41208	0.41168	0.00040
140	0.39788	0.39729	0.00059
145	0.38124	0.38078	0.00046
150	0.36119	0.36088	0.00031
155	0.33395	0.33430	−0.00035
160	0.27716	0.27919	−0.00203

[a] Exptl − Calcd.

The experimental results of Heichelheim (*8*) have been corrected by Silberberg et al. (*14*), who applied a graphical technique to reevaluate apparatus constants for the Burnet apparatus used by Heichelheim. The comparison to this work (Table VIII) shows divergences >1%.

Fugacity coefficients. The fugacity coefficients of neopentane were also 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 performed using Weddle's rule with an integrating interval of 0.25 atm. The fugacity coefficients so obtained are plotted in Figure 3 and presented in Table VI. The maximum error in values calculated from Equation 3 is estimated to be 0.1%.

Orthobaric Densities

The saturated state volumes were found by extrapolating each isotherm to the vapor pressure on large-scale graphs of pressure vs. volume. The resulting values are presented in Table IX and Figure 4. For smoothing, the results were fitted by the method of least squares to the equations:

$$\tfrac{1}{2}(d_l + d_g) = 0.23189 + 4.463 \times 10^{-4}(t_c - t) + 1.0485 \times 10^{-7}(t_c - t)^2 \qquad (4)$$

$$\tfrac{1}{2}(d_l - d_g) = 5.5606 \times 10^{-2}(t_c - t)^{1/3} + 2.1633 \times 10^{-4}(t_c - t) - 1.7190 \times 10^{-6}(t_c - t)^2 \qquad (5)$$

The value of the critical temperature used in Equations 4 and 5 was taken from Table XII. The standard errors of the regressions were 0.00011 g/ml for Equation 4 and 0.00057 g/ml for Equation 5. It may be seen from Table IX that the maximum deviation from the original data which results from using Equations 4 and 5 is less than 0.0006 g/ml except near the critical temperature.

Vapor Pressures

Data in the two-phase region for all four samples are reported in Table III. The average of the values for the largest samples was chosen as the vapor pressure for

Table X. Selected Vapor Pressures of Neopentane

Temp, °C	This work exptl, atm	Antoine equation, atm Calcd	Dev[a]	Nernst equation, atm Calcd	Dev[a]	Ref. 2, atm	Ref. 8, atm
50						3.509	
70	5.783	5.797	−0.014	5.779	0.004		
75	6.490	6.495	−0.005	6.490	0.000	6.493	6.493
80	7.262	7.257	0.005	7.263	−0.001		
85	8.097	8.086	0.011	8.100	−0.003		
90	9.002	8.985	0.017	9.004	−0.002		
95	9.975	9.958	0.017	9.979	−0.004		
100	11.027	11.009	0.018	11.029	−0.002	11.031	10.979
105	12.155	12.143	0.012	12.158	−0.003		
110	13.372	13.362	0.010	13.369	0.003		
115	14.670	14.671	−0.001	14.668	0.002		
120	16.068	16.074	−0.006	16.059	0.009		
125	17.553	17.573	−0.020	17.547	0.006	17.560	17.504
130	19.143	19.175	−0.032	19.139	0.004		
135	20.839	20.882	−0.043	20.839	0.000		
140	22.651	22.698	−0.047	22.655	−0.004		
145	24.589	24.627	−0.038	24.594	−0.005		
150	26.652	26.673	−0.021	26.663	−0.011	26.665	26.528
155	28.858	28.840	0.018	28.870	−0.012		
160	31.243	31.132	0.111	31.225	0.018		

[a] Exptl − Calcd.

Table XI. Latent Heats of Vaporization of Neopentane

	ΔH_v, cal/gram		
Temp, °C	Exptl (Eq 8)	Smoothed (Eq 9)	Dev[a]
70	62.524	62.439	0.084
75	61.096	61.031	0.065
80	59.458	59.578	−0.120
85	58.083	58.075	0.008
90	56.475	56.516	−0.040
95	54.814	54.894	−0.080
100	53.221	53.201	0.020
105	51.371	51.426	−0.055
110	49.499	49.556	−0.057
115	47.639	47.575	0.064
120	45.514	45.463	0.051
125	43.244	43.189	0.055
130	40.783	40.715	0.068
135	37.985	37.984	0.001
140	34.918	34.906	0.012
145	31.378	31.332	0.046
150	26.924	26.965	−0.041
155	20.888	21.043	−0.155
160	8.907	8.821	0.086

[a] Exptl − Smoothed.

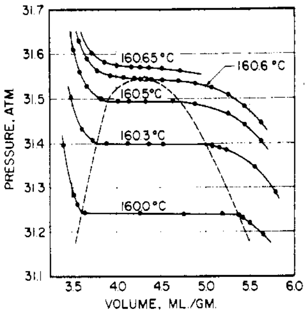

Figure 5. Specific volumes of neopentane in the critical region

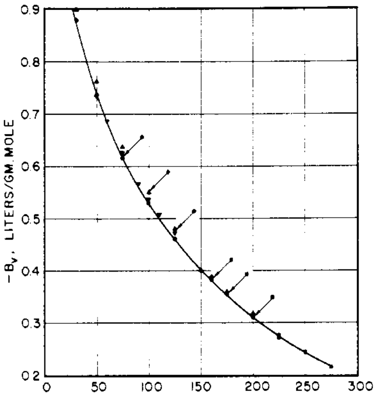

Figure 6. Second virial coefficients of neopentane

● This work
▲ Silberberg et al. (*14*)
■ Beattie et al. (*3*)
▼ Hamann and Lambert (*7*)
♦ Masia et al. (*13*)

each temperature, as it was felt that the largest sample would be relatively the least contaminated during the charging procedure. These values were then correlated by the least-squares method to the Antoine equation

$$\log_{10} P = 7.49038 - 1477.78/(314.2 + t) \quad (6)$$

Table XII. Critical Properties of Neopentane

	This work	Ref. *2*
t_c, °C	160.6 ± 0.05	160.6 ± 0.05
P_c, atm	31.545 ± 0.02	31.56 ± 0.03
V_c, ml/gram	4.312 ± 0.01	4.20 ± 0.04
Z_c	0.2758 ± 0.0006	0.2687

Table XIII. Second Virial Coefficients of Neopentane

	$-B_v$, l./g-mol				
Temp, °C	This work	Ref. *14*	Ref. *3*	Ref. *7*	Ref. *13*
30		0.900			0.881
50		0.763		0.734	0.737
60				0.686	
75	0.615[a]	0.637		0.626	0.618
90				0.566	
100	0.530	0.550		0.536	0.552
110				0.507	
125	0.460	0.479		0.472	0.476
150	0.401	0.417			
160.6	0.383		0.383		
161.5	0.381	0.385			
175	0.354	0.358	0.354		
200	0.311	0.318	0.311		
225	0.275		0.273		
250			0.243		
275			0.215		

[a] Graphically extrapolated.

and to the Nernst equation

$$\log_{10} P = 48.2788 - 2.89085 \times 10^3/T - 15.8043 \log_{10} T + 8.3142 \times 10^{-6} T^2 \quad (7)$$

Standard errors of the regression were, in logarithmic units, 0.00075 for Equation 6 and 0.00016 for Equation 7. A summary of the selected vapor pressures and the smoothed values calculated from these two equations is shown in Table X. The Nernst equation is seen to give the better fit to the original data, with a maximum deviation of 0.018 atm at 160°C, or 0.06%. Values reported in previous works (*2*, *8*) are also presented. The agreement with Beattie et al. (*2*) is satisfactory, as was the case with the other comparisons made previously.

Heats of Vaporization

Experimental saturated state densities and the Nernst equation were used to calculate heats of vaporization from the Clapeyron equation,

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

The results are presented in Table XI, with smoothed values calculated by fitting to the data the equation

$$\Delta H_v = -9.08888 \times 10^{-3}(t_c - t) + 9.81503 \times 10^{-5}(t_c - t)^2 + 10.77222\,(t_c - t)^{0.39} \quad (9)$$

by the method of least squares, using an iterative process to find the value of the exponent which minimized the sum of the squares of the residuals of ΔH_v. The standard error of this regression was 0.078 cal/g.

Critical Constants

The data in the critical region (Table IV) are plotted in Figure 5. The critical temperature was chosen as that of the isotherm which most closely exhibited the desired

Table XIV. Third Virial Coefficients of Neopentane

	C_v (l./g-mol)^2		
Temp, °C	This work	Ref. *14*	Ref. *3*
30		0.282	
50		0.150	
75	0.013	0.106	
100	0.0413	0.0919	
125	0.0462	0.0822	
150	0.0471	0.0690	
160.6	0.0498		0.0498
161.5	0.0498	0.0542	
175	0.0464	0.0510	0.0465
200	0.0415	0.0463	0.0416
225	0.0376		0.0370
250			0.0345
275			0.0317

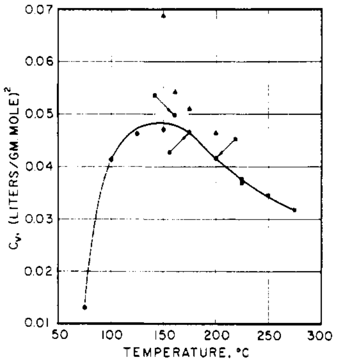

Figure 7. Third virial coefficients of neopentane

● This work
▲ Silberberg et al. (*14*)
■ Beattie et al. (*3*)

horizontal inflection point. The pressure corresponding to this inflection point was taken as the critical pressure. The critical volume was found on the orthobaric density plot, Figure 4, as the intersection between the saturated phase density curve and the line representing the average density. It is consistent with the critical density of 0.23189 g/ml from Equation 4. A comparison between these critical properties and those values reported by Beattie et al. (2) is made in Table XII. The agreement is satisfactory.

Virial Coefficients

The Leiden equation of state

$$PV/RT = 1 + B_v/V + C_v/V^2 + \cdots \qquad (10)$$

may be rewritten into the form

$$V(Z - 1) = B_v + C_v/V + \cdots \qquad (11)$$

It is seen that the limit of Equation 11 as $1/V \rightarrow 0$ is the second virial coefficient, B_v. To evaluate the virial coefficients, large-scale plots were made of the quantity $V(Z - 1)$ vs. $1/V$ for each isotherm. The value of the intercept was taken as the second virial coefficient, and the limiting value of the slope as $1/V \rightarrow 0$ was taken as the third virial coefficient. Random scatter in the experimental data precluded evaluation of higher-order coefficients. Total uncertainties in the virial coefficients are estimated to be 0.004 l./g-mol in B_v and 0.002 (l./g-mol)^2 in C_v up to the critical temperature and less at higher temperatures. The results of this work are compared with those of previous investigators in Tables XIII and XIV and in Figures 6 and 7. As was noted previously for other properties, the agreement with Beattie et al. (*3*) is excellent, whereas significant divergence from the values reported by Heichelheim (*8*) as modified by Silberberg et al. (*14*) is seen, particularly at the lower temperatures for the third virial coefficients.

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Nomenclature

B_v = second virial coefficient, l./g-mol
C_v = third virial coefficient, (l./g-mol)^2
d = density, gram/l.
f = fugacity, atm
ΔH_v = heat of vaporization, cal/gram
J = dimensional constant, 0.0242179 cal/ml atm
R = gas constant of neopentane, 1.137241 atm ml/K-gram
P = pressure, atm
T = absolute temperature, K
t = temperature, °C
V = specific volume, ml/gram
Z = compressibility factor, PV/RT
γ = volume residual, ml/gram
ν = fugacity coefficient, f/P

Subscripts

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

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