PVT Surface and Thermodynamic Properties of Neopentane

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Selected values of vapor pressure, specific volume, enthalpy, and entropy are presented for the saturated liquid and vapor states of neopentane from normal boiling point (282.628 K) to the critical point (433.75 K). Experimental values of the density, together with the saturated vapor densities, were fitted to a differential regional Benedict–Webb–Rubin (DR-BWR) equation of state; compressibility factors were generated from 282.628 to 600 K with pressure to 400 atm. Thermodynamic properties of the real gas, $H - H^0$, $(H - H^0)/T$, $A - A^0$, $S - S^0$, $S - S^\mathrm{I}$, $G - G^0$, $(G - G^0)/T$, $G - G^\mathrm{I}$, and f/P, were also calculated from the classical relationships.

Previous correlation studies (*5, 7*) present both vapor–liquid coexistence and superheated vapor thermodynamic properties of neopentane. The present compilation is part of a general revision of the j-tables of the API Research Project 44 (*22*) for C_1–C_5 alkanes.

Physical Constants

Table I is a list of the physical constants and conversion factors (*25*) used in this investigation. A summary of selected, experimentally determined, critical constants is shown in Table II. The present set of critical constants (T_c = 433.75 ± 0.05 K; P_c = 31.545 ± 0.02 atm; ρ_c = 0.232 ± 0.002 g cm^{-3}) is based on the modern measurements of Beattie et al. (*2*) and Dawson (*7*).

Table I. Physical Constants and Conversion Factors

Constants	Value
Critical temperature	433.75 K
Critical pressure	31.545 atm
Critical density	0.232 g cm^{-3}
Critical volume	311 cm^3 mol^{-1}
Normal boiling point	282.628 K
Triple point	256.6 K
Molecular weight	72.1514 mass units
Gas constant, R	82.05606 atm cm^3 K^{-1} mol^{-1}
Temperature conversions	0 °C = 273.15 K 0 °F = 459.67 °R
Pressure conversions	1 atm = 760 mmHg 1 psia = 0.068 045 96 atm
Energy conversions	1 defined thermochemical calorie = 4.1840 J (exact)

Table II. Critical Constants of Neopentane

Investigator	T_c, K	P_c, atm	ρ_c, g cm^{-3}
Beattie, Douslin, and Levine (*2*) (1951)	433.75	31.57	0.238
Kobe and Lynn (*14*) (1953)	433.75	31.57	0.238
Partington, Rowlinson, and Weston (*18*) (1960)	433.75		
Kudchadker, Alani, and Zwolinski (*15*) (1968)	433.75	31.57	0.238
Dawson (*7*) (1971)	433.75	31.545	0.2319
Selected values	433.75	31.545	0.232

Vapor Pressure

A Frost-Kalkwarf vapor-pressure equation was used with the parameters determined to fit the experimental literature values from the normal boiling point (NBP) to the CP.

$$\log P = 19.911\,10 - 1882.58/T - 5.411\,56 \log T + 1191.74(P/T^2) \qquad (1)$$

where P is in atm and T is in K.

This equation correlates the measurements of Aston and Messerly (*1*), Beattie et al. (*2*), Heichelheim et al. (*11*), Heichelheim and McKetta (*12*), and Whitemore and Fleming (*24*) with an average deviation of 0.052 atm. At the NBP of 282.628 K and the CP of 433.75 K, the equation agrees exactly with the experimental values. The equation is believed to be accurate to ±0.49% from 300 to CP, with a maximum uncertainty of ±0.08 atm near the CP. Table III, the selected saturation properties, contains the calculated vapor pressure and its temperature derivative from the NBP to the CP.

Saturated Liquid Volume

The available measurements are those of Bendiel (*4*) (293 K), Dawson (*7*) (344–433 K), and Phibbs (*19*) (257–302 K).

Selected data from the above references were fit to a modified Guggenheim equation (*9*) which was further modified as shown below to pass through the CP. The constants of the equation were evaluated for two temperature zones meeting at 333.15 K.

$$\rho_{SL} = (\rho_L + A\theta + B\theta^2)(1.0 + 1.0\theta + 0.25\theta^3) \qquad (2)$$

where $\theta = (1 - T/T_L)^{1/3}$, T is in K, and ρ is in g cm^{-3}. Constants of eq 2:

	ρ_L	A	B	T_L
Less than 333.15 K	0.368 46	−150.259 91 × 10^{-3}	174.359 30 × 10^{-3}	403.15
More than 333.15 K	0.232	168.872 66 × 10^{-3}	−295.718 04 × 10^{-4}	433.75

The selected data are represented by the equation with a standard deviation of 0.000 27 g cm^{-3} from 256 to 433 K. Values from eq 2 appear in Table III.

Saturated Vapor Volume

Dawson (*7*) (344–433 K) and Heichelheim and McKetta (*12*) (303–433 K) measured the vapor volumes. These values together with experimental superheated vapor volumes (*2, 3, 7, 11, 12*) were used to evaluate the DR-BWR equation of state constants.

The selected densities and temperatures near the critical point were tested with the method proposed by Davis and Rice (*6*) and

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[†] Deceased.

Table III. Saturated Properties of Neopentane

T, K	P, atm	dP/dT (atm K^{-1})	V_{SL}, cm^3 mol^{-1}	V_{SV}, cm^3 mol^{-1}	λ, cal mol^{-1}	H_{SL}, cal mol^{-1}	H_{SV}, cal mol^{-1}	S_{SL}, cal mol^{-1} K^{-1}	ΔS_S, cal mol^{-1} K^{-1}	S_{SV}, cal mol^{-1} K^{-1}
282.628	1.000	0.036 13	119.6	22 013	5411	0	5411	0	19.15	19.15
290.0	1.295	0.044 08	121.3	17 265	5304	408	5712	0.54	18.29	18.83
300.0	1.797	0.056 58	123.7	12 670	5154	924	6078	1.30	17.18	18.48
310.0	2.434	0.071 15	126.3	9 490	4999	1434	6433	2.04	16.12	18.16
320.0	3.227	0.087 89	129.0	7 234	4836	1950	6786	2.76	15.11	17.87
330.0	4.199	0.106 90	132.0	5 597	4666	2466	7132	3.51	14.14	17.65
340.0	5.373	0.128 30	135.2	4 385	4487	2977	7464	4.23	13.20	17.43
350.0	6.773	0.152 17	138.8	3 472	4297	3478	7875	4.99	12.28	17.27
360.0	8.425	0.178 68	142.8	2 772	4093	3974	8067	5.71	11.37	17.08
370.0	10.357	0.208 0	147.4	2 226	3879	4464	8343	6.44	10.48	16.92
380.0	12.596	0.240 4	152.8	1 794	3629	4966	8595	7.18	9.55	16.73
390.0	15.176	0.276 3	159.2	1 446	3356	5463	8819	7.90	8.61	16.51
400.0	18.134	0.316 1	167.1	1 161	3042	6001	9043	8.63	7.60	16.23
410.0	21.513	0.360 6	177.5	920.0	2657	6566	9223	9.39	6.48	15.87
415.0	23.377	0.385 0	184.3	809.9	2419	6895	9314	9.80	5.83	15.63
420.0	25.366	0.411 0	192.9	706.9	2147	7230	9377	10.22	5.11	15.33
425.0	27.489	0.439 0	204.9	603.6	1800	7595	9395	10.68	4.24	14.92
426.0	27.931	0.444 8	208.0	583.4	1721	7678	9399	10.79	4.04	14.83
427.0	28.380	0.450 8	211.4	561.9	1633	7765	9398	10.90	3.82	14.72
428.0	28.834	0.456 9	215.3	540.6	1539	7858	9397	11.02	3.60	14.62
429.0	29.294	0.463 0	219.8	517.5	1431	7958	9389	11.16	3.34	14.50
430.0	29.758	0.469 3	225.2	493.2	1309	8055	9364	11.31	3.04	14.35
431.0	30.232	0.475 7	231.9	466.9	1166	8162	9328	11.49	2.71	14.20
432.0	30.711	0.482 1	241.0	436.7	987	8275	9262	11.71	2.28	13.99
433.0	31.195	0.488 7	255.8	387.5	726	8429	9155	12.04	1.68	13.72
433.5	31.442	0.492 1	271.0	366.4	493	8562	9055	12.36	1.14	13.50
433.75	31.545	0.493 8	311	311	0	8849	8849	12.91	0	12.91

found to fit to a standard deviation of 4 × 10^{-4} the following equation:

$$(\rho_{SL} + \rho_{SV}) = 0.4629 + 0.702(\rho_{SL} - \rho_{SV})^3 \qquad (3)$$

with ρ (g cm^{-3}).

Enthalpy of Vaporization

The enthalpies of vaporization computed from eq 4 below with eq 1 and previously selected vapor and liquid volumes appear in Table IV in comparison with the values reported by other authors (*5*, *7*). The measured enthalpy of vaporization, 5438 cal mol^{-1}, of Aston and Messerly (*1*) at 282.61 K shows close agreement with the value of 5420 cal mol^{-1} which is calculated from the Clapeyron equation,

$$\frac{dP}{dT} = \frac{\lambda}{T(V_{SV} - V_{SL})} \qquad (4)$$

after extrapolating orthobaric volumes and the vapor pressure derivatives to below the NBP.

Enthalpy of Saturated Liquid and Vapor

As no specific heat of saturated liquid data are available from the normal boiling point to the critical point, the saturated liquid enthalpy data reported by Dawson (*7*) have been accepted after correction for the present reference state $H_{SL} = 0$ at 282.628 K.

From the NBP to CP, the vapor enthalpy was obtained by addition of the heat of vaporization to the liquid enthalpy calculated above. The locus of $\bar{H} = (H_{SL} + H_{SV})/2$ was checked for smoothness. Values of H_{SL} and H_{SV} indicated that the enthalpy locus was reasonably straight, and a plot of H_S vs. V_S allowed a check of the values obtained from the H_S vs. T diagram in the critical region.

Entropy of Saturated Liquid and Vapor

The saturated liquid entropy values reported by Dawson (*7*) are given in Table III after correction for the present reference state $S_{SL} = 0$ at 282.628 K. The vapor entropy was obtained by the addition of (λ/T) to S_{SL}. The entropy locus, $\bar{S}_S = (S_{SL} + S_{SV})/2$, was found to be reasonably straight. Again a plot of S_S vs. V_S provided a check of entropy values at densities near the critical point.

Table IV. Comparison of Enthalpies of Vaporization

T, K	λ, cal mol^{-1}		
	DK[b]	D[a,c]	This work
290	5365	—	5304
300	5259	—	5154
310	5127	—	4999
320	4979	—	4836
330	4808	—	4666
340	4624	—	4487
350	4414	4365	4297
360	4180	4150	4093
370	3933	3922	3879
380	3663	3665	3629
390	3374	3375	3356
400	3056	3052	3042
410	2673	2660	2657
420	2134	2155	2147
430	1148	1312	1309

[a] Values are interpolated. [b] Das and Kuloor (*5*). [c] Dawson (*7*).

Compressibility Data

The measurements of Beattie et al. (*3*) covered 434–548 K with pressures from 24 to 298 atm. Dawson (*7*) determined values over the temperature range of 343–498 K and pressure range of 5.6–312 atm. Heichelheim et al. (*11*) measured from 303 to 473 K and 1 to 73 atm. Heichelheim and McKetta (*12*) reported their data for the temperature range of 303–473 K and 0.5–70 atm of pressure. Figure 1 shows the P, T regions of these major data sources.

Table V. Thermodynamic Properties of Neopentane

Pressure (atm)	Z	$H - H^0$ (cal mol^{-1})	$(H - H^0)/T$ (cal mol^{-1} K^{-1})	$A - A^0$ (cal mol^{-1})	$S - S^0$ (cal mol^{-1} K^{-1})	$S - S^i$ (cal mol^{-1} K^{-1})	$G - G^0$ (cal mol^{-1})	$(G - G^0)/T$ (cal mol^{-1} K^{-1})	$G - G^i$ (cal mol^{-1})	(f/P)
Temperature = 290 K										
1	0.9541	−92.753	−0.320	0.506	−0.2304	−0.2304	−25.9	−0.089	−25.9	0.9560
1.30[a]	0.9398	−121.703	−0.420	149.889	−0.8170	−0.3032	115.2	0.397	−33.8	0.9430
Temperature = 310 K										
1	0.9640	−77.424	−0.250	0.324	−0.1792	−0.1792	−21.9	−0.071	−21.9	0.9651
2.43[a]	0.9080	−198.103	−0.639	549.748	−2.2297	−0.4635	493.1	1.591	−54.4	0.9154
Temperature = 330 K										
1	0.9712	−65.642	−0.199	0.214	−0.1423	−0.1423	−18.7	−0.057	−18.7	0.9719
4	0.8750	−286.087	−0.867	912.829	−3.3849	−0.6319	830.9	2.518	−77.6	0.8884
4.20[a]	0.8680	−302.338	−0.916	945.190	−3.5182	−0.6687	858.7	2.602	−81.7	0.8829
Temperature = 350 K										
1	0.9766	−56.385	−0.161	0.145	−0.1151	−0.1151	−16.1	−0.046	−16.1	0.9771
4	0.9005	−240.779	−0.688	966.326	−3.2514	−0.4984	897.2	2.563	−66.3	0.9090
6.77[a]	0.8189	−440.384	−1.258	1339.494	−4.7258	−0.9269	1213.7	3.468	−116.0	0.8463
Temperature = 370 K										
1	0.9808	−48.978	−0.132	0.101	−0.0945	−0.0945	−14.0	−0.038	−14.0	0.9811
4	0.9194	−206.192	−0.557	1020.453	−3.1552	−0.4022	961.2	2.598	−57.4	0.9249
8	0.8254	−449.333	−1.214	1537.287	−5.0224	−0.8930	1409.0	3.808	−118.9	0.8506
10.36[a]	0.7595	−621.745	−1.680	1736.456	−5.8959	−1.2537	1559.7	4.215	−157.9	0.8067
Temperature = 390 K										
1	0.9840	−42.958	−0.110	0.071	−0.0786	−0.0786	−12.3	−0.032	−12.3	0.9842
4	0.9337	−178.981	−0.459	1074.921	−3.0835	−0.3305	1023.6	2.625	−50.1	0.9374
8	0.8593	−381.922	−0.979	1616.538	−4.8448	−0.7153	1507.5	3.865	−102.9	0.8755
12	0.7720	−623.005	−1.597	1941.583	−6.1232	−1.1885	1765.0	4.526	−159.5	0.8139
15.18[a]	0.6861	−864.695	−2.217	2141.382	−7.0845	−1.6835	1898.2	4.867	−208.1	0.7643
Temperature = 410 K										
1	0.9866	−37.997	−0.093	0.051	−0.0662	−0.0662	−10.9	−0.026	−10.9	0.9868
4	0.9448	−157.095	−0.383	1129.598	−3.0287	−0.2757	1084.7	2.646	−44.0	0.9473
8	0.8845	−330.449	−0.806	1697.114	−4.7159	−0.5865	1603.1	3.910	−90.0	0.8954
12	0.8170	−526.804	−1.285	2033.912	−5.8823	−0.9476	1884.9	4.597	−138.3	0.8438
16	0.7384	−759.235	−1.852	2280.792	−6.8952	−1.3893	2067.8	5.043	−189.6	0.7922
20	0.6387	−1061.397	−2.589	2487.891	−7.9393	−1.9902	2193.7	5.351	−245.4	0.7398
21.51[a]	0.5893	−1214.942	−2.963	2564.649	−8.4029	−2.3090	2230.2	5.440	−268.2	0.7193
Temperature = 430 K										
1	0.9887	−33.861	−0.079	0.036	−0.0563	−0.0563	−9.6	−0.022	−9.6	0.9888
4	0.9536	−139.167	−0.324	1184.397	−2.9860	−0.2330	1144.8	2.662	−39.0	0.9554
8	0.9039	−289.759	−0.674	1778.430	−4.6190	−0.4895	1696.4	3.945	−79.3	0.9113
12	0.8499	−455.247	−1.059	2128.919	−5.7117	−0.7771	2000.8	4.653	−121.1	0.8678
16	0.7901	−641.270	−1.491	2381.934	−6.6139	−1.1080	2202.7	5.123	−164.8	0.8245
20	0.7217	−858.083	−1.996	2584.789	−7.4541	−1.5050	2347.2	5.459	−210.9	0.7811
24	0.6387	−1128.594	−2.625	2762.018	−8.3305	−2.0194	2453.5	5.706	−260.3	0.7373
28	0.5208	−1533.104	−3.565	2939.904	−9.4507	−2.8334	2530.7	5.885	−314.7	0.6917
29	0.4751	−1699.207	−3.952	2993.905	−9.8717	−3.1848	2545.6	5.920	−329.7	0.6797
29.76[a]	0.4229	−1897.972	−4.414	3048.361	−10.3571	−3.6190	2555.6	5.943	−341.8	0.6701
Temperature = 450 K										
1	0.9904	−30.375	−0.068	0.026	−0.0484	−0.0484	−8.6	−0.019	−8.6	0.9904
10	0.8975	−326.672	−0.726	2060.794	−5.1020	−0.5294	1969.2	4.376	−88.4	0.9058
20	0.7759	−727.355	−1.616	2693.361	−7.1565	−1.2075	2493.1	5.540	−184.0	0.8139
30	0.6143	−1293.136	−2.874	3093.439	−8.9819	−2.2277	2748.7	6.108	−290.7	0.7223
40	0.3322	−2578.651	−5.730	3472.025	−12.1198	−4.7943	2875.3	6.389	−421.2	0.6241
50	0.2908	−3225.710	−7.168	3567.833	−13.6883	−5.9197	2934.0	6.520	−561.9	0.5333
60	0.3193	−3397.022	−7.549	3591.805	−14.1789	−6.0482	2983.5	6.630	−675.3	0.4697
80	0.3910	−3550.516	−7.890	3618.418	−14.7216	−6.0196	3074.2	6.832	−841.7	0.3899
100	0.4654	−3624.930	−8.055	3637.012	−15.0761	−5.9310	3159.3	7.021	−956.0	0.3431
150	0.6490	−3696.552	−8.215	3672.830	−15.6793	−5.7290	3359.1	7.465	−1118.5	0.2860
200	0.8267	−3701.381	−8.225	3702.735	−16.1094	−5.5878	3547.9	7.884	−1186.9	0.2650
250	0.9993	−3675.699	−8.168	3730.016	−16.4557	−5.4909	3729.3	8.287	−1204.8	0.2597
300	1.1675	−3632.384	−8.072	3755.788	−16.7509	−5.4240	3905.5	8.679	−1191.6	0.2636
400	1.4937	−3514.730	−7.811	3804.649	−17.2457	−5.3476	4245.8	9.435	−1108.3	0.2893
Temperature = 500 K										
1	0.9934	−23.724	−0.047	0.011	−0.0344	−0.0344	−6.5	−0.013	−6.5	0.9934
10	0.9318	−248.249	−0.496	2287.499	−4.9361	−0.3635	2219.8	4.440	−66.5	0.9352
20	0.8581	−526.032	−1.052	2979.888	−6.7300	−0.7810	2839.0	5.678	−135.6	0.8724
30	0.7776	−844.292	−1.689	3390.403	−8.0277	−1.2735	3169.6	6.339	−207.6	0.8114
40	0.6898	−1218.358	−2.437	3687.899	−9.1965	−1.8710	3379.9	6.760	−282.9	0.7521

Table V. *Continued*

Pressure (atm)	Z	$H - H^0$ (cal mol^{-1})	$(H - H^0)/T$ (cal mol^{-1} K^{-1})	$A - A^0$ (cal mol^{-1})	$S - S^0$ (cal mol^{-1} K^{-1})	$S - S^{\mathrm{l}}$ (cal mol^{-1} K^{-1})	$G - G^0$ (cal mol^{-1})	$(G - G^0)/T$ (cal mol^{-1} K^{-1})	$G - G^{\mathrm{l}}$ (cal mol^{-1})	(f/P)
					Temperature = 500 K					
50	0.5998	−1656.786	−3.314	3920.438	−10.3597	−2.5910	3523.1	7.046	−361.3	0.6950
60	0.5286	−2107.920	−4.216	4092.989	−11.4656	−3.3349	3624.9	7.250	−440.5	0.6417
80	0.4935	−2707.887	−5.416	4271.144	−12.9522	−4.2501	3768.2	7.536	−582.8	0.5560
100	0.5290	−2985.308	−5.971	4348.424	−13.7320	−4.5869	3880.7	7.761	−691.9	0.4982
150	0.6744	−3250.762	−6.502	4443.233	−14.7414	−4.7911	4119.9	8.240	−855.2	0.4226
200	0.8314	−3332.187	−6.664	4501.297	−15.3322	−4.8105	4333.9	8.668	−926.9	0.3932
250	0.9874	−3348.627	−6.697	4547.280	−15.7668	−4.8021	4534.8	9.070	−947.6	0.3851
300	1.1408	−3332.231	−6.664	4587.262	−16.1186	−4.7917	14727.0	9.454	−936.4	0.3894
400	1.4393	−3246.936	−6.494	4657.579	−16.6814	−4.7833	5093.7	10.187	−855.3	0.4226
					Temperature = 600 K					
1	0.9967	−15.655	−0.026	0.000	−0.0195	−0.0195	−4.0	−0.007	−4.0	0.9967
10	0.9669	−159.586	−0.266	2743.507	−4.7727	−0.2001	2704.0	4.507	−39.5	0.9674
20	0.9340	−326.009	−0.543	3569.125	−6.3609	−0.4119	3490.5	5.818	−78.9	0.9359
30	0.9019	−499.135	−0.832	4051.388	−7.3894	−0.6352	3934.5	6.558	−118.0	0.9057
40	0.8711	−678.273	−1.130	4392.222	−8.1948	−0.8692	4238.6	7.064	−156.7	0.8767
50	0.8423	−861.865	−1.436	4654.359	−8.8805	−1.1118	4466.4	7.444	−194.8	0.8492
60	0.8166	−1047.196	−1.745	4865.168	−9.4897	−1.3590	4646.6	7.744	−231.8	0.8232
80	0.7787	−1406.686	−2.344	5183.417	−10.5441	−1.8421	4919.8	8.200	−301.4	0.7765
100	0.7632	−1722.585	−2.871	5406.515	−11.4115	−2.2664	5124.3	8.541	−362.8	0.7375
150	0.8052	−2246.268	−3.744	5730.832	−12.9084	−2.9581	5498.8	9.165	−471.4	0.6732
200	0.9038	−2502.798	−4.171	5904.703	−13.8214	−3.2998	5790.1	9.650	−522.9	0.6448
250	1.0197	−2629.540	−4.383	6021.542	−14.4575	−3.4928	6045.0	10.075	−533.9	0.6389
300	1.1412	−2686.986	−4.478	6111.059	−14.9437	−3.6169	6279.2	10.465	−516.9	0.6481
400	1.3869	−2693.373	−4.489	6249.548	−15.6731	−3.7750	6710.5	11.184	−428.4	0.6980

[a] Saturation pressure.

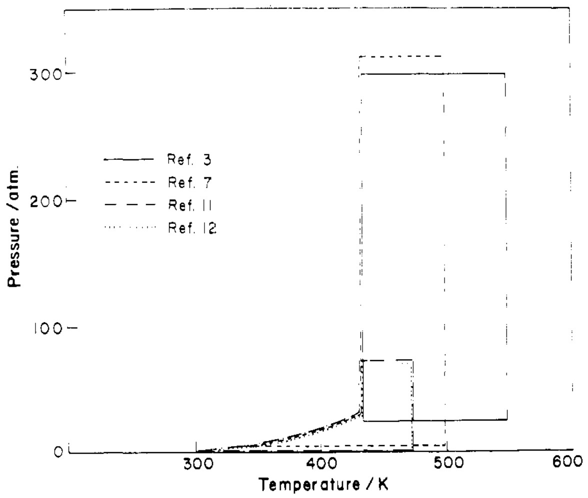

Figure 1. Regional block diagram of literature data for neopentane.

Correlation Procedure

Although agreement between the major data sources is not excellent, no sound reason was found for deletion of any point, and each was given equal weight. Saturated vapor volumes selected in Table III were added to the present PVT data sets and given a weight of four, except for the CP and the NBP which were each weighted ten. This procedure was used to constrain the fitted PVT surface to values consistent with the selected saturated properties which form a boundary condition. The differential regional BWR equation (*8*) is:

$$\phi = \sum_{r=1}^{N} \sum_{j=1}^{7} K_{jr}\theta_j^* \tag{5}$$

where $\phi = P - RT\rho$, $\theta_1^* = RT(\rho^*)^2$, $\theta_2^* = (\rho^*)^2$, $\theta_3^* = (\rho^*)^2T^{-2}$, $\theta_4^* = RT(\rho^*)^3$, $\theta_5^* = (\rho^*)^3$, $\theta_6^* = (\rho^*)^6$, $\theta_7^* = (\rho^*)^3[1 + K_{8r}(\rho^*)^2][\exp(-K_{8r}\rho^{*2})]T^{-2}$, and $\rho^* = \rho - \rho_{r-1,n_{r-1}}$, with $\rho_{r-1,n_{r-1}}$ equal to the density at the interface between regions r and $r - 1$ when the density falls in region r. An optimal fit is generally obtained when the interface between the first and second regions is equal to the critical density. For neopentane there were not sufficient data at densities above the critical to require more than one region. Standard BWR coefficients for the first region ($K_{11} = B_0$, $K_{21} = -A_0$, $K_{31} = -C_0$, $K_{41} = b$, $K_{51} = -a$, $K_{61} = a\alpha$, $K_{71} = c$, and $K_{81} = +\gamma$) and coefficients of eq 5 for the first and second regions are found in Table VI. The latter coefficients are used only with normalized densities. Table VI also provides the first region constants in the usual metric units for comparison to literature BWR coefficients.

Accuracy of Saturated Properties

The selected liquid volumes of Table III are considered accurate to a maximum of ±0.2% from the NBP to 370 K, 0.1% from 370 to 420 K, and 0.2% from 420 to 433 K. The error limits of vapor volume at the NBP are ±32 cm^3 mol^{-1}, providing the measurement of enthalpy of vaporization of Aston and Messerly (*1*) is correct. The accuracy of enthalpy of vaporization values in Table III depends on that of the vapor pressure slope and the vapor volume with error limits of 3.9% for dP/dT.

PVT Surface and Corresponding Thermodynamic Properties

Table VI shows the ability of the DR-BWR model to fit the available experimental PVT data. Both experimental data and isotherms from the model were plotted as compressibility factor $Z = (P/\rho RT)$ vs. pressure on large graphs such that the finest division was 0.0005 for Z. The Z–P graphs show that in all regions the model provides a smooth surface with reasonable compromise between the experimental results.

Thermodynamic properties were calculated from the PVT surface by the usual relationships and appear in Table V, a condensed version of the API Research Project 44 j-Tables (a complete version of Table V has been deposited in the ACS Microfilm Depository Service). Values of pressure in parentheses are at saturated conditions. The tables are thermodynamically

Table VI. Constants for the DR-BWR Equation: Neopentane

	Region I	Region II
No. of data points	740	144
Density range, g mol cm^{-3}	0.000 027 6 to 0.003 220 6	0.003 220 6 to 0.007 169
Normalized density range	0.003 85 to 0.449 242	0.449 242 1 to 1.0
Av percentage of deviation of Z	0.307 60	0.315 55
Max percentage of deviation of Z	1.544 46	2.489 57
Constants for eq 5[a]		
K_{1r}	$8.143\,81 \times 10^{-3}$	$7.547\,18 \times 10^{-3}$
K_{2r}	$-6.112\,08 \times 10^{2}$	$-3.602\,53 \times 10^{2}$
K_{3r}	$-7.306\,18 \times 10^{7}$	$1.583\,21 \times 10^{7}$
K_{4r}	$2.730\,92 \times 10^{-2}$	$-1.380\,49 \times 10^{-2}$
K_{5r}	$-1.484\,88 \times 10^{3}$	$5.743\,16 \times 10^{2}$
K_{6r}	$1.008\,90 \times 10^{3}$	$-2.666\,63 \times 10^{3}$
K_{7r}	$2.253\,38 \times 10^{8}$	$-1.324\,01 \times 10^{9}$
K_{8r}	2.55	$8.020\,51 \times 10^{3}$
BWR constants[b]		
1 A_0	$1.189\,26 \times 10^{7}$	
B_0	$1.584\,59 \times 10^{2}$	
C_0	$1.421\,60 \times 10^{12}$	
a	$4.030\,17 \times 10^{9}$	
b	$7.412\,09 \times 10^{4}$	
c	$6.115\,99 \times 10^{14}$	
α	$1.844\,11 \times 10^{6}$	
γ	$4.961\,67 \times 10^{4}$	

[a] Only for use in eq 5 with ρ normalized as (g mol cm^{-3}/0.007 169). [b] $P - RT\rho = (B_0RT - A_0 - C_0/T^2)\rho^2 + (bRT - A)\rho^3 + a\alpha\rho^6 + (c\rho^3/T^2)(1 + \gamma\rho^2)e^{-\gamma\rho^2}$, P (atm), T (K), ρ (g mol cm^{-3}).

Table VII. Compressibility Factors from Corresponding States

		Z				
T, K	P, atm	DK[b]	D[a,c]	Pitzer[d]	LGH[e]	This work
450	10	0.9018	0.9020	0.902	0.91	0.8960
	20	0.7854	0.7785	0.783	0.78	0.7713
500	80	0.4875	0.4865	0.487	0.47	0.4935
	100	0.5216	0.5266	0.525	0.54	0.5290
	200	0.8287	0.8326	0.831	0.82	0.8314
550	80	0.6266	—	0.631	0.63	0.6582
	100	0.6204	—	0.620	0.62	0.6477
	200	0.8442	—	0.846	0.85	0.8590

[a] Values are interpolated. [b] Das and Kuloor(*5*). [c] Dawson (*7*). [d] Pitzer (*20*); Pitzer et al. (*21*). [e] Lydersen et al. (*16*).

Table VIII. Second Virial Coefficient

	$-B$, cm^3 mol^{-1}						
T, K	Ref 2, 3	Ref 7	Ref 10	Ref 13	Ref 17	Ref 23	This work
303.15	—	—	842	885	881	900.4	941.6
323.15	—	—	734	766	737	764.0	803.5
333.15	—	—	686	—	—	—	745.2
348.15	—	—	626	—	618	637.2	668.4
363.15	—	—	566	591	—	—	602.4
373.15	—	530	536	—	552	548.7	563.4
383.15	—	—	507	—	—	—	527.9
398.15	—	460	472	—	476	477.5	480.1
423.15	—	401	—	—	—	413.5	412.7
448.15	354	354	—	—	—	357.7	357.5
473.15	311	311	—	—	—	318.0	311.4
498.15	273	275	—	—	—	—	272.7
523.15	243	—	—	—	—	—	239.6
548.15	215	—	—	—	—	—	211.6

consistent as the other functions were calculated from $A - A^0$ and $S - S^0$, where A is the energy function for density and temperature with S its temperature derivative. Table V extends only to 600 K or somewhat above the maximum experimental temperature of 548 K rather than 1500 K as in the revised API Research Project 44 Tables. The values above 548 K are an extrapolation of the present surface and further assume no decomposition of neopentane.

Discussion

Table VII is a comparison of present values with those calculated from corresponding states by two methods: The corresponding state tables of Lydersen et al. (*16*) and Pitzer's (*20, 21*) acentric factor procedure. Table VIII is a comparison of the literature second virial coefficients with the present values where:

$$B = B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3} \tag{6}$$

The present PVT surface was not constrained by the critical conditions:

$$\left(\frac{\partial P}{\partial \rho}\right)_{T_c} = 0 = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T_c} \tag{7}$$

However, the constants of Table VI for the region yield $(\partial P_r/\partial \rho_r)|_{T_r=1} = 0.0352$ and $(\partial^2 P_r/\partial {\rho_r}^2)|_{T_r=1} = 0.3176$.

Glossary

A	Helmholtz energy, cal mol^{-1}
A_0, B_0, C_0, a, b, c, α, γ	BWR constants in atm cm^3 K^{-1} mol^{-1} units
B	second virial coefficient, cm^3 mol^{-1}
CP	critical point, 433.75 K
f	fugacity, atm
G	Gibbs energy, cal mol^{-1}
H	enthalpy, cal mol^{-1}
K	constants of eq 5
N	total number of regions
NBP	normal boiling point, 282.628 K
n	number of data points in a given region
P	pressure, atm
R	gas constant, 82.05606 atm cm^3 K^{-1} mol^{-1}
S	entropy, cal K^{-1} mol^{-1}
T	temperature, K
V	specific volume, cm^3 mol^{-1}
Z	compressibility factor

Greek Letters

λ	latent heat of vaporization, cal mol^{-1}
θ	dimensionless temperature variable defined by eq 2
θ^*	density and temperature-dependent factors defined in eq 5
ρ	density, mol cm^{-3}
ρ_L	limiting density constant in eq 2
ϕ	$P - RT\rho$, atm

Superscripts

I	ideal gas state
0	standard state; ideal gas at 1 atm and temperature T
*	indicates difference between quantity in region i and the value of that quantity at the region $i - 1$/region i interface

Subscripts

c	critical point value
i	running index for BWR terms
r	divided by critical value
r	region
S	saturated property
SV	saturated vapor
SL	saturated liquid
T_L	limiting temperature constant in eq 2

Literature Cited

(1) Aston, J. G., Messerly, G. H., *J. Am. Chem. Soc.*, **58,** 2354 (1936).
(2) Beattie, J. A., Douslin, D. R., Levine, S. W., *J. Chem. Phys.*, **19,** 948 (1951).
(3) Beattie, J. A., Douslin, D. R., Levine, S. W., *J. Chem. Phys.*, **20,** 1619 (1952).
(4) Bendiel, R. W., M.S. Thesis, Pennsylvania State University, University Park, Pa., 1941.
(5) Das, T. R., Kuloor, N. R., *Indian J. Tech.*, **8,** 65 (1968).
(6) Davis, B. W., Rice O. K., *J. Chem. Phys.*, **47,** 5043 (1967).
(7) Dawson, P. P., Ph.D. dissertation, The University of Texas, Austin, Texas, 1971.
(8) Eubank, P. T., Fort, B. F., *Can. J. Chem. Eng.*, **47,** 177 (1969).
(9) Guggenheim, E. A., *J. Chem. Phys.*, **13,** 253 (1945).
(10) Hamann, S. D., Lambert, J. A., *Aust. J. Chem.*, **7,** 1 (1954).
(11) Heichelheim, H. R., Kobe, K. A., Silberberg, I. H., McKetta, J. J., *J. Chem. Eng. Data*, **7,** 507 (1962).
(12) Heichelheim, H. R., McKetta, J. J., *Chem. Eng. Prog. Symp. Ser.*, **59** (44), 23 (1963).
(13) Huff, J. A., Reed, T. M., *J. Chem. Eng. Data*, **8,** 306 (1963).
(14) Kobe, K. A., Lynn, R. E., *Chem. Rev.*, **52,** 117 (1953).
(15) Kudchadker, A. P., Alani, G. H., Zwolinski, B. J., *Chem. Rev.*, **68,** 659 (1968).
(16) Lydersen, A. L., Greenkorn, R. A., Hougen, O. A., "Generalized Thermodynamic Properties of Pure Liquids", University of Wisconsin, College of Engineering, Report 4, Oct 1955.
(17) Maisia, A. P., Pena, M. D., Lluna, J. A. B., *An. Fis. Quim., Ser. B*, **60,** 229 (1964).
(18) Partington, E. J., Rowlinson, J. S., Weston, J. F., *Trans. Faraday Soc.*, **56,** 479 (1960).
(19) Phibbs, M. K., private communication, E. I. Dupont, 16th June 1952.
(20) Pitzer, K. S., *J. Am. Chem. Soc.*, **77,** 3427 (1955).
(21) Pitzer, K. S., Lippmann, D. Z., Curl, R. F., Huggins, C. M., Petersen, D. E., *J. Am. Chem. Soc.*, **77,** 3433 (1955).
(22) "Selected Values of Properties of Hydrocarbons and Related Compounds", API Research Project 44, Thermodynamic Research Center, Texas A&M University, College Station, Texas (Looseleaf data sheets, extant 1971).
(23) Silberberg, I. H., Lin, D. C. K., McKetta, J. J., *J. Chem. Eng. Data*, **12,** 226 (1967).
(24) Whitemore, F. C., Fleming, G. H., *J. Am. Chem. Soc.*, **55,** 3803 (1933).
(25) Wilhoit, R. C., Hathaway, A. W., "Table of Conversion Factors Based on Accepted Constants as of 1965", Report of Investigation, API Research Project 44, Thermodynamic Research Center, Texas A&M University, College Station, Texas, 1965.

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Supplementary Material Available: The complete Table V thermodynamic properties of neopentane (76 pages). Ordering information is given on any current masthead page.