be seen from the values of ΔH^0 in different percentages of organic media that the ΔH^0 value in a medium with lower percentage of organic component is within experimental error and linear in composition and that such a value with higher percentage of organic component passes through a maximum. According to Arnett et al. (*1*), the addition of polar solvent (ethanol, methanol) up to a mole fraction of 0.1 increases the structure in the solution and at that composition the maximum order is obtained. Any addition in polar solvent can no longer build structure without interfering with the established order in the system. Thus many properties of the mixture such as molar volume, activity coefficient, sound velocity, and temperature at maximum density of water show maximum at this composition.

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Received for review June 26, 1975. Accepted August 30, 1976.

PVT Surface and Thermodynamic Properties of *n*-Pentane

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Selected values of vapor pressure, specific volume, enthalpy, and entropy are presented for the saturated liquid and vapor states of *n*-pentane from normal boiling point (309.19 K) to the critical point (469.65 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 309 to 600 K with pressure to 700 atm. Thermodynamic properties of the real gas, $H - H^0$, $(H - H^0)/T$, $A - A^0$, $S - S^0$, $S - S^{\mathrm{l}}$, $G - G^0$, $(G - G^0)/T$, $G - G^{\mathrm{l}}$, and f/P, were also calculated from the classical relationships.

A previous correlation study (*5*) presents both vapor–liquid coexistence and superheated vapor thermodynamic properties of *n*-pentane. The present compilation is part of a general revision of the j-tables of the API Research Project 44 (*26*) for C_1–C_5 alkanes.

Physical Constants

Table I is a list of the physical constants and conversion factors (*29*) used in this investigation. A summary of selected, experimentally determined, critical constants is shown in Table II. The present set of critical constants ($T_c = 469.65 \pm 0.15$ K; $P_c = 33.25 \pm 0.10$ atm; $\rho_c = 0.237 \pm 0.005$ g cm^{-3}) is based on the modern measurements of Beattie et al. (*2*), Jordan and Kay (*13*), Partington et al. (*20*), and Ambrose et al. (*1*). These critical constants are the same as those selected by Kudchadker et al. (*15*) and differ but slightly from those selected earlier by Kobe and Lynn (*14*).

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.

$$\log P = 17.306\,98 - 1971.73/T - 4.393\,06 \log T + 997.021(P/T^2) \qquad (1)$$

where P is in atm and T is in K.

This equation correlates the measurements of Beattie et al. (*2*), Li and Canjar (*16*), Sage and Lacey (*24*), Sage et al. (*25*), and Willingham et al. (*31*) with an average deivation of 0.037 atm. In addition, the equation is in approximate agreement (average deviation of 0.06 atm) with data of Messerly and Kennedy (*18*), Nicolini (*19*), and Tickner and Lossing (*28*), which were not used to determine the constants of eq 1.

At the NBP of 309.19 K and the CP of 469.65 K, the equation agrees exactly with the experimental values. The equation is believed to be accurate to ±0.29% from 300 K to CP, with a maximum uncertainty of ±0.1 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 Calengaert (*4*) (288 K), Carney (*6*) (243–293 K), Dornte and Smyth (*8*) (263–303 K), Li and Canjar (*16*) (423–448 K), Sage and Lacey (*24*) (311–444 K), Sage et al. (*25*) (294–378 K), NGAA (*27*) (228–334 K); Wibout et al. (*30*) (288–293 K), and Young (*32*) (273–466 K).

Selected data from the above references were fitted to a modified Guggenheim equation (*12*) 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 323.15 K.

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

where $\theta = (1 - T/T_{\mathrm{L}})^{1/3}$, T (K), and ρ (g cm^{-3}). Constants of eq

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[†] Deceased.

Table I. Physical Constants and Conversion Factors

Constants	Value
Critical temperature	496.65 K
Critical pressure	33.25 atm
Critical density	0.237 g cm^{-3}
Critical volume	304 cm^3 mol^{-1}
Normal boiling point	309.19 K
Triple point	143.429 K
Molecular weight	72.1514 mass units
Gas constant, R	82.056060 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 *n*-Pentane

Investigator	T_c, K	P_c, atm	ρ_c, g cm^{-3}
Young (*33*), 1910	470.35	33.03	0.2323
Sage and Lacey (*24*), 1942	470.35	33.60	0.229
Beattie, Levine, and Douslin (*2*), 1951	469.77	33.31	0.244
Kobe and Lynn (*14*), 1953	469.75	33.3	0.232
Partington, Rowlinson, and Weston (*20*), 1960	469.55	—	—
Ambrose, Cox, and Townsend (*1*), 1960	469.49	—	—
Jordan and Kay (*13*), 1968	469.75	33.30	0.232
Selected values (ref 15 and this work)	469.65	33.25	0.237

2 are shown below.

	ρ_L	A	B	T_L
Less than 323.15 K	0.595 813	−229.949 02 × 10^{-3}	184.651 29 × 10^{-3}	403.15
More than 323.15 K	0.237	171.983 51 × 10^{-3}	−312.454 42 × 10^{-4}	469.65

Table IV. Comparison of Enthalpies of Vaporization

T, K	λ/cal mol^{-1}				
	Y[a,b]	GA[a,c]	SLS[a,d]	SL[a,e]	This work
300	6154	6261	—	—	—
310	5983	6144	6151	—	6090
320	—	6033	6028	6016	5951
330	—	5882	5884	5863	5806
340	—	5716	5721	5701	5652
350	—	5530	5550	5536	5489
360	—	5328	5356	5357	5316
370	—	5113	(5143)[f]	5173	5131
380	—	4895	—	4981	4934
390	—	—	—	4756	4720
400	—	—	—	4516	4488
410	—	—	—	4273	4228
420	—	—	—	3978	3940
430	—	—	—	3669	3608
440	—	—	—	3249	3215
450	—	—	—	(2698)[f]	2723

[a] Values are interpolated. [b] Young (*33*). [c] Griffiths and Awbery (*11*). [d] Sage, Lacey, and Schaafsma (*25*). [e] Sage and Lacey (*24*). [f] Values in parentheses are extrapolated.

The selected data are represented by the equation with a standard deviation of 0.000 24 g cm^{-3} from 225 to 469 K. Values from eq 2 appear in Table III.

Saturated Vapor Volume

Li and Canjar (*16*) (423–448 K), Sage and Lacey (*24*) (311–444 K), Sage et al. (*25*) (294–378 K), and Young (*32*) (273–466 K) measured the vapor volumes. These values together with experimental superheated vapor volumes (*16*, *23–25*) 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 (*7*) and

Table III. Saturated Properties of *n*-Pentane

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}
309.19	1.000	0.03399	118.2	24104	6101	0	6101	0	19.73	19.73
310.0	1.029	0.03473	118.4	23491	6090	55	6145	0.16	19.65	19.81
320.0	1.425	0.04477	120.4	17283	5951	524	6475	1.68	18.60	20.28
330.0	1.931	0.05662	122.6	12961	5806	1006	6812	3.21	17.59	20.80
340.0	2.564	0.07039	124.9	9881	5652	1524	7176	4.67	16.62	21.29
350.0	3.345	0.08620	127.4	7644	5489	2070	7559	6.22	15.68	21.90
360.0	4.295	0.10417	130.2	5987	5316	2606	7922	7.67	14.77	22.44
370.0	5.436	0.12440	133.2	4739	5131	3154	8285	9.29	13.87	23.16
380.0	6.791	0.14703	136.5	3785	4934	3753	8687	10.82	12.98	23.80
390.0	8.385	0.17219	140.1	3044	4720	4183	8903	12.50	12.10	24.60
400.0	10.244	0.2001	144.3	2461	4488	4754	9242	14.10	11.22	25.32
410.0	12.396	0.2308	149.0	1995	4228	5366	9594	15.60	10.31	25.91
420.0	14.871	0.2647	154.6	1619	3940	6015	9955	17.20	9.38	26.58
430.0	17.702	0.3021	161.3	1309	3608	6660	10268	18.70	8.39	27.09
440.0	20.927	0.3434	169.8	1049	3215	7276	10491	19.82	7.31	27.13
450.0	24.586	0.3892	181.4	823.8	2723	7904	10627	20.80	6.05	26.85
455.0	26.593	0.4141	189.4	719.2	2416	8179	10595	21.32	5.31	26.63
460.0	28.729	0.4404	200.2	615.5	2036	8476	10512	21.85	4.43	26.28
461.0	29.172	0.4458	202.9	594.4	1947	8542	10489	21.94	4.22	26.16
462.0	29.621	0.4513	205.9	573.0	1853	8615	10468	22.04	4.01	26.05
463.0	30.075	0.4569	209.3	551.2	1751	8688	10439	22.16	3.78	25.94
464.0	30.534	0.4625	213.1	528.8	1640	8769	10409	22.28	3.53	25.81
465.0	31.000	0.4683	217.5	505.7	1519	8859	10378	22.40	3.27	25.67
466.0	31.471	0.4741	222.8	481.6	1384	8966	10350	22.52	2.97	25.49
467.0	31.948	0.4800	229.4	454.9	1223	9082	10305	22.65	2.62	25.27
468.0	32.431	0.4859	238.5	424.4	1023	9215	10238	22.82	2.19	25.01
469.0	32.919	0.4919	253.7	388.7	754	9397	10151	23.00	1.61	24.61
469.5	33.166	0.4949	271.6	350.4	443	9621	10064	23.21	0.94	24.15
469.65	33.250	0.4960	304	304	0	9886	9886	23.60	0	23.60

found to fit to a standard deviation of 7×10^{-4} the following equation:

$$(\rho_{SL} + \rho_{SV}) = 0.4713 + 0.4401(\rho_{SL} - \rho_{SV})^3 \qquad (3)$$

with ρ in 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 (*11, 24, 25, 33*). The measured enthalpy of vaporization, 6262 cal mol^{-1}, of Messerly and Kennedy (*18*) at 298.16 K shows close agreement with the value of 6265 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 Sage et al. (*25*) have been accepted after correction for the present reference state $H_{SL} = 0$ at 309.192 K.

From the NBP to 370 K, the vapor enthalpy was obtained by addition to the heat of vaporization to the liquid enthalpy calculated above. To establish the enthalpy envelope up to the critical temperature, the following graphical procedures were employed. Starting at 380 K, the enthalpy of vaporization was marked on an overlay to the H_S vs. T diagram and adjusted upward and downward until a position was obtained where both H_{SL} and H_{SV} would result in increased curvature of the envelope at the successive temperatures of Table III; as a second criterion, the locus of $\bar{H} = (H_{SL} + H_{SV})/2$ was checked for smoothness. Values of H_{SL} and H_{SV} below 380 K 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 Sage et al. (*25*) were accepted after correction for the present reference state $S_{SL} = 0$ at 309.192 K. The changes along the liquid portion of the saturation envelope, obtained after being smoothed graphically, are reported in Table III. From NBP to 370 K, the vapor entropy was obtained by the addition of (λ/T) to S_{SL}. Above 370 K, a graphical method identical with that for enthalpy was used with entropy locus, $\bar{S}_S = (S_{SL} + S_{SV})/2$, 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.

Compressibility Data

The measurements of Rose-Innes and Young (*23*) covered 313–553 K with pressures from 1 to 75 atm. Sage et al. (*25*) covered a higher pressure range of 0.7–204 atm with a temperature range of 294–375 K. Sage and Lacey (*24*) extended the coverage to 0.7–680 atm and 311–511 K. Beattie et al. (*2, 3*) determined values over the temperature range 473–573 K and pressure range 26–348 atm. Li and Canjar (*16*) reported their data for 373–573 K and 10–217 atm; their data are in approximate agreement with those of Beattie et al. (*2, 3*) and Sage and Lacey (*24*). Figure 1 shows the P, T regions of these major data sources.

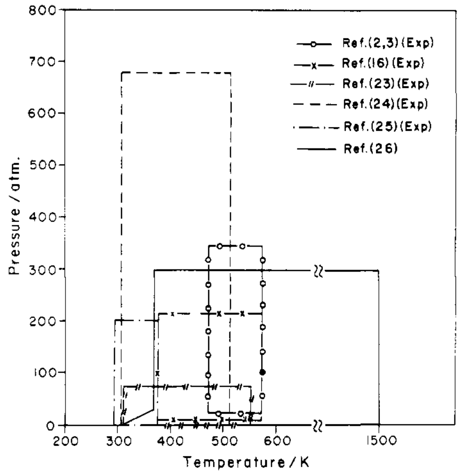

Figure 1. Regional block diagram of literature data for *n*-pentane.

Table V. Constants for the DR-BWR Equation: *n*-Pentane

	Region I	Region II
No. of data points	679	98
Density range, g cm^{-3}	0.001 612 7 to 0.237	0.237 to 0.570 051 8
Normalized density range	0.002 829 to 0.426 715	0.426 715 to 1.0
Av percentage of deviation of Z	0.533 02	0.892 48
Max percentage deviation of Z	1.789 14	3.990 28
Constants for eq 5[a]		
K_{1r}	$9.440\,20 \times 10^{-3}$	$-4.667\,90 \times 10^{-2}$
K_{2r}	$-7.587\,66 \times 10^{2}$	$4.228\,13 \times 10^{3}$
K_{3r}	$-1.292\,19 \times 10^{8}$	$-5.887\,46 \times 10^{8}$
K_{4r}	$4.951\,33 \times 10^{-2}$	$-7.920\,68 \times 10^{-2}$
K_{5r}	$-3.038\,93 \times 10^{3}$	$-1.148\,87 \times 10^{3}$
K_{6r}	$2.498\,26 \times 10^{3}$	$-8.151\,82 \times 10^{2}$
K_{7r}	$4.964\,32 \times 10^{8}$	$1.228\,85 \times 10^{9}$
K_{8r}	3.2	5.332 62
BWR constants[b]		
A_0	$1.215\,54 \times 10^{7}$	
B_0	$1.512\,31 \times 10^{2}$	
C_0	$2.070\,08 \times 10^{12}$	
a	$6.161\,86 \times 10^{9}$	
b	$1.003\,95 \times 10^{5}$	
c	$1.006\,58 \times 10^{15}$	
α	$1.666\,90 \times 10^{6}$	
γ	$5.126\,38 \times 10^{4}$	

[a] Only for use in eq 5 with ρ normalized as (g cm^{-3}/0.570 051 8). [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}).

Correlation Procedure

Although agreement between the major data sources is not perfect, 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 force the fitted PVT surface to values consistent with the selected saturated properties which form a boundary condition. The differential regional BWR equation is (*10*):

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

where $\phi = P - RT\rho$, $\theta_1{}^* = RT(\rho^*)^2$, $\theta_2{}^* = (\rho^*)^2$, $\theta_3{}^* = (\rho^*)^2T^{-2}$, $\theta_4{}^* = RT(\rho^*)^3$, $\theta_5{}^* = (\rho^*)^3$, $\theta_6{}^* = (\rho^*)^6$, $\theta_7{}^* = (\rho^*)^3[1$

Table VI. Thermodynamic Properties of *n*-Pentane

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 = 310 K										
1	0.9520	−105.751	−0.341	0.588	−0.2477	−0.2477	−29.0	−0.093	−29.0	0.9541
1.03^{a}	0.9505	−108.994	−0.352	18.397	−0.3127	−0.2554	−12.1	−0.039	−29.8	0.9527
Temperature = 330 K										
1	0.9619	−88.835	−0.269	0.382	−0.1948	−0.1948	−24.6	−0.074	−24.6	0.9632
1.93^{a}	0.9241	−177.336	−0.537	432.726	−1.6980	−0.3915	383.0	1.161	−48.1	0.9292
Temperature = 350 K										
1	0.9693	−75.678	−0.216	0.256	−0.1560	−0.1560	−21.1	−0.060	−21.1	0.9701
3.35^{a}	0.8904	−271.360	−0.775	842.818	−2.9657	−0.5676	766.6	2.190	−72.7	0.9007
Temperature = 370 K										
1	0.9749	−65.240	−0.176	0.176	−0.1270	−0.1270	−18.3	−0.049	−18.3	0.9755
4	0.8928	−280.017	−0.757	1022.031	−3.3061	−0.5532	943.2	2.549	−75.3	0.9025
5.44^{a}	0.8486	−396.453	−1.071	1251.134	−4.1522	−0.7899	1139.9	3.081	−104.2	0.8678
Temperature = 390 K										
1	0.9793	−56.820	−0.146	0.124	−0.1048	−0.1048	−15.9	−0.041	−15.9	0.9796
4	0.9126	−240.219	−0.616	1075.966	−3.2013	−0.4483	1008.3	2.585	−65.4	0.9190
8	0.8089	−528.514	−1.355	1622.498	−5.1358	−1.0064	1474.5	3.781	−136.0	0.8389
8.39^{a}	0.7975	−560.209	−1.436	1660.536	−5.2922	−1.0693	1503.7	3.856	−143.2	0.8312
Temperature = 410 K										
1	0.9827	−49.929	−0.122	0.088	−0.0876	−0.0876	−14.0	−0.034	−14.0	0.9829
4	0.9277	−208.771	−0.509	1130.306	−3.1225	−0.3696	1071.5	2.613	−57.2	0.9321
8	0.8455	−448.677	−1.094	1700.856	−4.9360	−0.8065	1575.1	3.842	−118.0	0.8651
12	0.7465	−741.612	−1.809	2045.995	−6.2956	−1.3609	1839.6	4.487	−183.6	0.7981
12.40^{a}	0.7352	−775.264	−1.891	2074.767	−6.4254	−1.423	1859.2	4.535	−190.5	0.7914
Temperature = 430 K										
1	0.9854	−44.221	−0.103	0.064	−0.0740	−0.0740	−12.4	−0.029	−12.4	0.9856
4	0.9396	−183.385	−0.426	1184.899	−3.0620	−0.3091	1133.3	2.636	−50.5	0.9426
8	0.8728	−387.929	−0.902	1780.915	−4.7912	−0.6617	1672.3	3.889	−103.4	0.8860
12	0.7966	−623.854	−1.451	2136.154	−6.0147	−1.0801	1962.5	4.564	−159.4	0.8297
16	0.7046	−913.766	−2.125	2400.119	−7.1200	−1.6141	2147.8	4.995	−219.7	0.7731
17.70^{a}	0.6567	−1067.076	−2.482	2499.855	−7.6134	−1.9067	2206.7	5.132	−247.2	0.7487
Temperature = 450 K										
1	0.9876	−39.439	−0.088	0.047	−0.0631	−0.0631	−11.1	−0.025	−11.1	0.9877
4	0.9490	−162.523	−0.361	1239.640	−3.0146	−0.2616	1194.0	2.653	−44.8	0.9511
8	0.8938	−339.938	−0.755	1861.887	−4.6820	−0.5525	1766.9	3.927	−91.3	0.9029
12	0.8329	−537.543	−1.195	2230.012	−5.8183	−0.8837	2080.7	4.624	−139.9	0.8551
16	0.7640	−764.657	−1.699	2497.529	−6.7806	−1.2747	2286.6	5.081	−191.1	0.8075
20	0.6817	−1041.029	−2.313	2715.789	−7.7164	−1.7673	2431.3	5.403	−245.7	0.7596
24	0.5704	−1427.418	−3.172	2918.156	−8.8037	−2.4926	2534.3	5.632	−305.8	0.7102
24.59^{a}	0.5485	−1505.508	−3.346	2949.753	−9.0040	−2.6450	2546.3	5.658	−315.2	0.7027
Temperature = 460 K										
1	0.9885	−37.335	−0.081	0.040	−0.0585	−0.0585	−10.4	−0.023	−10.4	0.9886
4	0.9530	−153.447	−0.334	1267.048	−2.9946	−0.2417	1224.1	2.661	−42.3	0.9548
8	0.9025	−319.526	−0.695	1902.595	−4.6371	−0.5077	1813.5	3.942	−86.0	0.9101
12	0.8476	−502.130	−1.092	2277.690	−5.7405	−0.8059	2138.5	4.649	−131.4	0.8660
16	0.7867	−707.640	−1.538	2548.659	−6.6552	−1.1493	2353.8	5.117	−179.0	0.8221
20	0.7167	−947.823	−2.060	2766.271	−7.5115	−1.5624	2507.4	5.451	−229.1	0.7782
24	0.6310	−1249.662	−2.717	2957.283	−8.4127	−2.1016	2620.2	5.696	−282.9	0.7336
28	0.5051	−1716.046	−3.731	3153.342	−9.6028	−2.9856	2701.2	5.872	−342.7	0.6872
28.73^{a}	0.4685	−1859.153	−4.042	3198.224	−9.9388	−3.2705	2712.7	5.897	−354.7	0.6782
Temperature = 470 K										
1	0.9894	−35.395	−0.075	0.034	−0.0543	−0.0543	−9.9	−0.021	−9.9	0.9895
10	0.8859	−383.909	−0.817	2153.336	−5.1719	−0.5993	2046.9	4.355	−102.2	0.8962
20	0.7453	−871.750	−1.855	2819.392	−7.3478	−1.3987	2581.7	5.493	−214.3	0.7948
30	0.5292	−1674.913	−3.566	3269.530	−9.5873	−2.8331	2830.1	6.022	−344.4	0.6915
40	0.2047	−3888.489	−8.273	3647.699	−14.4551	−7.1295	2905.4	6.182	−537.6	0.5621
50	0.2440	−3985.110	−8.479	3657.539	−14.7596	−6.9910	2951.9	6.281	−699.3	0.4727
60	0.2840	−4037.150	−8.590	3664.990	−14.9657	−6.8350	2996.7	6.376	−824.7	0.4133
80	0.3634	−4088.527	−8.699	3677.314	−15.2590	−6.5570	3083.2	6.560	−1006.8	0.3401
100	0.4414	−4106.236	−8.737	3688.102	−15.4744	−6.3292	3166.7	6.738	−1131.5	0.2975
150	0.6304	−4086.467	−8.695	3712.345	−15.8592	−5.9089	3367.4	7.165	−1309.3	0.2459
200	0.8128	−4023.460	−8.561	3734.824	−16.1351	−5.6135	3560.1	7.575	−1385.1	0.2267
250	0.9901	−3938.980	−8.381	3756.438	−16.3536	−5.3888	3747.2	7.973	−1406.2	0.2216
300	1.1634	−3841.710	−8.174	3777.524	−16.5356	−5.2088	3930.0	8.362	−1393.6	0.2247

Table VI. *Continued*

Temperature = 470 K

400	1.5004	−3624.466	−7.712	3818.715	−16.8302	−4.9321	4285.7	9.119	−1306.4	0.2467
500	1.8272	−3389.456	−7.212	3859.058	−17.0651	−4.7239	4631.1	9.853	−1169.2	0.2857
600	2.1460	−3144.197	−6.690	3898.840	−17.2610	−4.5577	4968.5	10.571	−1002.1	0.3418
700	2.4582	−2892.534	−6.154	3938.206	−17.4292	−4.4198	5299.2	11.275	−815.2	0.4175

Temperature = 500 K

1	0.9915	−30.404	−0.061	0.022	−0.0440	−0.0440	−8.4	−0.017	−8.4	0.9916
10	0.9106	−323.262	−0.647	2288.786	−5.0466	−0.4740	2200.0	4.400	−86.2	0.9168
20	0.8084	−704.043	−1.408	2986.729	−7.0011	−1.0521	2796.5	5.593	−178.0	0.8359
30	0.6850	−1186.976	−2.374	3412.540	−8.5735	−1.8192	3099.8	6.200	−277.4	0.7563
40	0.5211	−1901.383	−3.803	3749.922	−10.3516	−3.0261	3274.4	6.549	−388.4	0.6763
50	0.3567	−2915.118	−5.830	4009.146	−12.5710	−4.8024	3370.4	6.741	−513.9	0.5959
60	0.3299	−3459.164	−6.918	4096.263	−13.7802	−5.6495	3430.9	6.862	−634.4	0.5278
80	0.3842	−3756.504	−7.513	4143.210	−14.5765	−5.8745	3531.7	7.063	−819.3	0.4382
100	0.4523	−3864.008	−7.728	4167.918	−14.9761	−5.8310	3624.1	7.248	−948.5	0.3847
150	0.6263	−3939.616	−7.879	4209.913	−15.5570	−5.6066	3838.9	7.678	−1136.3	0.3184
200	0.7970	−3919.763	−7.840	4242.630	−15.9217	−5.4000	4041.1	8.082	−1219.7	0.2927
250	0.9636	−3861.024	−7.722	4271.609	−16.1931	−5.2283	4235.5	8.471	−1246.9	0.2849
300	1.1267	−3781.251	−7.563	4298.527	−16.4111	−5.0843	4424.3	8.849	−1239.1	0.2871
400	1.4439	−3586.771	−7.174	4348.783	−16.7526	−4.8545	4789.5	9.579	−1159.5	0.3111
500	1.7516	−3366.281	−6.733	4396.172	−17.0174	−4.6762	5142.4	10.285	−1028.2	0.3550
600	2.0516	−3131.284	−6.263	4441.777	−17.2345	−4.5312	5486.0	10.972	−865.7	0.4182
700	2.3453	−2887.381	−5.775	4486.145	−17.4187	−4.4092	5821.9	11.644	−682.8	0.5028

Temperature = 600 K

1	0.9957	−19.654	−0.033	0.003	−0.0242	−0.0242	−5.1	−0.009	−5.1	0.9957
10	0.9563	−201.974	−0.337	2743.851	−4.8230	−0.2504	2691.8	4.486	−51.7	0.9575
20	0.9117	−416.953	−0.695	3570.576	−6.4705	−0.5215	3465.4	5.776	−104.1	0.9164
30	0.8665	−646.260	−1.077	4054.757	−7.5698	−0.8156	3895.6	6.493	−156.9	0.8766
40	0.8213	−890.521	−1.484	4398.168	−8.4596	−1.1341	4185.3	6.975	−210.1	0.8384
50	0.7776	−1148.482	−1.914	4662.960	−9.2441	−1.4754	4398.0	7.330	−263.2	0.8018
60	0.7376	−1415.149	−2.359	4875.248	−9.9629	−1.8322	4562.6	7.604	−315.8	0.7672
80	0.6800	−1931.215	−3.219	5186.248	−11.2270	−2.5250	4805.0	8.008	−416.2	0.7052
100	0.6610	−2352.399	−3.921	5386.506	−12.2249	−3.0798	4982.5	8.304	−504.5	0.6548
150	0.7238	−2941.438	−4.902	5641.215	−13.7559	−3.8055	5312.1	8.853	−658.1	0.5756
200	0.8317	−3218.422	−5.364	5777.818	−14.6594	−4.1378	5577.2	9.295	−735.7	0.5393
250	0.9522	−3342.320	−5.571	5870.521	−15.2599	−4.2951	5813.6	9.689	−765.2	0.5261
300	1.0776	−3380.718	−5.635	5941.160	−15.6906	−4.3638	6033.6	10.056	−762.5	0.5273
400	1.3310	−3328.154	−5.547	6049.944	−16.2875	−4.3894	6444.4	10.741	−694.5	0.5583
500	1.5821	−3190.354	−5.317	6136.933	−16.7014	−4.3602	6830.5	11.384	−574.3	0.6176
600	1.8290	−3010.182	−5.017	6212.487	−17.0174	−4.3141	7200.2	12.000	−421.7	0.7019
700	2.0717	−2805.718	−4.676	6281.001	−17.2728	−4.2634	7558.0	12.597	−247.7	0.8123

[a] Saturation pressure.

$+ K_{8r}(\rho^*)^2][\exp(-K_{8r}\rho^{*2})]T^{-2}$, $\rho^* = \rho - \rho_{r-1,n_{r-1}}$, 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.

Anomalies were observed in preliminary fits at the regional interface. This was caused by lack of constraint on the region I fitting surface by data beyond the interface and could not be corrected by the region II equation. This problem was solved by an overlap fitting technique in which about 10% of the points in the next higher region adjacent to the interface were included in the fit of the region. The interface between the first and second regions was chosen to be critical density. For *n*-pentane 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 V. The latter coefficients are used only with normalized densities. Table V 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 ±0.1% from the NBP to 320 K, 0.3% from 320 to 410 K, and 0.2% from 410 to 450 K. The error limits of vapor volume at the NBP are ±12 cm^3 mol^{-1}, providing the measurement of enthalpy of vaporization of Messerly and Kennedy (*18*) 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 2.3% for dP/dT. The uncertainty is ±60 cal mol^{-1} from NBP to 370 K. Above 370 K, the prime source of error is dP/dT rather than the vapor volume or liquid volume. The liquid enthalpies of Table III are judged accurate to 0.2% as reported by Sage et al. (*25*). Liquid entropy values are likewise considered accurate within ±0.2% from NBP to 370 K.

Table VII. Compressibility Factors from Corresponding States

		Z			
T, K	*P*, atm	CGM[a]	Pitzer[b]	LGH[c]	This work
400	1	0.982	0.984	0.98	0.9811
	3	0.944	0.953	0.94	0.9415
	6	0.882	0.906	0.88	0.8783
500	100	0.440	0.438	0.45	0.4523
	200	0.767	0.763	0.77	0.7970
	300	1.072	1.067	1.05	1.1267
600	100	0.646	0.688	0.65	0.6610
	200	0.813	0.824	0.80	0.8317
	300	1.056	1.055	1.05	1.0776

[a] Canjar, Gensini, and Manning (*4*). [b] Pitzer (*19*); Pitzer et al. (*20*). [c] Lydersen et al. (*15*).

Table VIII. Second Virial Coefficient

T, K	$-B$, cm^3 mol^{-1}	
	Ref *9*	This work
310	1135 ± 60	1173
320	1030 ± 50	1082
340	852 ± 20	926
360	735 ± 20	801
380	645 ± 20	698
400	575 ± 15	613
425	505 ± 15	526
450	445 ± 15	455
475	393 ± 15	396
500	347 ± 15	347
550	276 ± 15	270

PVT Surface and Corresponding Thermodynamic Properties

Table V 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 VI, a condensed version of the API Research Project 44 j-tables (a complete version of Table VI has been deposited in the ACS Microfilm Depository Service). Values of pressure in parentheses are at saturated conditions. The tables are thermodynamically consistent as the other functions were calculated from $A - A^0$ and $S - S^0$, where A is the energy function for density and termperature with S its temperature derivative. Table VI extends only to 600 K or slightly above the maximum experimental temperature of 573 K rather than 1500 K as in the revised API Research Project No. 44 tables. The values above 573 K are an extrapolation of the present surface and further assume no decomposition of *n*-pentane.

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. (*17*) and Pitzer's (*21, 22*) acentric factor procedure. Table VIII is a comparison of the selected second virial coefficients of Dymond and Smith (*9*) 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:

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

However, the constants of Table V for the region yield $(\partial P_r/\partial \rho_r)|_{T_r=1} = 0.0373$ and $(\partial^2 P_r/\partial \rho_r{}^2)|_{T_r=1} = 0.3251$.

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, 469.65 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, 309.19 K
n	number of data points in a given region
P	pressure, atm
R	gas constant, 82.056 06 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

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Received for review March 15, 1976. Accepted September 20, 1976. The support of the American Petroleum Institute Research Project 44 of the Thermodynamics Research Center is acknowledged, together with that of Texas Engineering Experiment Station, both of Texas A&M University.

Supplementary Material Available: The complete Table VI, thermodynamic properties of *n*-pentane (78 pages). Ordering information is given on any current masthead page.

PVT Surface and Thermodynamic Properties of Isopentane

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Selected values of vapor pressure, specific volume, enthalpy, and entropy are presented for the saturated liquid and vapor states of isopentane from normal boiling point (301.025 K) to the critical point (460.39 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 301 to 600 K with pressure to 300 atm. Thermodynamic properties of the real gas, $H - H^0$, $(H - H^0)/T$, $A - A^0$, $S - S^0$, $S - S^l$, $G - G^0$, $(G - G^0)/T$, $G - G^l$, and f/P, were also calculated from the classical relationships.

Previous correlation studies (*2, 6*) present both vapor–liquid coexistence and superheated vapor thermodynamic properties of isopentane. The present compilation is part of a general revision of the j-tables of the API Research Project 44 (*26*) for C_1–C_5 alkanes.

Physical Constants

Table I is a list of the physical constants and conversion factors (*34*) used in this investigation. A summary of selected, experimentally determined, critical constants is shown in Table II. The present set of critical constants ($T_c = 460.39 \pm 0.10$ K; $P_c = 33.37 \pm 0.10$ atm; $\rho_c = 0.236 \pm 0.005$ g cm^{-3}) is based on the measurements of Vohra and Kobe (*31*) and Ambrose et al. (*3*). These critical constants are the same as those selected by Kudchadker et al. (*15*) and differ but slightly from those selected earlier by Kobe and Lynn (*14*).

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.

$$\log P = 22.670\,65 - 2152.74/T - 6.267\,84 \log T + 1401.44\,(P/T^2) \quad (1)$$

where P is in atm and T is in K.

Table I. Physical Constants and Conversion Factors

Constants	Value
Critical temperature	460.39 K
Critical pressure	33.37 atm
Critical density	0.236 g cm^{-3}
Critical volume	306 cm^3 mol^{-1}
Normal boiling point	301.025 K
Triple point	113.25 K
Molecular weight	72.1514 mass units
Gas constant, R	82.056 06 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 Isopentane

Investigator	T_c, K	P_c, atm	ρ_c, g cm^{-3}
Powlewski (*22*) (1882)	467.95	—	—
Altschul (*1*) (1893)	460.25	33.3	—
Young (*37*) (1910)	460.95	32.9	0.2343
Sugden (*29*) (1927)	—	—	0.2343
Kobe and Lynn (*14*) (1953)	460.95	32.9	0.234
Vohra and Kobe (*31*) (1959)	460.95	33.66	0.236
Ambrose, Cox, and Townsend (*3*) (1960)	460.39	—	—
Selected values (ref 15 and this work)	460.39	33.37	0.236

This equation correlates the measurements of Isaac, Li, and Canjar (*13*); Silberberg, McKetta, and Kobe (*28*); Willingham et al. (*35*); and Young (*37*) with an average deviation of 0.021 atm. In addition, the equation is in approximate agreement (average deviation of 0.04 atm) with the data of Echols and Gelus (*8*) and Schumann et al. (*24*) which were not used to determine the constants of eq 1. At the NBP of 301.025 K and the CP of 460.39

[†] Deceased.