PVT Surface and Thermodynamic Properties of *n*-Butane

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Selected values of vapor pressure, specific volume, enthalpy, and entropy are presented for saturated liquid and vaporous *n*-butane from the normal boiling point (272.67K) to the critical point (425.16K). 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 280 to 600K with pressure to 700 atm. Thermodynamic properties of the real gas, $H - H°$, $(H - H°)/T$, $A - A°$, $S - S°$, $S - S^I$, $G - G°$, $(G - G°)/T$, $G - G^I$, and f/P, were also calculated from the classical relationships. These results illustrate the inconsistency of different experimental data sets for *n*-butane and the need for new density and enthalpy data.

A number of correlational studies (*6, 11, 28*) present both vapor-liquid coexistence and superheated vapor thermodynamic properties of *n*-butane. The present compilation is part of a general revision of the j-Tables of the API Research Project 44 (*31*) for C_1–C_5 alkanes.

Physical Constants

Table I is a list of the physical conversion constants (*36*) 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 = 425.16 ± 0.01K, P_C = 37.47 ± 0.01 atm, ρ_C = 0.228 ± 0.001 g cm^{-3}) is based on the saturated vapor and liquid-density measurements of Kay (*19*) near the critical point (CP) with support from the recent liquid and vapor-density measurements of Sliwinski (*32*). The critical temperature and pressure of Beattie et al. (*2*), Kay (*19*), and Klipping and Schmidt (*20*) are acceptable within their error limits. The selected critical density and temperature, 0.228 g cm^{-3} and 425.16K, respectively, were tested with the method proposed by Davis and Rice (*12*) together with all the experimental density data (*10, 19, 29, 32*) available. As shown in Figure 1, the data fit the following equation:

$$(\rho_{SL} + \rho_{SV}) = 0.455403 + 0.675121\,(\rho_{SL} - \rho_{SV})^3 \quad (1)$$

Vapor Pressure

A Frost-Kalkwarf vapor-pressure equation was used with the parameters determined to fit the experimental literature values from 255K to the CP.

$$\log P = 19.21706 - 1694.10/T - 4.15954 \log T + 0.98593\,(P/T^2) \quad (2)$$

where P (mm Hg) and T (K).

This equation correlated the measurements of Dana et al. (*10*); Young (*37*); Sage et al. (*29*); Beattie et al. (*2*); Kay (*19*), and Wackher et al. (*35*) with an average deviation of 0.045 atm in P. In addition, the equation is also in

Table I. Physical and Conversion Constants

Constants	Value
Critical temperature	425.16K
Critical pressure	37.47 atm
Critical density	0.228 g cm^{-3}
Critical volume	254.9 cm^3 mol^{-1}
Normal boiling point	272.67K
Triple point	134.86K
Molecular weight	58.1243 mass units
Gas constant, *R*	82.056060 atm cm^3 K^{-1} mol^{-1}
Temperature conversions	0°C = 273.15K 459.67°R = 0°F
Pressure conversions	1 atm = 760 mm Hg 1 psia = 0.06804596 atm
Energy conversions	1 defined thermochemical calorie = 4.1840 J (exact)

Table II. Critical Constants of *n*-Butane

Investigator	T_c, K	P_c, atm	ρ_c, g cm^{-3}
Kuenen (*22*), 1901	423.96	37.5	
Visser (*34*), 1913	423.95	37.5	
Seibert and Burrell (*30*), 1915	426.15	35.67	
Harand (*17*), 1935	423.85		
Beattie et al. (*2*), 1939	425.16	37.47	0.225
Kay (*19*), 1940	425.35	37.46	0.228
Oldenburg (*24*), 1955	425.15	35.0	
Connolly (*9*), 1962	425.12	37.35	
Klipping and Schmidt (*20*), 1965	425.17	37.47	
Selected values (Kudchadker et al.) (*21*), 1968	425.16	37.47	0.228
Selected values (this work), 1973	425.16	37.47	0.228

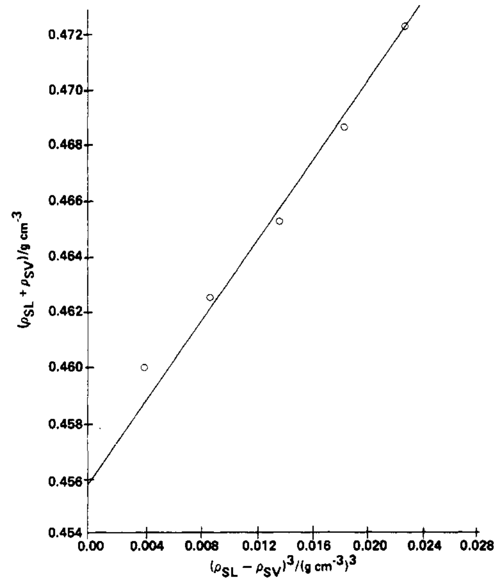

Figure 1. Cubic plot of Sliwinski densities near CP

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agreement with data of Seibert and Burrell (*30*), Aston and Messerly (*1*), and Connolly (*9*), which were not used to determine the constants of Equation 2. At the normal boiling point of 272.67K and the critical point 425.16K, the equation agrees with the experimental values. The equation is believed to be accurate to ±0.2% from 255K to CP. Figure 2 shows increased data scatter in the higher temperature range, resulting in maximum uncertainties of ±0.1 atm. Table III, the selected saturation properties, contains the pressure and its temperature derivative from NBP to the CP.

Saturated Liquid Volume

The available measurements are those of Dana et al. (*10*) (273–329K); Coffin and Maass (*7*) (239–306K); Sage et al. (*29*) (294–394K); Kay (*19*) (325–422K); NGAA (*33*) (227–333K); Olds et al. (*25*) (311–411K); Foehr and Fenske (*15*) (293K); Connolly (*8*) (293–298K); Helmkamp et al. (*18*) (298K), and Sliwinski (*32*) (283–368K).

For the present investigation, the data of Sliwinski (*32*) were selected and heavily weighted (a factor of 4) in comparison with other available literature data (*5, 7, 8, 15, 18, 19, 25, 33*). In fitting the data, the Guggenheim (*16*) equation was modified as shown below and force fitted through the critical point. The constants of the equation were evaluated for two temperature zones meeting at a common temperature of 303.15K, and optimal fit is obtained.

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

where $\theta = (1 - T/T_L)^{1/3}$, T (K), and ρ (g cm^{-3}).

Constants of Equation 3:

	ρ_L	A
Less than 303.15K	0.318406	$-222.89021 \times 10^{-4}$
More than 303.15K	0.228	173.86647×10^{-3}

	B	T_L
Less than 303.15K	787.04586×10^{-4}	403.15
More than 303.15K	$-348.38276 \times 10^{-4}$	425.16

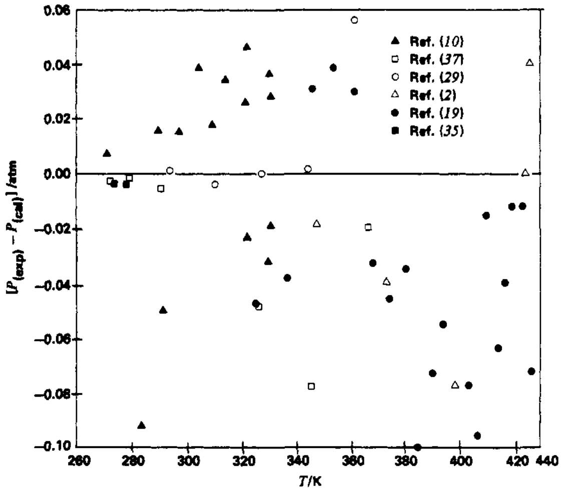

Figure 2. *n*-Butane vapor-pressure difference near CP

Table III. Saturated Properties of *n*-Butane

T, K	P, atm	dP/dT	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}
272.67	1.000	0.0381	96.66	21384	5352	0	5352	0	19.628	19.628
280.0	1.317	0.0470	97.96	16636	5267	210	5477	0.822	18.811	19.633
290.0	1.856	0.0613	99.83	12070	5150	510	5660	1.94	17.758	19.698
300.0	2.552	0.0782	101.8	8958	5028	835	5863	3.06	16.761	19.821
310.0	3.430	0.0979	104.0	6778	4902	1185	6087	4.18	15.812	19.992
320.0	4.518	0.1204	106.4	5216	4764	1555	6319	5.30	14.888	20.188
330.0	5.848	0.1460	109.0	4056	4602	1930	6532	6.42	13.946	20.366
340.0	7.449	0.1748	111.9	3182	4416	2310	6726	7.54	12.988	20.528
350.0	9.355	0.2069	115.1	2511	4199	2695	6894	8.66	11.997	20.657
360.0	11.60	0.2426	118.8	1992	3959	3110	7069	9.79	10.998	20.788
370.0	14.22	0.2821	123.0	1584	3691	3530	7221	10.92	9.974	20.894
380.0	17.25	0.3257	128.1	1262	3396	3955	7351	12.05	8.938	20.988
390.0	20.75	0.3737	134.3	1004	3068	4400	7468	13.18	7.866	21.046
400.0	24.75	0.4269	142.5	790.7	2679	4877	7556	14.31	6.697	21.007
405.0	26.95	0.4556	147.7	696.3	2450	5140	7590	14.93	6.049	20.979
410.0	29.31	0.4859	154.3	609.6	2195	5414	7609	15.57	5.354	20.924
411.0	29.79	0.4921	155.8	593.7	2143	5467	7610	15.70	5.215	20.915
412.0	30.29	0.4985	157.5	577.0	2085	5522	7607	15.83	5.061	20.891
413.0	30.79	0.5049	159.2	560.5	2025	5581	7606	15.96	4.904	20.864
414.0	31.30	0.5113	161.1	543.1	1957	5643	7600	16.11	4.727	20.837
415.0	31.81	0.5179	163.2	526.0	1887	5710	7597	16.26	4.547	20.807
416.0	32.33	0.5245	165.4	507.7	1808	5776	7584	16.43	4.345	20.775
417.0	32.86	0.5312	167.9	489.6	1725	5847	7572	16.60	4.136	20.736
418.0	33.40	0.5380	170.6	470.6	1633	5922	7555	16.77	3.906	20.676
419.0	33.94	0.5449	173.7	451.1	1533	5998	7531	16.96	3.659	20.619
420.0	34.49	0.5518	177.2	429.3	1414	6089	7503	17.18	3.367	20.547
421.0	35.04	0.5589	181.3	405.7	1278	6190	7468	17.41	3.035	20.445
422.0	35.60	0.5660	186.3	379.4	1116	6306	7422	17.67	2.645	20.315
423.0	36.17	0.5732	192.9	353.8	944	6422	7366	17.92	2.232	20.152
423.5	36.46	0.5768	197.1	340.4	847	6487	7334	18.06	2.000	20.060
424.0	36.75	0.5805	202.6	326.0	735	6560	7295	18.21	1.734	19.944
424.5	37.04	0.5842	210.3	308.6	590	6650	7240	18.40	1.390	19.790
425.16	37.47	0.5900	254.9	254.9	0	7033	7033	19.18	0	19.18

The equations represent the selected data very well over the temperature range from 227K to the CP with the standard deviations of 0.00043 g cm^{-3}. The values reported by Dana et al. (*10*) are lower, and the values reported by Sage et al. (*29*) are higher than the other data; hence, both sets of data were excluded in fitting the equation. Figure 3 shows how Equation 3 deviates from the experimental data. The values accepted near the critical point are shown in Figure 4 by a solid line; selected values from Equation 3 appear in Table III.

Saturated Vapor Volume

Dana et al. (*10*) (273-329K); Sage et al. (*29*) (289-390K); Kay (*19*) (325 to CP); Olds et al. (*25*) (311-411K); and Sliwinski (*32*) (283-368K) measured the vapor volumes. At normal boiling point, the vapor volume calculated from the heat of vaporization measurement of Aston and Messerly (*1*) via the Clapeyron equation was used. This value, together with other selected saturated vapor volumes (*10, 19, 25, 29, 32*) and the experimental gaseous volumes (*2, 3, 19, 29*), were used to evaluate the Benedict-Webb-Rubin (BWR) equation of state constants. In the evaluation of these constants, the data of Aston and Messerly (*1*) and Sliwinski (*32*) were weighted five times heavier than the other data.

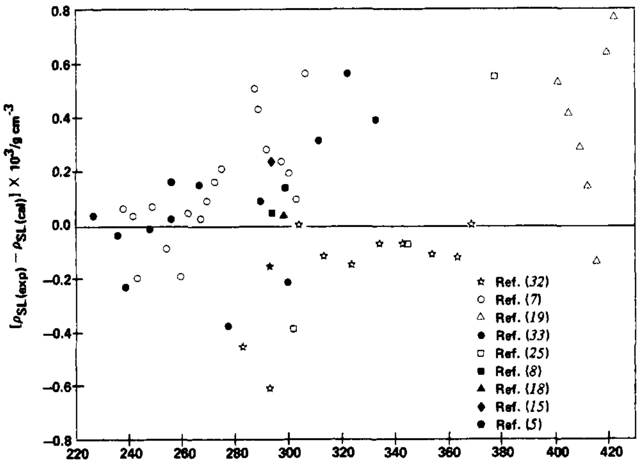

Figure 3. *n*-Butane saturated liquid-density difference

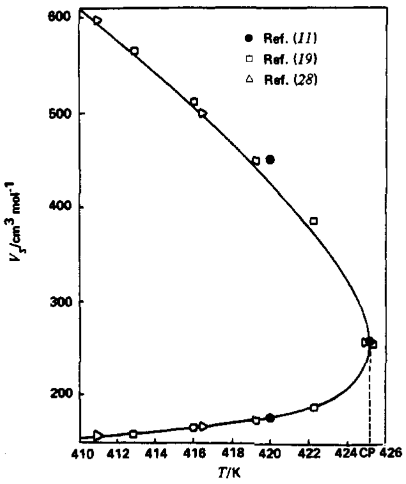

Figure 4. Saturated volume near CP

Figure 5 illustrates the agreement between all the sources cited above. The base volumes for Figure 5 are supplied by the Equation 2 in conjunction with a preliminary BWR equation of state with constants reported in Table VII. The graphically smoothed values of Figure 5 were accepted and appear in Table III.

Enthalpy of Vaporization

The enthalpies of vaporization computed from Equation 4 with Equation 2 and previously selected vapor and liquid volumes appear in Table IV in comparison of the present values to those reported by other authors (*10, 11, 28, 29*). The measured enthalpy of vaporization 5351 cal mol^{-1} of Aston and Messerly (*1*) at NBP shows close agreement with the value of 5352 cal mol^{-1} which is calculated from the Clapeyron equation:

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

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. (*29*) have been accepted after making the correction

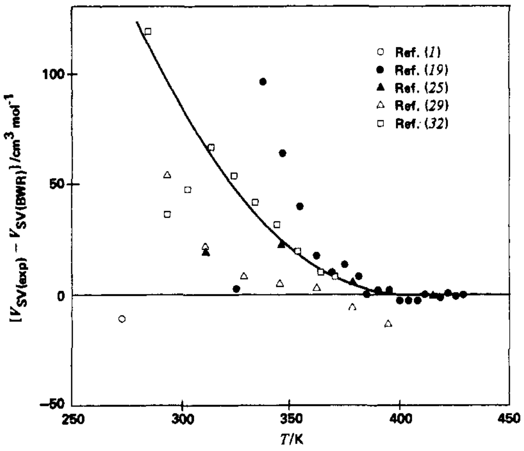

Figure 5. Saturated vapor-volume difference

Table IV. Comparison of Enthalpies of Vaporization

	λ/cal mol^{-1}				
T, K	DJBT[a,b]	DK[c]	PGY[a,d]	SWL[a,e]	This work
280.0	5260	5262	5264		5267
290.0	5136	5134	5136		5150
300.0	5002	4992	4992	(5050)[f]	5028
310.0	4850	4840	4842	4883	4902
320.0	4677	4680	4682	4704	4764
330.0	4497	4518	4518	4531	4602
340.0		4346	4345	4338	4416
350.0		4160	4158	4092	4199
360.0		3956	3960	3874	3959
370.0		3722	3722	3626	3691
380.0		3453	3450	3317	3396
390.0		3140	3147	(2976)[f]	3068
400.0		2750	2752		2679
405.0			2507		2450
410.0		2214	2235		2195
415.0			1888		1887
420.0		1467	1428		1414

[a] Values are interpolated. [b] Dana et al. (*10*). [c] Das and Kuloor (*11*). [d] Prengle et al. (*28*). [e] Sage et al. (*29*). [f] Values in parentheses are extrapolated.

with the reference state $H_{SL} = 0$ at 272.67K, which allows calculation of enthalpy changes along the saturated liquid envelope. A comparison of the saturated liquid enthalpies is made in Table V.

From the NBP to 390K, the vapor enthalpy was obtained by addition of 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 (Figure 6): Starting at 390K, the enthalpy of vaporization was marked on an overlay to Figure 6 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 390K 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 Figure 6 in the critical region.

Entropy of Saturated Liquid and Vapor

By accepting the saturated liquid entropy reported by Sage et al. (*29*), after making the correction with the reference state $S_{SL} = 0$ at 272.67K, the calculation of entropy changes along the saturated liquid envelope is allowed. The change along the saturation liquid envelope thus obtained is smoothed graphically and reported in Table III. The data are compared in Table VI with the other data available in the literature. From NBP to 390K, the vapor entropy was obtained by addition of (λ/T) to S_{SL}. Above 390K, a graphical method identical to that for enthalpy was used with entropy locus, $\bar{S}_S = (S_{SL} + S_{SV})/2$, found to be reasonably straight (Figure 7). 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 Sage et al. (*29*) covered 297 to 394K with pressures from 1 to 204 atm. Beattie et al. (*2*, *3*) covered a higher temperature range from 433 to 573K in the pressure range 14.7–310 atm. Kay (*19*) determined values over the temperature range 311–589K and pressure range 2–81 atm. Olds et al. (*25*) extended the coverage 0.68–680 atm and 311–511K; their data are in approximate agreement with those of Beattie et al. (*2*, *3*) and Kay (*19*) but not with Sage et al. (*29*). Figure 8 shows the *P*, *T* regions of these major data sources.

Table V. Comparison of Saturated Liquid Enthalpies

	H_{SL}/cal mol^{-1}				
T, K	DJBT[a,b]	DK[c]	PGY[a,d]	SWL[a,e]	This work
272.67	0	0	0	(0)[f]	0
280.0	247	226	244	(210)[f]	210
290.0	564	540	570	(510)[f]	510
300.0	911	876	924	(835)[f]	835
310.0	1270	1217	1280	1185	1185
320.0	1646	1567	1640	1555	1555
330.0	2024	1918	2005	1930	1930
340.0		2280	2380	2310	2310
350.0		2640	2756	2695	2695
360.0		3033	3125	3110	3110
370.0		3443	3516	3530	3530
380.0		3869	3925	3955	3955
390.0		4329	4370	(4400)[f]	4400
400.0		4816	4830		4877
405.0			5165		5140
410.0		5435	5445		5414
415.0			5760		5710
420.0		6083	6170		6089

[a] Values are interpolated. [b] Dana et al. (*10*). [c] Das and Kuloor (*11*). [d] Prengle et al. (*28*). [e] Sage et al. (*29*). [f] Values in parentheses are extrapolated.

Table VI. Comparison of Saturated Liquid Entropies

	S_{SL}/cal K^{-1} mol^{-1}				
T, K	DJBT[a,b]	DK[c]	PGY[a,d]	SWL[a,e]	This work
272.67	0	0	0	(0)[f]	0
280.0	0.84	1.04	0.795	(0.822)[f]	0.822
290.0	2.01	2.18	1.83	(1.94)[f]	1.94
300.0	3.15	3.33	3.01	(3.06)[f]	3.06
310.0	4.32	4.46	4.16	4.18	4.18
320.0	5.51	5.55	5.31	5.30	5.30
330.0	6.71	6.61	6.42	6.42	6.42
340.0		7.68	7.54	7.54	7.54
350.0		8.74	8.64	8.66	8.66
360.0		9.80	9.76	9.79	9.79
370.0		10.92	10.83	10.92	10.92
380.0		12.02	12.02	12.05	12.05
390.0		13.19	13.18	(13.18)[f]	13.18
400.0		14.38	14.44		14.31
405.0			15.08		14.93
410.0		15.87	15.80		15.57
415.0			16.57		16.26
420.0		17.32	17.42		17.18

[a] Values are interpolated. [b] Dana et al. (*10*). [c] Das and Kuloor (*11*). [d] Prengle et al. (*28*). [e] Sage et al. (*29*). [f] Values in parentheses are extrapolated.

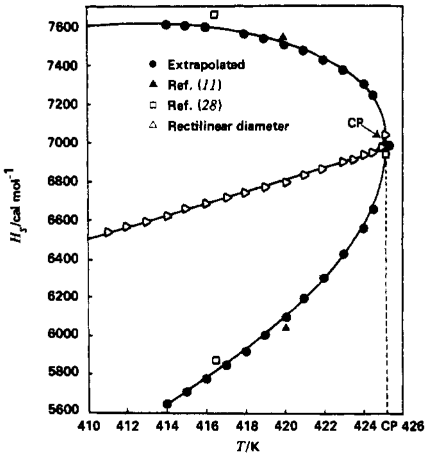

Figure 6. Enthalpy envelope

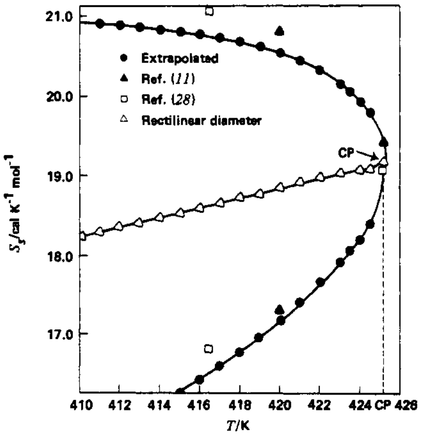

Figure 7. Entropy envelope

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 five, except for the critical point and the boiling point which were 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 (*14*) is:

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

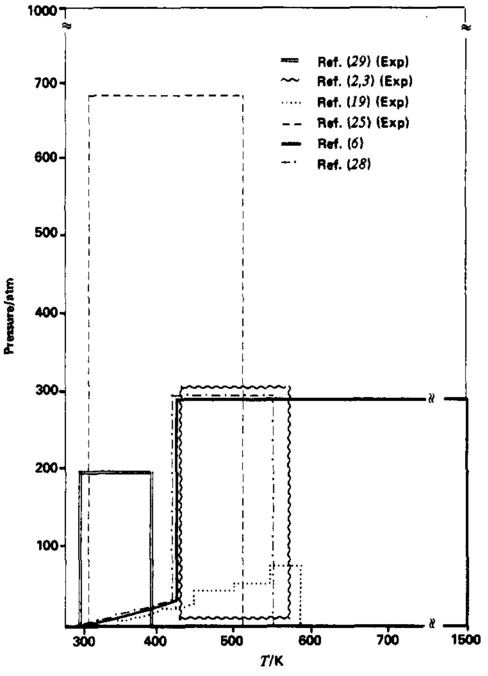

Figure 8. Regional block diagram of literature data for *n*-butane

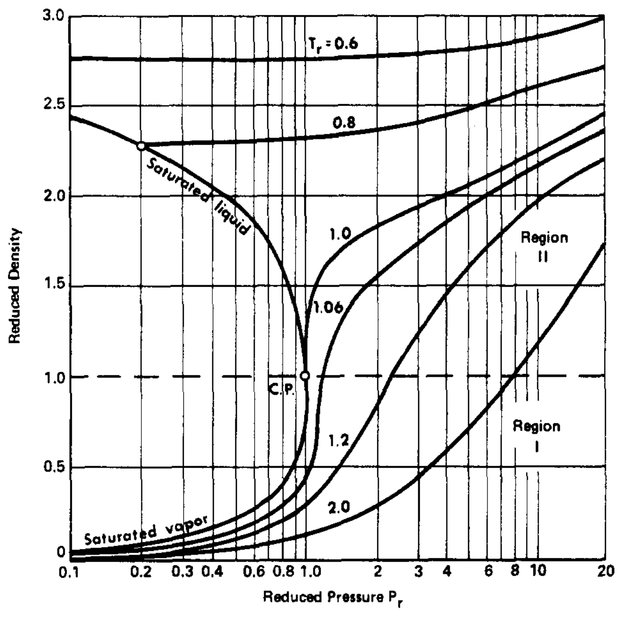

Figure 9. *n*-Butane PVT regions

where

$\varphi = P - RT\rho, \theta_1^* = RT(\rho^*)^2, \theta_2^* = (\rho^*)^2$

$\theta_3^* = (\rho^*)^2 T^{-2}, \theta_4^* = RT(\rho^*)^3, \theta_5^* = (\rho^*)^3$
$\theta_6^* = (\rho^*)^6, \theta_7^* = (\rho^*)^3[1 + K_{8r}(\rho^*)^2][\exp(-K_{8r}\rho^{*2})]T^{-2}$

$\rho^* = \rho - \rho_{r-1,\, n_{r-1}}$

with $\rho_{r-1,\, n(r-1)}$ equal to the density at the interface between regions r and $r - 1$ when the density ρ 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 *n*-butane there were not sufficient data at densities above the critical point to require more than one region to provide an optimal fit as shown by Figure 9. 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 Equation 5 for the first and second regions are found in Table VII. The latter coefficients are used only with normalized densities. Table VII 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 ±0.2% from the NBP to 300K, 0.5% from 300 to 330K, 0.2% from 330 to 380K, and 0.05% from 380K to CP. The error limits of vapor volume at NBP are ±10 $cm^3\ mol^{-1}$, providing the measurement of enthalpy of vaporization of Aston and Messerly (*1*) is correct. Figure 5 indicates the uncertainty with respect to the equation of state in the vapor volume. The accuracy of enthalpy of vaporization values in Table III depends on that of vapor-pressure slope and vapor volume with error limits of 1.0% for dP/dT. The uncertainty is ±50 cal mol^{-1} from NBP to 380K. Above 380K, the prime source of

Table VII. Constants for the DR-BWR Equation

	Region I	Region II
Number of data points	670	87
Density range, g mol cm^{-3}	0.0 to 0.00392267	0.00392267 to 0.0094444751
Normalized density range	0.0017241 to 0.41534	0.41534 to 1
Av % deviation for Z	0.2376	0.3961
Max % deviation for Z	0.3961	1.2215
Constants for Equation 5[a]		
K_{1r}	7.83440×10^{-3}	2.91398×10^{-2}
K_{2r}	-6.85637×10^{2}	-1.30266×10^{3}
K_{3r}	-1.05335×10^{8}	6.79792×10^{6}
K_{4r}	3.52403×10^{-2}	-7.85591×10^{-3}
K_{5r}	-1.67070×10^{3}	4.41673×10^{3}
K_{6r}	4.09316×10^{2}	1.09300×10^{3}
K_{7r}	2.67269×10^{8}	-4.66951×10^{8}
K_{8r}	1.80000	6.20000
BWR constants[b]		
A_0	7.68668×10^{6}	
B_0	8.78314×10	
C_0	1.18091×10^{12}	
a	1.98319×10^{9}	
b	4.18317×10^{4}	
c	3.17260×10^{14}	
α	2.90822×10^{5}	
γ	2.01798×10^{4}	

[a] Only for use in Equation 5 with ρ normalized as (g mol cm^{-3}/0.0094444751). [b] $P - RT\rho = (B_0RT - A_0 - C_0/T^2)\rho^2 + (bRT - a)\rho^3 + a\alpha\rho_6{}^6 + (c\rho^3/T^2)[(1 + \gamma\rho^2)e^{-\gamma\rho^2}]$; P (atm), T (K), ρ (g mol cm^{-3}).

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. (*29*), except near the critical point. Liquid entropy values are likewise considered accurate within ±0.2% from NBP to 380K.

PVT Surface and Corresponding Thermodynamic Properties

Table VII 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 VIII, a condensed version of the API Research Project 44 j-tables (a complete version of Table VIII 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 $A - A^\circ$ and $S - S^\circ$, where A is the energy function for density and temperature with S its temperature derivative. Table VIII extends only to 600K or slightly above the maximum experimental temperature of 589K rather than 1500K as in the revised API Research Project 44 tables. The values above 589K are an extrapolation of the present surface and further assume no decomposition of the *n*-butane.

Discussion

Table IX is a comparison of present values with those calculated from corresponding states by two methods:

Table VIII (Condensed). Thermodynamic Properties of *n*-Butane

Press, atm	Z	$H - H^\circ$, cal mol^{-1}	$(H - H^\circ)/T$, cal mol^{-1} K^{-1}	$A - A^\circ$, cal mol^{-1}	$S - S^\circ$, cal mol^{-1} K^{-1}	$S - S^I$, cal mol^{-1}	$G - G^\circ$, cal mol^{-1}	$(G - G^\circ)/T$, cal mol^{-1} K^{-1}	$G - G^I$, cal mol^{-1}	(f/p)
					280K					
1	0.9593	−80.413	−0.287	0.396	−0.2078	−0.2078	−22.2	−0.079	−22.2	0.9608
1.316[a]	0.9458	−107.196	−0.383	153.601	−0.8238	−0.2778	123.5	0.441	−29.4	0.9485
					300K					
1	0.9684	−66.400	−0.221	0.248	−0.1594	−0.1594	−18.6	−0.062	−18.6	0.9693
2.552[a]	0.9156	−177.853	−0.593	559.888	−2.2915	−0.4314	509.6	1.699	−48.4	0.9219
					320K					
1	0.9750	−55.743	−0.174	0.161	−0.1250	−0.1250	−15.7	−0.049	−15.7	0.9755
4	0.8925	−240.379	−0.751	884.124	−3.3006	−0.5477	815.8	2.549	−65.1	0.9026
4.518[a]	0.8768	−275.664	−0.861	962.591	−3.6250	−0.6301	884.3	2.764	−74.0	0.8900
					340K					
1	0.9798	−47.452	−0.140	0.108	−0.0998	−0.0998	−13.5	−0.040	−13.5	0.9802
4	0.9149	−200.977	−0.591	938.027	−3.1810	−0.4281	880.6	2.590	−55.4	0.9212
7.449[a]	0.8287	−406.652	−1.196	1364.591	−4.8695	−0.8818	1249.0	3.673	−106.9	0.8536
					360K					
1	0.9835	−40.880	−0.114	0.074	−0.0810	−0.0810	−11.7	−0.033	−11.7	0.9838
4	0.9313	−170.970	−0.475	992.396	−3.0952	−0.3422	943.3	2.620	−47.8	0.9354
8	0.8532	−367.477	−1.021	1493.082	−4.8766	−0.7472	1388.1	3.856	−98.5	0.8713
11.60[a]	0.7697	−580.183	−1.612	1769.325	−6.0690	−1.2018	1604.7	4.457	−147.5	0.8135
					380K					
1	0.9864	−35.584	−0.094	0.051	−0.0667	−0.0667	−10.2	−0.027	−10.2	0.9865
4	0.9437	−147.473	−0.388	1047.028	−3.0316	−0.2786	1004.5	2.643	−41.6	0.9464
8	0.8816	−311.537	−0.820	1573.379	−4.7252	−0.5958	1484.0	3.905	−85.1	0.8933
12	0.8113	−499.785	−1.315	1886.440	−5.9047	−0.9701	1744.0	4.590	−131.1	0.8405
16	0.7272	−728.307	−1.917	2117.627	−6.9476	−1.4417	1911.8	5.031	−180.5	0.7873
17.25[a]	0.6962	−813.902	−2.142	2181.639	−7.2796	−1.6237	1952.3	5.138	−196.9	0.7704
					400K					
1	0.9886	−31.258	−0.078	0.036	−0.0556	−0.0556	−9.0	−0.023	−9.0	0.9887
4	0.9532	−128.663	−0.322	1101.810	−2.9833	−0.2303	1064.7	2.662	−36.5	0.9551
8	0.9028	−268.572	−0.671	1654.576	−4.6149	−0.4855	1577.4	3.943	−74.4	0.9106
12	0.8477	−423.422	−1.059	1981.033	−5.7086	−0.7740	1860.0	4.650	−113.8	0.8665
16	0.7858	−599.494	−1.499	2217.306	−6.6166	−1.1107	2047.2	5.118	−155.2	0.8225
20	0.7135	−809.146	−2.023	2408.086	−7.4741	−1.5250	2180.5	5.451	−199.1	0.7782
24	0.6208	−1084.991	−2.712	2578.897	−8.4066	−2.0955	2277.7	5.694	−246.8	0.7329
24.75[a]	0.5990	−1151.097	−2.878	2611.012	−8.6090	−2.2371	2292.5	5.731	−256.3	0.7242
					410K					
1	0.9895	−29.386	−0.072	0.031	−0.0510	−0.0510	−8.5	−0.021	−8.5	0.9896
4	0.9572	−120.625	−0.294	1129.237	−2.9634	−0.2105	1094.4	2.669	−34.3	0.9587
8	0.9115	−250.627	−0.611	1695.381	−4.5706	−0.4411	1623.3	3.959	−69.8	0.9179
12	0.8621	−392.660	−0.958	2029.018	−5.6327	−0.6980	1916.7	4.675	−106.5	0.8774
16	0.8078	−550.894	−1.344	2269.224	−6.4966	−0.9907	2112.7	5.153	−144.7	0.8372
20	0.7464	−732.626	−1.787	2460.710	−7.2850	−1.3360	2254.2	5.498	−184.9	0.7969
24	0.6737	−952.881	−2.324	2625.683	−8.0802	−1.7690	2360.0	5.756	−227.6	0.7562
28	0.5771	−1255.528	−3.062	2783.314	−9.0111	−2.3938	2439.0	5.949	−274.1	0.7142
29.30[a]	0.5330	−1398.934	−3.412	2839.872	−9.4112	−2.7035	2459.6	5.999	−290.5	0.6999

(Continued on page 250)

Table VIII (Condensed). Continued

Press, atm	Z	$H - H^\circ$, cal mol^{-1}	$(H - H^\circ)/T$, cal mol^{-1} K^{-1}	$A - A^\circ$, cal mol^{-1}	$S - S^\circ$, cal mol^{-1} K^{-1}	$S - S^I$, cal mol^{-1}	$G - G^\circ$, cal mol^{-1}	$(G - G^\circ)/T$, cal mol^{-1} K^{-1}	$G - G^I$, cal mol^{-1}	(f/p)
					420K					
1	0.9904	−27.679	−0.066	0.026	−0.0469	−0.0469	−8.0	−0.019	−8.0	0.9905
4	0.9607	−113.341	−0.270	1156.682	−2.9459	−0.1929	1123.9	2.676	−32.3	0.9620
8	0.9191	−234.557	−0.558	1736.280	−4.5319	−0.4024	1668.8	3.973	−65.5	0.9244
12	0.8746	−365.580	−0.870	2077.295	−5.5674	−0.6328	1972.7	4.697	−99.8	0.8872
16	0.8264	−509.267	−1.213	2321.922	−6.3963	−0.8903	2177.2	5.184	−135.3	0.8502
20	0.7733	−670.163	−1.596	2515.374	−7.1344	−1.1854	2326.3	5.539	−172.3	0.8134
24	0.7130	−856.342	−2.039	2678.911	−7.8474	−1.5363	2439.6	5.808	−211.1	0.7764
28	0.6411	−1084.819	−2.583	2826.275	−8.5993	−1.9821	2526.9	6.016	−252.3	0.7389
32	0.5438	−1407.725	−3.352	2973.869	−9.5264	−2.6440	2593.4	6.175	−297.2	0.7002
33	0.5099	−1525.404	−3.632	3015.694	−9.8388	−2.8953	2606.9	6.207	−309.4	0.6901
34	0.4650	−1686.368	−4.015	3065.267	−10.2511	−3.2483	2619.1	6.236	−322.1	0.6796
34.49[a]	0.4331	−1805.651	−4.299	3097.242	−10.5478	−3.5167	2624.4	6.249	−328.6	0.6744
					424K					
1	0.9907	−27.038	−0.064	0.024	−0.0453	−0.0453	−7.8	−0.018	−7.8	0.9908
4	0.9620	−110.617	−0.261	1167.665	−2.9394	−0.1865	1135.7	2.679	−31.6	0.9632
8	0.9219	−228.591	−0.539	1752.660	−4.5177	−0.3883	1686.9	3.979	−64.0	0.9268
12	0.8792	−355.630	−0.839	2096.669	−5.5438	−0.6092	1994.9	4.705	−97.3	0.8908
16	0.8332	−494.205	−1.166	2343.162	−6.3606	−0.8546	2202.7	5.195	−131.8	0.8551
20	0.7828	−648.128	−1.529	2537.631	−7.0822	−1.1332	2354.7	5.554	−167.7	0.8194
24	0.7264	−823.839	−1.943	2701.191	−7.7704	−1.4593	2470.8	5.827	−205.1	0.7838
28	0.6606	−1033.914	−2.438	2846.802	−8.4787	−1.8614	2561.0	6.040	−244.7	0.7478
32	0.5575	−1309.952	−3.090	2986.717	−9.2947	−2.4123	2631.0	6.205	−287.2	0.7110
33	0.5516	−1399.179	−3.300	3023.200	−9.5396	−2.5961	2645.6	6.240	−298.4	0.7016
34	0.5218	−1503.903	−3.547	3061.799	−9.8185	−2.8157	2659.1	6.272	−310.1	0.6919
35	0.4855	−1635.051	−3.856	3104.641	−10.1568	−3.0964	2671.4	6.301	−322.2	0.6821
36	0.4349	−1826.831	−4.309	3158.214	−10.6350	−3.5187	2682.4	6.326	−334.9	0.6718
36.75[a]	0.2038	−3095.947	−7.302	3359.329	−13.6436	−6.4863	2688.9	6.342	−345.8	0.6632
					426K					
1	0.9908	−26.726	−0.063	0.023	−0.0446	−0.0446	−7.7	−0.018	−7.7	0.9909
4	0.9627	−109.293	−0.257	1173.157	−2.9363	−0.1834	1141.6	2.680	−31.2	0.9638
8	0.9233	−225.699	−0.530	1760.855	−4.5109	−0.3815	1695.9	3.981	−63.2	0.9280
12	0.8814	−350.826	−0.824	2106.368	−5.5325	−0.5979	2006.0	4.709	−96.1	0.8926
16	0.8364	−486.975	−1.143	2353.811	−6.3436	−0.8376	2215.4	5.200	−130.1	0.8574
20	0.7873	−637.643	−1.497	2548.826	−7.0576	−1.1085	2368.9	5.561	−165.4	0.8224
24	0.7326	−808.618	−1.898	2712.492	−7.7346	−1.4234	2486.3	5.836	−202.2	0.7874
28	0.6696	−1010.794	−2.373	2857.483	−8.4243	−1.8070	2577.9	6.052	−241.0	0.7521
32	0.5917	−1269.620	−2.980	2994.851	−9.1998	−2.3174	2649.5	6.219	−282.4	0.7162
33	0.5682	−1350.381	−3.170	3029.857	−9.4248	−2.4813	2664.6	6.255	−293.4	0.7070
34	0.5420	−1442.230	−3.386	3066.103	−9.6733	−2.6705	2678.6	6.288	−304.6	0.6976
35	0.5117	−1550.710	−3.640	3104.665	−9.9583	−2.8980	2691.5	6.318	−316.2	0.6882
36	0.4746	−1687.937	−3.962	3147.824	−10.3081	−3.1918	2703.3	6.346	−328.2	0.6784
37	0.4221	−1892.533	−4.443	3202.613	−10.8129	−3.6422	2713.8	6.370	−341.0	0.6683
38	0.2757	−2606.619	−6.119	3334.706	−12.5085	−5.2848	2722.0	6.390	−355.3	0.6571
39	0.2113	−3117.547	−7.318	3393.920	−13.7189	−6.4437	2726.7	6.401	−372.5	0.6438
40	0.2085	−3189.408	−7.487	3400.749	−13.8981	−6.5726	2731.2	6.411	−389.5	0.6310
41	0.2082	−3239.659	−7.605	3405.417	−14.0263	−6.6517	2735.5	6.421	−406.0	0.6188
42	0.2089	−3279.108	−7.697	3409.043	−14.1289	−6.7065	2739.8	6.431	−422.2	0.6071
43	0.2103	−3311.868	−7.774	3412.044	−14.2156	−6.7464	2744.0	6.441	−437.9	0.5959
44	0.2121	−3339.991	−7.840	3414.622	−14.2912	−6.7764	2748.1	6.451	−453.2	0.5852
45	0.2142	−3364.682	−7.898	3416.894	−14.3587	−6.7993	2752.1	6.460	−468.2	0.5750
46	0.2165	−3386.715	−7.950	3418.935	−14.4198	−6.8168	2756.1	6.470	−482.8	0.5651
47	0.2190	−3406.617	−7.997	3420.792	−14.4759	−6.8301	2760.1	6.479	−497.0	0.5557
48	0.2216	−3424.767	−8.039	3422.503	−14.5277	−6.8401	2764.0	6.488	−510.9	0.5467
52	0.2329	−3484.635	−8.180	3428.302	−14.7043	−6.8578	2779.4	6.524	−563.2	0.5139
56	0.2451	−3530.780	−8.288	3433.018	−14.8478	−6.8541	2794.4	6.560	−610.9	0.4857
60	0.2576	−3568.120	−8.376	3437.069	−14.9699	−6.8391	2809.0	6.594	−654.6	0.4612
64	0.2704	−3599.266	−8.449	3440.668	−15.0768	−6.8179	2823.4	6.628	−694.8	0.4398
68	0.2833	−3625.803	−8.511	3443.940	−15.1724	−6.7931	2837.6	6.661	−731.9	0.4210
72	0.2963	−3648.767	−8.565	3446.966	−15.2592	−6.7664	2851.7	6.694	−766.3	0.4042
76	0.3093	−3668.875	−8.612	3449.798	−15.3389	−6.7388	2865.5	6.727	−798.2	0.3893
80	0.3224	−3686.641	−8.654	3452.475	−15.4128	−6.7108	2879.2	6.759	−827.9	0.3758
100	0.3873	−3751.205	−8.806	3464.304	−15.7211	−6.5759	2946.0	6.915	−949.9	0.3254
120	0.4514	−3790.545	−8.898	3474.583	−15.9649	−6.4577	3010.5	7.067	−1039.6	0.2926
140	0.5147	−3815.047	−8.956	3483.992	−16.1701	−6.3567	3073.4	7.215	−1107.1	0.2702
160	0.5770	−3829.711	−8.990	3492.852	−16.3491	−6.2706	3135.0	7.359	−1158.4	0.2543
180	0.6385	−3837.346	−9.008	3501.328	−16.5090	−6.1966	3195.5	7.501	−1197.6	0.2428

Table VIII (Condensed). Continued

Press, atm	Z	$H - H°$, cal mol^{-1}	$(H - H°)/T$, cal mol^{-1} K^{-1}	$A - A°$, cal mol^{-1}	$S - S°$, cal mol^{-1} K^{-1}	$S - S^I$, cal mol^{-1}	$G - G°$, cal mol^{-1}	$(G - G°)/T$, cal mol^{-1} K^{-1}	$G - G^I$, cal mol^{-1}	(f/p)
					426K					
200	0.6992	−3839.699	−9.013	3509.525	−16.6544	−6.1328	3255.1	7.641	−1227.1	0.2344
220	0.7592	−3837.933	−9.009	3517.508	−16.7882	−6.0773	3313.8	7.779	−1249.0	0.2285
240	0.8186	−3832.863	−8.997	3525.325	−16.9125	−6.0288	3371.9	7.915	−1264.6	0.2243
260	0.8774	−3825.083	−8.979	3533.007	−17.0290	−5.9864	3429.3	8.050	−1274.9	0.2216
280	0.9356	−3815.040	−8.955	3540.578	−17.1388	−5.9490	3486.1	8.183	−1280.8	0.2200
300	0.9933	−3803.080	−8.927	3548.058	−17.2428	−5.9160	3542.4	8.315	−1282.9	0.2195
350	1.1353	−3766.447	−8.841	3566.441	−17.4821	−5.8492	3680.9	8.641	−1274.7	0.2216
400	1.2747	−3722.421	−8.738	3584.487	−17.6980	−5.7999	3816.9	8.960	−1251.7	0.2277
450	1.4118	−3672.892	−8.622	3602.287	−17.8956	−5.7636	3950.6	9.274	−1217.6	0.2371
500	1.5467	−3619.123	−8.496	3619.903	−18.0787	−5.7375	4082.4	9.583	−1175.0	0.2493
550	1.6797	−3561.999	−8.361	3637.375	−18.2498	−5.7193	4212.4	9.888	−1125.6	0.2643
600	1.8110	−3502.163	−8.221	3654.731	−18.4107	−5.7075	4340.8	10.190	−1070.8	0.2820
650	1.9407	−3440.097	−8.075	3671.992	−18.5631	−5.7009	4467.8	10.488	−1011.5	0.3025
700	2.0689	−3376.174	−7.925	3689.173	−18.7080	−5.6986	4593.4	10.783	−948.6	0.3259
					480K					
1	0.9940	−20.006	−0.042	0.009	−0.0297	−0.0297	−5.8	−0.012	−5.8	0.9940
20	0.8705	−440.205	−0.917	2860.018	−6.6183	−0.6692	2736.6	5.701	−119.0	0.8826
40	0.7166	−1008.933	−2.102	3538.425	−8.9109	−1.5854	3268.3	6.809	−248.0	0.7710
60	0.5399	−1807.642	−3.766	3951.944	−11.0854	−2.9547	3513.4	7.319	−389.4	0.6646
80	0.4481	−2542.190	−5.296	4172.407	−12.8927	−4.1907	3646.3	7.596	−530.6	0.5731
100	0.4632	−2863.805	−5.966	4253.836	−13.7624	−4.6173	3742.2	7.796	−647.5	0.5070
120	0.5066	−3018.564	−6.289	4296.422	−14.2598	−4.7526	3826.1	7.971	−737.3	0.4614
140	0.5567	−3113.739	−6.487	4326.695	−14.6206	−4.8072	3904.1	8.134	−806.3	0.4292
160	0.6090	−3177.789	−6.620	4350.963	−14.9084	−4.8299	3978.2	8.288	−859.4	0.4059
180	0.6620	−3222.465	−6.713	4371.666	−15.1500	−4.8376	4049.5	8.436	−900.4	0.3888
200	0.7153	−3253.908	−6.779	4390.015	−15.3595	−4.8378	4118.6	8.580	−931.7	0.3763
220	0.7685	−3275.718	−6.824	4406.694	−15.5452	−4.8343	4186.0	8.721	−955.2	0.3671
240	0.8214	−3290.217	−6.855	4422.129	−15.7127	−4.8291	4251.9	8.858	−972.3	0.3606
260	0.8741	−3298.991	−6.873	4436.602	−15.8657	−4.8231	4316.6	8.993	−983.9	0.3562
280	0.9264	−3303.163	−6.882	4450.310	−16.0069	−4.8170	4380.1	9.125	−991.0	0.3536
300	0.9783	−3303.565	−6.882	4463.394	−16.1381	−4.8113	4442.7	9.256	−994.1	0.3524
350	1.1067	−3291.812	−6.858	4494.019	−16.4323	−4.7994	4595.7	9.574	−988.1	0.3547
400	1.2329	−3266.658	−6.806	4522.461	−16.6898	−4.7917	4744.4	9.884	−966.7	0.3627
450	1.3571	−3231.951	−6.733	4549.345	−16.9201	−4.7881	4889.7	10.187	−933.7	0.3755
500	1.4794	−3190.132	−6.646	4575.063	−17.1296	−4.7883	5032.1	10.483	−891.7	0.3924
550	1.6001	−3142.833	−6.548	4599.875	−17.3223	−4.7918	5171.9	10.775	−842.8	0.4131
600	1.7191	−3091.202	−6.440	4623.961	−17.5014	−4.7981	5309.4	11.061	−788.1	0.4374
650	1.8368	−3036.073	−6.325	4647.452	−17.6690	−4.8068	5445.1	11.344	−728.8	0.4655
700	1.9530	−2978.072	−6.204	4670.445	−17.8270	−4.8175	5578.9	11.623	−665.7	0.4974
					600K					
1	0.9973	−11.892	−0.020	−0.009	−0.0144	−0.0144	−3.3	−0.005	−3.3	0.9973
20	0.9456	−245.531	−0.409	3569.122	−6.2498	−0.3007	3504.3	5.841	−65.1	0.9468
40	0.8934	−506.167	−0.844	4393.027	−7.9536	−0.6281	4266.0	7.110	−129.3	0.8971
60	0.8461	−777.850	−1.296	4870.110	−9.1076	−0.9768	4686.7	7.811	−191.8	0.8513
80	0.8074	−1050.826	−1.751	5199.557	−10.0348	−1.3328	4970.1	8.283	−251.1	0.8100
100	0.7810	−1310.272	−2.184	5441.980	−10.8189	−1.6738	5181.1	8.635	−306.0	0.7735
120	0.7682	−1542.585	−2.571	5625.302	−11.4862	−1.9790	5349.2	8.915	−355.2	0.7422
140	0.7674	−1742.036	−2.903	5767.126	−12.0534	−2.2401	5490.0	9.150	−398.0	0.7160
160	0.7764	−1908.243	−3.180	5879.107	−12.5349	−2.4564	5612.7	9.354	−434.4	0.6945
180	0.7963	−2034.400	−3.391	5965.654	−12.9288	−2.6164	5722.9	9.538	−464.5	0.6771
200	0.8243	−2127.170	−3.545	6033.884	−13.2528	−2.7312	5824.5	9.708	−488.5	0.6637
220	0.8573	−2196.217	−3.660	6089.970	−13.5269	−2.8160	5919.9	9.867	−506.6	0.6537
240	0.8933	−2248.439	−3.747	6137.796	−13.7651	−2.8814	6010.6	10.018	−519.6	0.6466
260	0.9310	−2288.371	−3.814	6179.750	−13.9766	−2.9340	6097.6	10.163	−528.0	0.6420
280	0.9699	−2319.003	−3.865	6217.348	−14.1675	−2.9777	6181.5	10.302	−532.4	0.6397
300	1.0094	−2342.362	−3.904	6251.593	−14.3420	−3.0152	6262.8	10.438	−533.3	0.6392
350	1.1096	−2377.387	−3.962	6326.616	−14.7243	−3.0913	6457.2	10.762	−522.6	0.6449
400	1.2101	−2388.799	−3.981	6391.135	−15.0505	−3.1524	6641.5	11.069	−497.3	0.6588
450	1.3103	−2383.918	−3.973	6448.534	−15.3370	−3.2049	6818.3	11.364	−460.9	0.6792
500	1.4097	−2367.053	−3.945	6500.757	−15.5932	−3.2520	6988.9	11.648	−415.9	0.7054
550	1.5081	−2341.012	−3.902	6549.042	−15.8258	−3.2953	7154.5	11.924	−363.8	0.7369
600	1.6056	−2307.736	−3.846	6594.227	−16.0393	−3.3360	7315.8	12.193	−306.2	0.7734
650	1.7021	−2268.623	−3.781	6636.905	−16.2369	−3.3746	7473.5	12.456	−243.8	0.8149
700	1.7977	−2224.719	−3.708	6677.513	−16.4212	−3.4117	7628.0	12.713	−177.7	0.8615

[a] Saturation pressure.

the corresponding state tables of Lyderson et al. (*23*) and Pitzer's (*26, 27*) acentric factor procedure.

Table X is a comparison of the selected second virial coefficients of Dymond and Smith (*13*) 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 VII for the region yield $(\partial P_r/\partial \rho_r)_{T(r=1)} = 0.0441$ and $(\partial^2 P_r/\partial \rho_r^2)_{T(r=1)} = 0.4069$.

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Nomenclature

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 (*4*)
B = second virial coefficient, cm^3 mol^{-1}
CP = critical point, 425.16K
f = fugacity, atm
G = Gibbs energy, cal mol^{-1}
H = enthalpy, cal mol^{-1}
K = constants of Equation 5
NBP = normal boiling point, 272.67K
n = number of data points in a given region
P = pressure, atm
R = gas constant, 82.05606 atm cm^3 K^{-1} mol^{-1}
N = total number of regions
S = entropy, cal K^{-1} mol^{-1}
T = temperature, K
Z = compressibility factor
V = specific volume, cm^3 mol^{-1}

Greek Letters

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

Superscripts

I = ideal gas state
° = 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
j = 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 Equation 3

Table IX. Compressibility Factors from Corresponding States

		Z				
T, K	P, atm	CGM[a]	DK[b]	This work	LGH[c]	Pitzer[d] et al.
400	4	0.9553	0.9543	0.9532	0.952	0.953
	8	0.9063	0.9052	0.9028	0.906	0.904
	20	0.7153	0.7227	0.7135	0.711	0.706
500	100	0.5214	0.5242	0.5160	0.523	0.522
	200	0.7251	0.7271	0.7284	0.724	0.728
	300	0.9745	1.0036	0.9789	0.974	0.985
600	100	0.7780	0.7875	0.7810	0.767	0.791
	200	0.8327	0.8306	0.8243	0.826	0.825
	300	1.0051	1.0097	1.0094	0.998	1.024

[a] Canjar et al. (*6*). [b] Das and Kuloor (*11*). [c] Lyderson et al. (*23*). [d] Pitzer (*26*); Pitzer et al. (*27*).

Table X. Second Virial Coefficients

	$-B$, cm^3 mol^{-1}		
T, K	Ref. *13*	Ref. *31*	This work
280	852 ± 20	853	902
290	780 ± 20	781	825
300	718 ± 20	719	757
320	609 ± 20	615	644
340	527 ± 20	533	554
360	462 ± 20	467	481
380	414 ± 20	412	421
400	370 ± 20	366	371
420	331 ± 15	327	329
440	298 ± 15	293	294
470	254 ± 10	251	250
500	219 ± 10	216	215
530	189 ± 10	187	186
560	165 ± 10	162	161

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Supplementary Material Available. The complete Table VIII will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JCED-73-244.

PVT Surface and Thermodynamic Properties of Isobutane

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Selected values of vapor pressure, specific volume, enthalpy, and entropy are presented for the saturated liquid and vapor states of isobutane from the normal boiling point (261.32K) to the critical point (408.13K). 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 270 to 600K with pressure to 400 atm. Thermodynamic properties of the real gas, $H - H^\circ$, $(H - H^\circ)/T$, $A - A^\circ$, $S - S^\circ$, $S - S^{\mathrm{I}}$, $G - G^\circ$, $(G - G^\circ)/T$, $G - G^{\mathrm{I}}$, and f/P, were also calculated from the classical relationships. These results illustrate the inconsistency of different experimental data sets for isobutane and the need for new density and enthalpy data.

A number of correlation studies (*6, 12, 28*) present both vapor-liquid coexistence and superheated vapor thermodynamic properties of isobutane. The present compilation is part of a general revision of the j-tables of real gas properties of the API Research Project 44 (*30*) for C_1–C_5 alkanes.

Physical Constants

Table I is a list of the physical conversion constants (*35*) 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 = 408.13 ± 0.01K; P_C = 36.00 ± 0.01 atm; ρ_C = 0.221 ± 0.005 g cm^{-3}) is based on the relation $(\partial P/\partial V)_T = 0$ at the critical point of Beattie et al. (*2*). The selected critical density and critical temperature, 0.221 g cm^{-3} and 408.13K, respectively, were tested with the method proposed by Davis and Rice (*13*) together with all the experimental density data (*11, 28, 31*) available. Because of the unavailability of experimental density data near the critical point, the values reported by Beattie et al. (*2*) were accepted.

The data fit the following equation:

$$(\rho_{\mathrm{SL}} + \rho_{\mathrm{SV}}) = 0.4421 + 0.7414\,(\rho_{\mathrm{SL}} - \rho_{\mathrm{SV}})^3 \qquad (1)$$

Vapor Pressure

A Frost-Kalkwarf vapor-pressure equation was used with the parameters determined to fit the experimental literature values from 255K to the CP.

$$\log P = 18.54662 - 1583.23/T - 3.97829 \log T + 0.95173\,(P/T^2) \qquad (2)$$

where P (mm HG) and T (K).

This equation correlated the measurements of Dana et al. (*11*), Sage and Lacey (*28*), Morris et al. (*25*), Aston

Table I. Physical and Conversion Constants

Constants	Value
Critical temperature	408.13K
Critical pressure	36.0 atm
Critical density	0.221 g cm^{-3}
Critical volume	263.0 cm^3 mol^{-1}
Normal boiling point	261.32K
Triple point	113.55K
Molecular weight	58.1243 mass units
Gas constant, R	82.056060 atm cm^3 K^{-1} mol^{-1}
Temperature conversions	0°C = 273.15K 0°F = 459.67°R
Pressure conversions	1 atm = 760 mm Hg 1 psia = 0.06804596 atm
Energy conversions	1 defined thermochemical calorie = 4.1840 J (exact)

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