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Received for review November 22, 1972. Accepted April 2, 1973. 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 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, $H - H^\circ$, $(H - H^\circ)/T$, $A - A^\circ$, $S - S^\circ$, $S - S^I$, $G - G^\circ$, $(G - G^\circ)/T$, $G - G^I$, and f/P, were also calculated from the classical relationships. These results illustrate the inconsistency of different experimental data sets for 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:

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

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.

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

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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Table II. Critical Constants of Isobutane

Investigator	T_c, K	P_c, atm	ρ_c, g cm^{-3}
Seibert and Burrell (*29*), 1915	406.85	36.54	
Harand (*21*), 1935	406.95		
Gilliland and Scheeline (*17*), 1940	407.61	37.0	0.249
Grunberg and Nissan (*18*), 1948	407.15		
Beattie et al. (*2*), 1949	408.13	36.0	0.221
Selected values, Kudchadker et al. (*23*), 1968	408.13	36.0	0.221
Selected values (this work), 1973	408.13	36.0	0.221

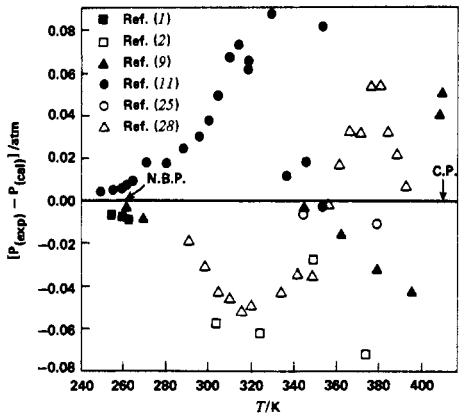

Figure 1. Isobutane vapor-pressure difference near CP

et al. (*1*), Wackher et al. (*34*), Beattie et al. (*2*), and Connolly (*9*) with an average deviation of 0.033 atm in *P*. In addition, the equation is also in agreement with data of Seibert and Burrell (*29*) and Gilliland and Scheeline (*17*), which were not used to determine the constants of Equation 2. At the normal boiling point of 261.32K and the critical point 408.13K, the equation agrees with the experimental values. The equation is believed to be accurate to 0.36% from 249 to CP. Figure 1 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 vapor pressure and its temperature derivative from the NBP to the CP.

Saturated Liquid Volume

The available measurements are those of (*2, 5, 7, 8, 10, 11, 15, 16, 25, 28, 31–34*) who reported their data in different temperature ranges from 224 to 398K.

For the present investigation, the data of Sliwinski (*31*) were selected and heavily weighted (a factor of 4) in comparison with other available literature data (*2, 5, 7, 10, 11, 15, 16, 32–34*). In fitting the data, the modified Guggenheim (*19*) equation was further 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 298.15K, and optimal fit is obtained.

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

Table III. Saturated Properties of Isobutane

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}
261.32	1.000	0.0391	97.80	20682	5090	0	5090	0	19.478	19.478
270.0	1.390	0.0503	99.44	15202	4964	290	5254	0.96	18.385	19.345
280.0	1.968	0.0657	101.4	10921	4817	626	5443	2.06	17.204	19.264
290.0	2.714	0.0839	103.6	8032	4669	955	5624	3.16	16.100	19.260
300.0	3.656	0.1051	105.9	6031	4521	1288	5809	4.26	15.070	19.330
310.0	4.826	0.1293	108.5	4615	4372	1626	5998	5.39	14.103	19.493
320.0	6.254	0.1569	111.3	3577	4211	1975	6186	6.48	13.159	19.639
330.0	7.975	0.1878	114.5	2801	4029	2337	6366	7.59	12.209	19.799
340.0	10.02	0.2224	118.1	2209	3826	2719	6545	8.71	11.253	19.963
350.0	12.44	0.2608	122.2	1750	3596	3115	6711	9.84	10.274	20.114
360.0	15.25	0.3033	127.1	1387	3329	3533	6862	11.01	9.247	20.257
370.0	18.52	0.3504	133.1	1094	3015	3965	6980	12.23	8.149	20.379
380.0	22.28	0.4025	140.8	849.7	2624	4429	7053	13.56	6.905	20.465
385.0	24.36	0.4306	145.6	745.3	2406	4670	7076	14.21	6.249	20.459
390.0	26.59	0.4603	151.6	647.6	2155	4928	7083	14.89	5.526	20.416
395.0	28.97	0.4917	159.2	556.1	1866	5204	7070	15.60	4.724	20.324
396.0	29.46	0.4982	161.1	539.1	1805	5261	7066	15.74	4.558	20.298
397.0	29.96	0.5048	163.0	521.6	1739	5317	7056	15.87	4.380	20.250
398.0	30.47	0.5115	165.2	505.3	1676	5375	7051	16.01	4.211	20.221
399.0	30.98	0.5182	167.5	488.2	1605	5433	7038	16.16	4.023	20.183
400.0	31.51	0.5250	170.1	471.0	1529	5496	7025	16.31	3.823	20.133
401.0	32.03	0.5319	172.9	453.3	1447	5560	7007	16.46	3.608	20.068
402.0	32.57	0.5389	176.1	435.1	1358	5627	6985	16.62	3.378	19.998
403.0	33.11	0.5460	179.8	416.1	1258	5698	6956	16.79	3.122	19.912
404.0	33.66	0.5531	184.2	396.6	1149	5772	6921	16.97	2.844	19.814
405.0	34.22	0.5604	189.5	376.1	1025	5847	6872	17.15	2.531	19.681
406.0	34.78	0.5677	196.5	354.4	881	5933	6814	17.34	2.170	19.510
406.5	35.07	0.5715	201.1	341.8	791	5983	6774	17.45	1.946	19.396
407.0	35.35	0.5752	207.0	327.3	682	6042	6724	17.58	1.676	19.256
407.5	35.64	0.5790	215.4	309.3	536	6116	6652	17.74	1.315	19.055
408.13	36.00	0.5835	263.0	263.0	0	6443	6443	18.49	0	18.49

where

$\theta = [1 - (T/T_L)]^{1/3}$, T (K) and ρ (g cm^{-3}) constants of Equation 3.

	ρ_L	A
Less than 298.15K	0.304533	$-155.57356 \times 10^{-4}$
More than 298.15K	0.221	185.22760×10^{-3}

	B	T_L
Less than 298.15K	837.55384×10^{-4}	393.15
More than 298.15K	$-456.33640 \times 10^{-4}$	408.13

The equation represents the selected data very well over the temperature range from 224 to 398K with the standard deviation of 0.00056 g cm^{-3}. The values reported by Morris et al. (*25*), Coffin and Maass (*8*), and Sage and Lacey (*28*) are higher than the other data; hence, these sets of data were excluded in fitting the equation. Figure 2 shows how Equation 3 deviates from the experimental data. Very near the critical point, there are no data available; hence, the values accepted near the critical point are shown in Figure 3 by a solid line by use of graphical extrapolation based on rectilinear diameters and the Clapeyron equation. Selected orthobaric volumes appear in Table III.

Saturated Vapor Volume

Dana et al. (*11*) (273–329K), Sage and Lacey (*28*) (290–391K), and Sliwinski (*31*) (283–368K) measured the vapor volumes. At the normal boiling point, the vapor volume was calculated from the enthalpy of vaporization measurement of Aston et al. (*1*) via the Clapeyron equation. This value, together with other selected saturated vapor volumes (*11, 31*) and experimental gaseous volumes (*3, 25, 28*), were used to evaluate Benedict-Webb-Rubin (BWR) constants. In the evaluation of these constants, the data of Aston et al. (*1*) and Sliwinski (*31*) were weighted five times.

Figure 4 illustrates the agreement between the values (*1, 28, 31*). The base volumes for Figure 4 are supplied by the Equation 2 in conjunction with the BWR constants reported in Table VII. The graphically smoothed values of Figure 4 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 (*11, 12, 28*). The measured enthalpy of vaporization 5089.6 cal mol^{-1} of Aston et al. (*1*) at NBP shows close agree-

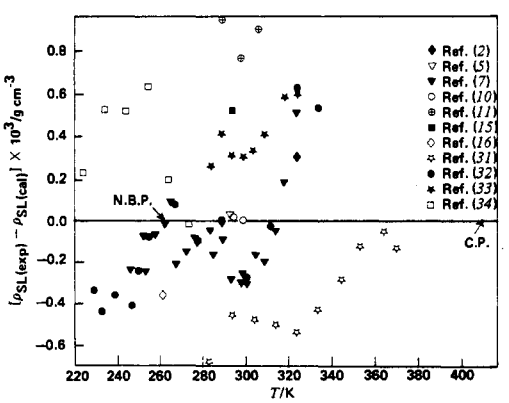

Figure 2. Isobutane saturated liquid-density difference

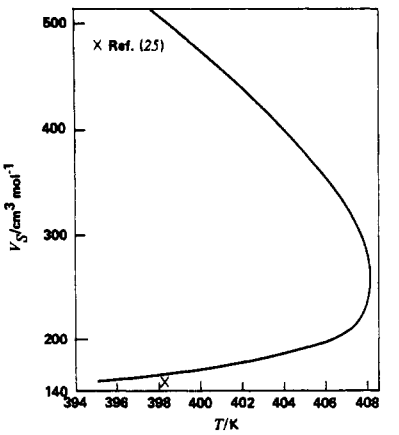

Figure 3. Saturated volume near CP

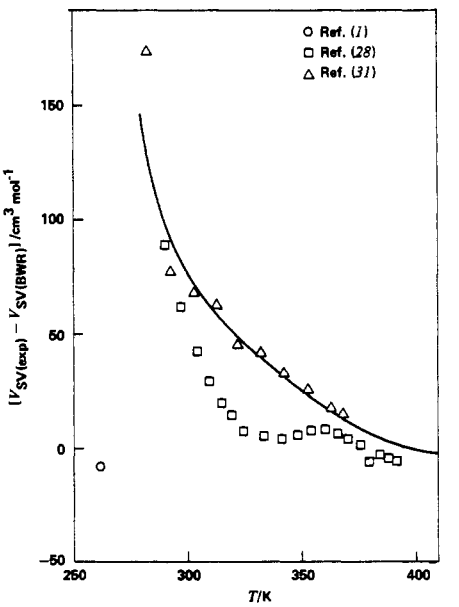

Figure 4. Saturated vapor-volume difference

Table IV. Comparison of Enthalpies of Vaporization

	λ, cal mol^{-1}			
T, K	DJBT[a,b]	SL[a,c]	DK[d]	This work
261.32	5166		5090	5090
270.0	4979		4976	4964
280.0	4839		4840	4817
290.0	4691	(4678)[e]	4691	4669
300.0	4534	4548	4534	4521
310.0	4358	4393	4372	4372
320.0	4160	4214	4188	4211
330.0	3952	4019	3991	4029
340.0		3808	3778	3826
350.0		3574	3551	3596
360.0		3301	3294	3329
370.0		2997	2991	3015
380.0		2607	2617	2624
385.0		2364		2406
390.0		2098	2144	2155
395.0				1866
400.0			1500	1529

[a] Values are interpolated. [b] Dana et al. (*11*). [c] Sage and Lacey (*28*). [d] Das and Kuloor (*12*). [e] Value in parentheses is extrapolated.

ment with the value 5090 cal mol^{-1} which is calculated from the Clapeyron equation.

$$dP/dT = \lambda/[T(V_{SV} - V_{SL})] \quad (4)$$

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 and Lacey (*28*) have been accepted after correction to the reference state $H_{SL} = 0$ at 261.32K. 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 enthalpy of vaporization to the liquid enthalpy calculated above. To establish the enthalpy envelope up to the critical temperature, the following graphical procedures were employed in Figure 5. Starting at 390K, the enthalpy of vaporization was marked on an overlay to Figure 5 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 404K indicated that the enthalpy locus was reasonably straight. A plot of H_s vs. V_s allowed a check of the values obtained from Figure 5 in the critical region.

Entropy of Saturated Liquid and Vapor

By accepting the saturated liquid entropy data reported by Sage and Lacey (*28*), entropy changes along the saturated liquid envelope may be found. The values are smoothed graphically, reported in Table III, and compared in Table VI with literature data available. 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 the entropy locus, $\bar{S}_s = (S_{SL} + S_{SV})/2$, reasonably straight (Figure 6) up to 405K. 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 and Lacey (*28*) covered 294–394K with pressures 0.68 and 204 atm. Morris et al. (*25*) covered a higher temperature range (311–511K) and pressure range 0.68 to 340 atm, and Beattie et al. (*3*) determined values over the temperature range 423–573K and pressure range 25–304 atm. The data reported by Beattie et al. (*3*) are in good agreement with those of Morris et al. (*25*). Figure 7 shows the P,T regions of these major data sources.

Correlation Procedure

Although agreement between the major data sources is not good in some regions, no sound reason was found for deletion of any point, and each point 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 boiling point which were weighted ten. This procedure was used to constrain the PVT surface to values consistent with the selected saturated properties which form a boundary condition. The differential regional BWR equation (*14*) is

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

Table V. Comparison of Saturated Liquid Enthalpies

	H_{SL}, cal mol^{-1}			
T, K	DJBT[a,b]	SL[a,c]	DK[d]	This work
261.32	0	(0)[e]	0	0
270.0	318	(290)[e]	267	290
280.0	635	(626)[e]	587	626
290.0	990	(955)[e]	920	955
300.0	1385	1288	1258	1288
310.0	1809	1626	1604	1626
320.0	2273	1975	1967	1975
330.0	2774	2337	2340	2337
340.0		2719	2725	2719
350.0		3115	3115	3115
360.0		3533	3527	3533
370.0		3965	3966	3965
380.0		4429	4445	4429
385.0		4657		4670
390.0		4923	4969	4928
395.0				5204
400.0			5570	5496

[a] Values are interpolated. [b] Dana et al. (*11*). [c] Sage and Lacey (*28*). [d] Das and Kuloor (*12*). [e] Values in parentheses are extrapolated.

Table VI. Comparison of Saturated Liquid Entropies

	S_{SL}, cal K^{-1} mol^{-1}			
T, K	DJBT[a,b]	SL[a,c]	DK[d]	This work
261.32	0	0	0	0
270.0	1.02	0.96	1.03	0.96
280.0	2.18	2.06	2.18	2.06
290.0	3.40	3.16	3.36	3.16
300.0	4.74	4.26	4.49	4.26
310.0	6.12	5.39	5.62	5.39
320.0	7.56	6.48	6.74	6.48
330.0	9.13	7.59	7.87	7.59
340.0		8.71	8.99	8.71
350.0		9.84	10.10	9.84
360.0		11.01	11.23	11.01
370.0		12.23	12.41	12.23
380.0		13.56	13.64	13.56
385.0		14.21		14.21
390.0		14.82	14.87	14.89
395.0				15.60
400.0			16.45	16.31

[a] Values are interpolated. [b] Dana et al. (*11*). [c] Sage and Lacey (*28*). [d] Das and Kuloor (*12*).

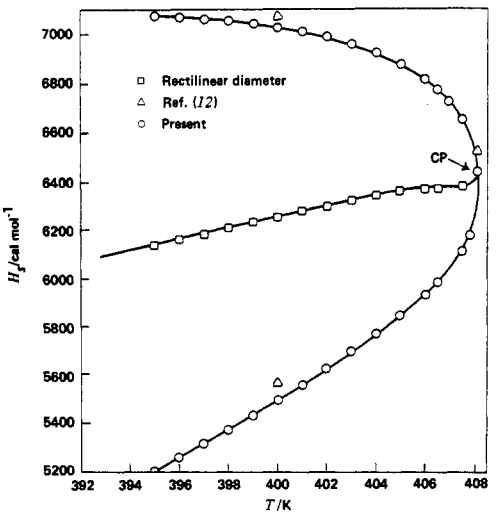

Figure 5. Enthalpy envelope

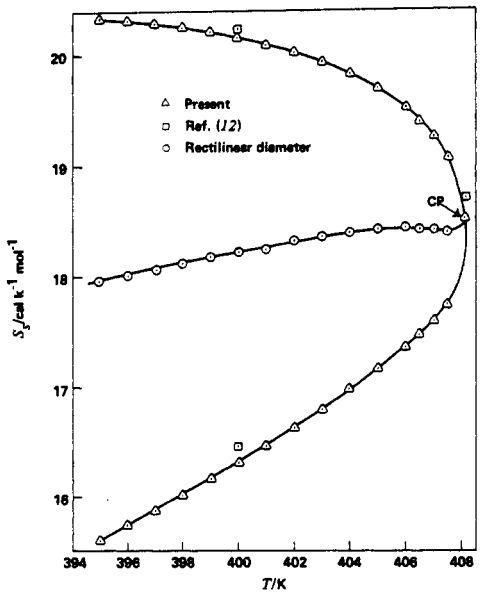

Figure 6. Entropy envelope

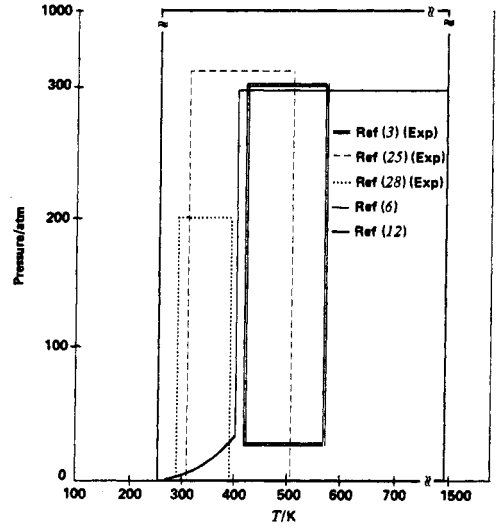

Figure 7. Regional block diagram of literature data for isobutane

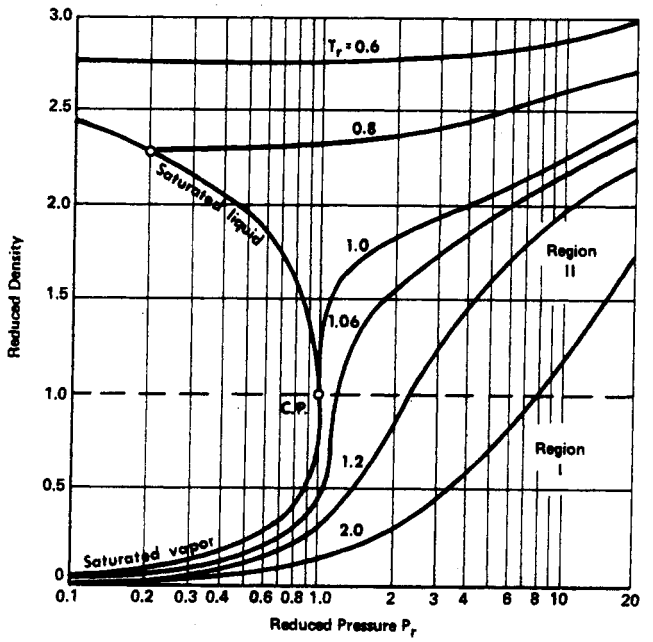

Figure 8. Isobutane gas PVT regions

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 isobutane 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 8. 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 a maximum of ±0.2% from NBP to 320K and maximum of 0.5% from 320 to 370K. The error limit of vapor volume at NBP is 14 cm^3 mol^{-1}, providing the measurement of enthalpy of vaporization of Aston and Kennedy (*1*) is correct. Figure 4 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 uncer-

Table VII. Constants for the DR-BWR Equation

	Region I	Region II
Number of data points	308	75
Density range, g mol cm^{-3}	0.0 to 0.0038022	0.0038022 to 0.008710174
Normalized density range	0.00244 to 0.4365	0.4365 to 1
Av % deviation for Z	0.4731	0.3205
Max % deviation for Z	0.6787	1.3260
Constants for Equation 1[a]		
K_{1r}	6.06741×10^{-3}	2.56545×10^{-2}
K_{2r}	-5.07260×10^{2}	-8.55723×10^{2}
K_{3r}	-8.64777×10^{7}	-1.06304×10^{7}
K_{4r}	3.00792×10^{-2}	-5.99536×10^{-2}
K_{5r}	-1.45155×10^{3}	4.53234×10^{3}
K_{6r}	4.89167×10^{2}	-1.57375×10^{3}
K_{7r}	2.10348×10^{8}	-2.62513×10^{8}
K_{8r}	2.00000	8.00000
BWR constants[b]		
A_0	6.68616×10^{6}	
B_0	7.99741×10	
C_0	1.13986×10^{12}	
a	2.19660×10^{9}	
b	4.55183×10^{4}	
c	3.18315×10^{14}	
α	5.09970×10^{5}	
γ	2.63619×10^{4}	

[a] Only for use in Equation 5 with ρ normalized as (g mol cm^{-3}/0.008710174). [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}).

tainty is ±40 cal mol^{-1} from NBP to 385K. Above 385K, 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 0.3% as reported by Sage and Lacey (*28*) except near the critical point. The H_S vs. V_S and S_S vs. V_S diagrams were drawn to check these extrapolated values from 390K to CP. Liquid entropy values are likewise considered accurate within ±0.3% from NBP to 385K.

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 $A - A°$ and $S - S°$ 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 573K rather than 1500K as in the revised API Research Project 44 tables. The values above 573K are an extrapolation of the present surface and further assume no decomposition of the isobutane.

Discussion

Table IX is a comparison of these values with values calculated from corresponding states by two methods: the corresponding state tables of Lyderson et al. (*24*) and Pitzer's (*26, 27*) acentric factor procedure.

Table X is a comparison of the selected second virial coefficients of Jessen and Lightfoot (*22*), Connolly (*9*), Gunn (*20*), and API (h-tables) (*30*) with the present value where

$$B = B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3} \qquad (6)$$

Table VIII (Condensed). Thermodynamic Properties of Isobutane

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)
					270K					
1	0.9566	−84.203	−0.312	0.434	−0.2272	−0.2272	−22.9	−0.085	−22.9	0.9583
1.390[a]	0.9386	−119.030	−0.441	177.560	−0.9766	−0.3222	144.7	0.536	−32.0	0.9420
					280K					
1	0.9621	−75.908	−0.271	0.337	−0.1970	−0.1970	−20.7	−0.074	−20.7	0.9634
1.968[a]	0.9228	−154.922	−0.553	377.931	−1.7497	−0.4051	335.0	1.196	−41.5	0.9281
					300K					
1	0.9706	−62.579	−0.209	0.210	−0.1510	−0.1510	−17.3	−0.058	−17.3	0.9714
3.656[a]	0.8842	−247.756	−0.826	775.859	−3.1821	−0.6075	706.9	2.356	−65.5	0.8959
					320K					
1	0.9768	−52.441	−0.164	0.135	−0.1182	−0.1182	−14.6	−0.046	−14.6	0.9773
4	0.9011	−224.364	−0.701	883.549	−3.2658	−0.5129	820.7	2.565	−60.2	0.9095
6.254[a]	0.8360	−373.601	−1.168	1172.517	−4.5059	−0.8653	1068.3	3.338	−96.7	0.8589
					340K					
1	0.9813	−44.555	−0.131	0.089	−0.0943	−0.0943	−12.5	−0.037	−12.5	0.9816
4	0.9218	−187.562	−0.552	937.653	−3.1541	−0.4011	884.8	2.602	−51.2	0.9270
8	0.8307	−408.562	−1.202	1412.309	−5.0193	−0.8898	1298.0	3.818	−106.0	0.8547
10.02[a]	0.7767	−541.078	−1.591	1571.343	−5.7695	−1.1924	1420.6	4.178	−135.7	0.8180
					360K					
1	0.9848	−38.306	−0.106	0.060	−0.0764	−0.0764	−10.8	−0.030	−10.8	0.9850
4	0.9370	−159.433	−0.443	992.142	−3.0736	−0.3207	947.1	2.631	−44.0	0.9403
8	0.8665	−339.473	−0.943	1491.705	−4.8215	−0.6921	1396.3	3.879	−90.3	0.8813
12	0.7846	−551.570	−1.532	1790.691	−6.0786	−1.1440	1636.7	4.546	−139.7	0.8224
15.25[a]	0.7032	−766.171	−2.128	1977.030	−7.0306	−1.6196	1764.8	4.902	−183.1	0.7740
					380K					
1	0.9875	−33.276	−0.088	0.042	−0.0628	−0.0628	−9.4	−0.025	−9.4	0.9876
4	0.9484	−137.358	−0.361	1046.849	−3.0139	−0.2609	1007.9	2.652	−38.2	0.9506
8	0.8923	−288.124	−0.758	1572.471	−4.6825	−0.5531	1491.2	3.924	−78.0	0.9019
12	0.8301	−457.394	−1.204	1883.750	−5.8236	−0.8890	1755.6	4.620	−119.6	0.8534
16	0.7588	−654.528	−1.722	2110.622	−6.7978	−1.2918	1928.6	5.075	−163.6	0.8051
20	0.6715	−901.051	−2.371	2297.492	−7.7650	−1.8159	2049.6	5.394	−211.0	0.7561
22.28[a]	0.6074	−1086.721	−2.860	2398.073	−8.3909	−2.2277	2101.8	5.531	−240.2	0.7274
					390K					
1	0.9886	−31.121	−0.080	0.035	−0.0572	−0.0572	−8.8	−0.023	−8.8	0.9887
4	0.9531	−128.044	−0.328	1074.252	−2.9897	−0.2367	1037.9	2.661	−35.7	0.9549
8	0.9027	−267.076	−0.685	1613.149	−4.6278	−0.4984	1537.8	3.943	−72.7	0.9104
12	0.8476	−420.620	−1.079	1931.321	−5.7280	−0.7934	1813.3	4.650	−111.2	0.8663
16	0.7862	−594.575	−1.525	2161.410	−6.6420	−1.1360	1995.8	5.117	−151.5	0.8223

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)
					390K					
20	0.7148	−800.250	−2.052	2346.752	−7.5030	−1.5539	2125.9	5.451	−194.2	0.7782
24	0.6253	−1065.782	−2.733	2511.211	−8.4277	−2.1166	2221.0	5.695	−240.3	0.7332
26.59[a]	0.5441	−1315.783	−3.374	2620.701	−9.1883	−2.6739	2267.6	5.814	−273.0	0.7030
					400K					
1	0.9895	−29.169	−0.073	0.029	−0.0522	−0.0522	−8.3	−0.021	−8.3	0.9896
4	0.9573	−119.667	−0.299	1101.679	−2.9685	−0.2155	1067.7	2.669	−33.5	0.9587
8	0.9117	−248.417	−0.621	1653.955	−4.5806	−0.4511	1583.8	3.960	−68.0	0.9180
12	0.8626	−388.737	−0.972	1979.317	−5.6473	−0.7127	1870.2	4.675	−103.7	0.8776
16	0.8089	−544.476	−1.361	2213.381	−6.5151	−1.0092	2061.6	5.154	−140.8	0.8376
20	0.7486	−722.193	−1.805	2399.607	−7.3052	−1.3562	2199.9	5.500	−179.7	0.7975
24	0.6782	−934.762	−2.337	2559.183	−8.0957	−1.7846	2303.5	5.759	−220.9	0.7572
28	0.5883	−1215.698	−3.039	2708.504	−8.9930	−2.3758	2381.5	5.954	−265.4	0.7160
29	0.5599	−1307.625	−3.269	2747.122	−9.2628	−2.5759	2397.5	5.994	−277.3	0.7054
30	0.5267	−1417.134	−3.543	2788.151	−9.5732	−2.8190	2412.2	6.030	−289.5	0.6945
31	0.4847	−1559.408	−3.899	2834.661	−9.9619	−3.1426	2425.4	6.063	−302.4	0.6834
31.51[a]	0.4564	−1658.466	−4.146	2863.209	−10.2248	−3.3732	2431.4	6.079	−309.2	0.6776
					406K					
1	0.9901	−28.084	−0.069	0.026	−0.0495	−0.0495	−8.0	−0.020	−8.0	0.9902
4	0.9595	−115.038	−0.283	1118.145	−2.9570	−0.2040	1085.5	2.674	−32.2	0.9608
8	0.9166	−238.208	−0.587	1678.486	−4.5552	−0.4258	1611.2	3.969	−65.3	0.9222
12	0.8706	−371.544	−0.915	2008.264	−5.6046	−0.6700	1903.9	4.689	−99.5	0.8839
16	0.8208	−518.072	−1.276	2244.961	−6.4496	−0.9436	2100.4	5.174	−135.0	0.8459
20	0.7657	−682.647	−1.681	2432.339	−7.2071	−1.2580	2243.4	5.526	−171.9	0.8080
24	0.7030	−873.988	−2.153	2591.060	−7.9449	−1.6338	2351.6	5.792	−210.7	0.7700
28	0.6279	−1110.756	−2.736	2734.679	−8.7325	−2.1153	2434.6	5.997	−252.0	0.7316
29	0.6059	−1181.774	−2.911	2769.860	−8.9504	−2.2635	2452.1	6.040	−262.8	0.7218
30	0.5819	−1260.187	−3.104	2805.395	−9.1836	−2.4293	2468.3	6.080	−273.9	0.7120
31	0.5554	−1348.656	−3.322	2841.841	−9.4385	−2.6191	2483.4	6.117	−285.3	0.7020
32	0.5251	−1451.843	−3.576	2880.115	−9.7268	−2.8443	2497.2	6.151	−297.0	0.6918
33	0.4887	−1579.418	−3.890	2922.058	−10.0720	−3.1285	2509.8	6.182	−309.3	0.6814
34	0.4397	−1758.918	−4.332	2972.756	−10.5417	−3.5389	2521.0	6.209	−322.1	0.6706
34.78[a]	0.3657	−2054.975	−5.062	3039.961	−11.2895	−4.2414	2528.6	6.228	−333.0	0.6617
					408K					
1	0.9903	−27.735	−0.068	0.025	−0.0487	−0.0487	−7.9	−0.019	−7.9	0.9903
4	0.9602	−113.556	−0.278	1123.635	−2.9533	−0.2004	1091.4	2.675	−31.8	0.9615
8	0.9181	−234.953	−0.576	1686.670	−4.5472	−0.4178	1620.3	3.971	−64.5	0.9235
12	0.8731	−366.098	−0.897	2017.933	−5.5913	−0.6566	1915.1	4.694	−98.2	0.8859
16	0.8245	−509.788	−1.249	2255.540	−6.4292	−0.9233	2113.3	5.180	−133.1	0.8485
20	0.7710	−670.436	−1.643	2443.378	−7.1771	−1.2280	2257.8	5.534	−169.4	0.8113
24	0.7105	−855.754	−2.097	2602.009	−7.9001	−1.5890	2367.5	5.803	−207.5	0.7741
28	0.6391	−1081.465	−2.651	2744.462	−8.6605	−2.0433	2452.0	6.010	−247.8	0.7365
29	0.6185	−1147.950	−2.814	2778.995	−8.8673	−2.1804	2469.9	6.054	−258.4	0.7270
30	0.5964	−1220.420	−2.991	2813.603	−9.0858	−2.3316	2486.6	6.095	−269.1	0.7174
31	0.5723	−1300.667	−3.188	2848.674	−9.3206	−2.5012	2502.1	6.133	−280.2	0.7077
32	0.5455	−1391.544	−3.411	2884.782	−9.5786	−2.6962	2516.5	6.168	−291.5	0.6978
33	0.5148	−1498.084	−3.672	2922.883	−9.8721	−2.9286	2529.7	6.200	−303.2	0.6878
34	0.4778	−1630.802	−3.997	2964.908	−10.2269	−3.2241	2541.8	6.230	−315.4	0.6776
35	0.4277	−1819.730	−4.460	3016.172	−10.7161	−3.6558	2552.4	6.256	−328.2	0.6669
35.93[a]	0.3069	−2352.159	−5.765	3122.311	−12.0413	−4.9287	2560.7	6.276	−341.3	0.6563
					410K					
1	0.9904	−27.393	−0.067	0.024	−0.0478	−0.0478	−7.8	−0.019	−7.8	0.9905
20	0.7761	−658.655	−1.606	2454.471	−7.1483	−1.1992	2272.1	5.542	−167.0	0.8146
30	0.6096	−1184.495	−2.889	2822.533	−8.9980	−2.2438	2504.7	6.109	−264.6	0.7226
40	0.2148	−3118.417	−7.606	3245.775	−13.9631	−6.6376	2606.5	6.357	−397.0	0.6141
52	0.2430	−3389.541	−8.267	3270.990	−14.7419	−6.8953	2654.6	6.475	−562.5	0.5012
60	0.2695	−3464.068	−8.449	3279.157	−14.9963	−6.8656	2684.4	6.547	−649.2	0.4505
72	0.3109	−3534.330	−8.620	3288.496	−15.2725	−6.7797	2727.4	6.652	−754.6	0.3958
80	0.3386	−3566.620	−8.699	3293.766	−15.4192	−6.7171	2755.2	6.720	−812.6	0.3686
100	0.4074	−3620.148	−8.830	3305.273	−15.7145	−6.5693	2822.8	6.885	−926.7	0.3204
120	0.4751	−3651.131	−8.905	3315.480	−15.9495	−6.4423	2888.1	7.044	−1009.8	0.2893
140	0.5417	−3668.974	−8.949	3324.982	−16.1484	−6.3351	2951.9	7.200	−1071.6	0.2682
160	0.6072	−3678.176	−8.971	3334.052	−16.3230	−6.2445	3014.3	7.352	−1117.9	0.2533
180	0.6717	−3681.243	−8.979	3342.834	−16.4799	−6.1675	3075.5	7.501	−1152.6	0.2428
200	0.7352	−3679.729	−8.975	3351.413	−16.6233	−6.1017	3135.8	7.648	−1178.0	0.2353

(Continued on page 260)

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)
					410K					
220	0.7979	−3674.665	−8.963	3359.845	−16.7560	−6.0451	3195.3	7.793	−1196.2	0.2301
240	0.8597	−3666.773	−8.943	3368.167	−16.8799	−5.9962	3254.0	7.937	−1208.3	0.2267
260	0.9209	−3656.576	−8.918	3376.405	−16.9964	−5.9538	3312.0	8.078	−1215.5	0.2247
280	0.9813	−3644.467	−8.889	3384.578	−17.1068	−5.9170	3369.3	8.218	−1218.5	0.2239
300	1.0410	−3630.748	−8.855	3392.700	−17.2119	−5.8851	3426.1	8.356	−1217.9	0.2241
350	1.1879	−3590.852	−8.758	3412.846	−17.4552	−5.8223	3565.8	8.697	−1203.7	0.2280
400	1.3313	−3544.889	−8.646	3432.842	−17.6768	−5.7787	3702.6	9.031	−1175.6	0.2360
					440K					
1	0.9925	−22.939	−0.052	0.014	−0.0373	−0.0373	−6.5	−0.015	−6.5	0.9926
20	0.8354	−520.024	−1.182	2625.099	−6.8211	−0.8721	2481.3	5.639	−136.3	0.8556
40	0.6147	−1291.334	−2.935	3268.845	−9.5989	−2.2733	2932.2	6.664	−291.1	0.7167
60	0.3749	−2540.856	−5.775	3650.868	−12.8307	−4.7000	3104.6	7.056	−472.9	0.5821
80	0.3859	−2984.909	−6.784	3734.690	−14.0523	−5.3503	3198.1	7.268	−630.8	0.4858
100	0.4381	−3153.223	−7.166	3769.016	−14.6165	−5.4713	3278.0	7.450	−745.8	0.4259
120	0.4968	−3243.431	−7.371	3792.005	−14.9903	−5.4831	3352.3	7.619	−830.9	0.3864
140	0.5570	−3297.793	−7.495	3810.239	−15.2749	−5.4616	3423.2	7.780	−894.7	0.3592
160	0.6174	−3331.904	−7.573	3825.927	−15.5080	−5.4295	3491.6	7.935	−942.9	0.3399
180	0.6774	−3353.088	−7.621	3840.047	−15.7074	−5.3950	3558.2	8.087	−979.3	0.3260
200	0.7369	−3365.347	−7.649	3853.115	−15.8832	−5.3615	3623.2	8.235	−1006.3	0.3161
220	0.7958	−3371.083	−7.662	3865.431	−16.0412	−5.3303	3687.0	8.380	−1025.8	0.3091
240	0.8541	−3371.860	−7.663	3877.185	−16.1854	−5.3017	3749.7	8.522	−1039.1	0.3045
260	0.9118	−3368.745	−7.656	3888.505	−16.3186	−5.2760	3811.5	8.662	−1047.3	0.3016
280	0.9689	−3362.501	−7.642	3899.482	−16.4428	−5.2530	3872.3	8.801	−1051.2	0.3003
300	1.0255	−3353.692	−7.622	3910.181	−16.5594	−5.2325	3932.4	8.937	−1051.4	0.3002
350	1.1645	−3323.021	−7.552	3936.004	−16.8244	−5.1914	4079.7	9.272	−1038.8	0.3046
400	1.3004	−3283.281	−7.462	3960.875	−17.0605	−5.1624	4223.3	9.599	−1011.8	0.4141
					520K					
1	0.9959	−15.254	−0.029	0.003	−0.0212	−0.0212	−4.3	−0.008	−4.3	0.9959
20	0.9158	−322.133	−0.619	3094.459	−6.4032	−0.4542	3007.5	5.784	−86.0	0.9201
40	0.8293	−684.590	−1.317	3812.006	−8.3082	−0.9827	3635.7	6.992	−173.6	0.8453
60	0.7463	−1086.281	−2.089	4228.365	−9.7166	−1.5859	3966.4	7.628	−261.6	0.7762
80	0.6813	−1495.496	−2.876	4507.363	−10.9110	−2.2090	4178.2	8.035	−346.8	0.7147
100	0.6471	−1852.951	−3.563	4695.186	−11.8918	−2.7467	4330.8	8.328	−424.7	0.6628
120	0.6455	−2116.811	−4.071	4818.002	−12.6322	−3.1250	4451.9	8.561	−491.8	0.6211
140	0.6700	−2284.958	−4.394	4897.123	−13.1564	−3.3430	4556.4	8.762	−546.6	0.5890
160	0.7057	−2400.335	−4.616	4954.952	−13.5604	−3.4819	4651.1	8.944	−589.8	0.5649
180	0.7466	−2483.889	−4.777	5000.931	−13.8908	−3.5784	4739.3	9.114	−623.1	0.5469
200	0.7903	−2545.934	−4.896	5039.401	−14.1707	−3.6491	4822.9	9.275	−648.4	0.5337
220	0.8355	−2592.364	−4.985	5072.699	−14.4138	−3.7029	4902.8	9.428	−666.9	0.5243
240	0.8816	−2626.925	−5.052	5102.228	−14.6285	−3.7449	4979.9	9.577	−679.6	0.5178
260	0.9281	−2652.210	−5.100	5128.906	−14.8209	−3.7783	5054.7	9.721	−687.5	0.5139
280	0.9749	−2670.092	−5.135	5153.366	−14.9953	−3.8055	5127.5	9.861	−691.2	0.5120
300	1.0218	−2681.966	−5.158	5176.060	−15.1549	−3.8281	5198.6	9.997	−691.4	0.5120
350	1.1387	−2691.764	−5.176	5227.060	−15.5040	−3.8711	5370.3	10.328	−678.8	0.5182
400	1.2546	−2681.233	−5.156	5272.285	−15.8008	−3.9026	5535.2	10.645	−651.9	0.5319
					600K					
1	0.9976	−10.872	−0.018	−0.008	−0.0133	−0.0133	−2.9	−0.005	−2.9	0.9976
20	0.9522	−223.085	−0.372	3568.795	−6.2248	−0.2758	3511.8	5.853	−57.6	0.9528
40	0.9076	−456.342	−0.761	4391.733	−7.8966	−0.5710	4281.6	7.136	−113.7	0.9090
60	0.8687	−695.169	−1.159	4867.521	−9.0103	−0.8796	4711.0	7.852	−167.4	0.8689
80	0.8383	−931.197	−1.552	5196.194	−9.8912	−1.1892	5003.5	8.339	−217.7	0.8330
100	0.8189	−1153.697	−1.923	5439.483	−10.6290	−1.4838	5223.7	8.706	−263.4	0.8017
120	0.8109	−1353.791	−2.256	5625.793	−11.2572	−1.7500	5400.5	9.001	−303.8	0.7749
140	0.8132	−1527.760	−2.546	5772.123	−11.7955	−1.9822	5549.5	9.249	−338.5	0.7527
160	0.8239	−1675.341	−2.792	5889.484	−12.2583	−2.1798	5679.6	9.466	−367.5	0.7346
180	0.8453	−1786.857	−2.978	5980.932	−12.6391	−2.3267	5796.6	9.661	−390.8	0.7204
200	0.8740	−1870.773	−3.118	6054.608	−12.9587	−2.4371	5904.4	9.841	−408.5	0.7097
220	0.9067	−1935.806	−3.226	6116.612	−13.2355	−2.5246	6005.5	10.009	−421.0	0.7023
240	0.9420	−1987.147	−3.312	6170.454	−13.4807	−2.5970	6101.3	10.169	−428.9	0.6977
260	0.9786	−2028.054	−3.380	6218.280	−13.7015	−2.6588	6192.8	10.321	−432.7	0.6955
280	1.0163	−2060.685	−3.434	6261.482	−13.9026	−2.7128	6280.9	10.468	−433.0	0.6953
300	1.0545	−2086.544	−3.478	6301.011	−14.0875	−2.7607	6366.0	10.610	−430.1	0.6970
350	1.1515	−2128.137	−3.547	6387.801	−14.4941	−2.8612	6568.3	10.947	−411.4	0.7080
400	1.2492	−2145.008	−3.575	6462.236	−14.8402	−2.9421	6759.1	11.265	−379.7	0.7271

[a] Saturation pressure.

Table IX. Compressibility Factors from Corresponding States

T, K	P, atm	Z CM[a]	DK[b]	This work	Pitzer[c]	LGH[d]
400	3	0.9687	0.9686	0.9683	0.968	0.964
	6	0.9360	0.9358	0.9346	0.935	0.928
	15	0.8260	0.8254	0.8230	0.820	0.832
500	100	0.5944	0.5957	0.5852	0.582	0.582
	200	0.7688	0.7687	0.7714	0.760	0.757
	300	1.0158	1.0504	1.0179	1.020	1.004
600	100	0.8309	0.8275	0.8189	0.800	0.802
	200	0.8907	0.8904	0.8740	0.880	0.871
	300	1.0579	1.1361	1.0545	1.110	1.053

[a] Canjar and Manning (*6*). [b] Das and Kuloor (*12*). [c] Pitzer (*26*); Pitzer et al. (*27*). [d] Lyderson et al. (*24*).

Table X. Second Virial Coefficients

T, K	−B, cm³ mol⁻¹ Literature values	API	This work
273.16	889[a]	786.0	899.9
303.16	699[a]	608.2	687.4
344.26	457.2[b]	449.8	497.2
360.93	412.7[b]	402.6	441.2
377.59	374.0[b]	362.2	393.9
394.26	341.1[b]	327.1	353.4
406.87	318.3[b]	303.6	326.5
410.93	311.5[b]	296.5	318.5
444.26	259.6[b]	245.7	261.9
477.6	230.2[c]	205.2	218.1
510.9	191.6[c]	172.2	183.7

[a] Jessen and Lightfoot (*22*). [b] Connolly (*9*). [c] Gunn (*20*).

The present PVT surface was not constrained by the critical conditions

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

However, the constants of Table VII for the first region yield $(\partial P_r/\partial \rho_r)_{T(r=1)} = 0.0136$ and $(\partial^2 P_r/\partial \rho_r{}^2)_{T(r=1)} = 0.3055$.

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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, 408.13K
f = fugacity, atm
G = Gibbs energy, cal mol^{-1}
H = enthalpy, cal mol^{-1}
K = constants of Equation 5
NBP = normal boiling point, 261.32K
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
$\varphi = P - RT\rho$, 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

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Received for review November 22, 1972. Accepted April 2, 1973. 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 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-73-253.

Heat of Mixing and Vapor-Liquid Equilibrium of Acetophenone–2-Butanol System

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The heat of mixing of the acetophenone–2-butanol system exhibits an endothermic maximum of 541 cal/mol of solution close to 0.50 mole fraction at temperatures close to 25°C. Vapor-liquid equilibrium data of this system are reported at 1 atm pressure over the entire composition range.

The acetophenone–2-butanol system can be expected to deviate from ideality owing to hydrogen bonding between both like and unlike species. This work is part of a continuing study of phase equilibria and heat of mixing of alcohol–ketone systems. The heat of mixing absorbed in this system indicates the degree of the formation of alcohol–ketone hydrogen bonds with the loss of alcohol–alcohol hydrogen bonds, with the endothermic heat of mixing indicating a net decrease in number of hydrogen bonds. Activity coefficients calculated from the vapor-liquid equilibria data of this system also indicate solution nonideality.

Experimental

Details of the apparatus and the experimental methods used in this work have been described (*2, 6*). The 2-butanol used was reagent grade, obtained from Eastman Kodak Co., acetophenone used was chromatoquality, obtained from Matheson Coleman & Bell. Reagents were purified by fractional distillation. Boiling points and refractive indices at 25°C of 2-butanol and acetophenone used were 99.5°C and 1.3946 and 202.1°C and 1.5313, respectively. Equilibrium data were obtained by use of an improved Othmer still, and refractive index measurements were used for analysis. The overall reliability of equilibrium data is estimated to be ±0.005 mole fraction.

The calorimeter consisted of a 500-cm^3 Dewar flask fitted with a Beckman and a standardized calorimetric thermometer and a stirrer. Liquids were mixed in all cases by crushing a thin-walled bulb of a capsule containing one component against the bottom of the Dewar flask which contained the other component. Heat capacity of the system was determined by passing a known current through a calibrated resistance wire which was wound about the glass stirrer. The power supply used was a Kepco unit, Model 430D, and was voltage regulated. The calorimeter was warmed prior to mixing to give a temperature change with an average temperature of 25°C.

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Results and Discussion

Experimental results are shown in Figures 1 and 2 and tabulated in Tables I and II. The activity coefficients calculated and shown in Table I indicate considerable nonideality. The latter nonideality is supported by the heat of mixing absorbed for the system at 25°C as seen in Figure 2, which exhibits a maximum of 541 cal/mol of solution at approximately 0.5 mole fraction.

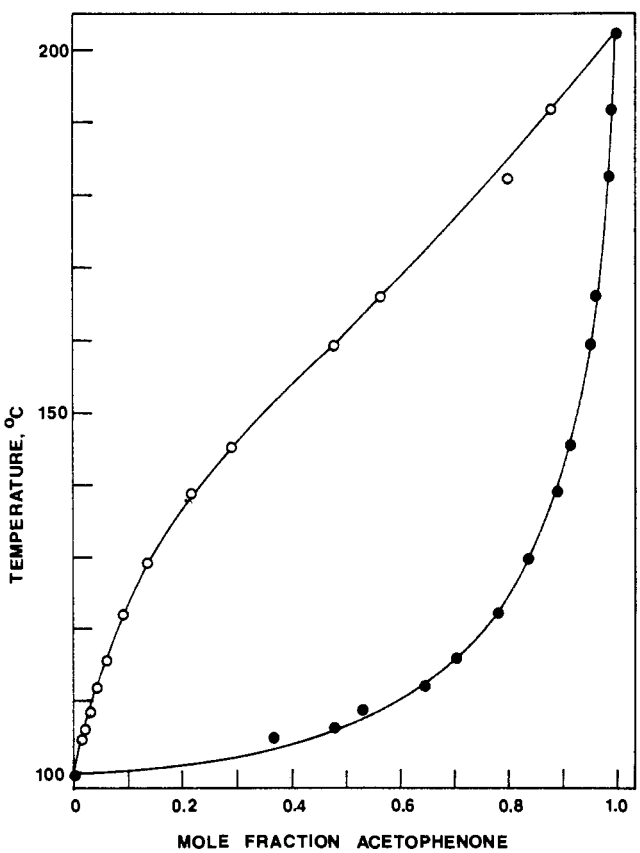

Figure 1. Boiling point–composition curve for acetophenone–2-butanol system