However, branching effects an increase in enthalpy over the value for the straight chain isomer. The trend in entropy seems to depend on whether the branching occurs on the carbon bearing the nitro group. For all the branched molecules, the carbon atom bearing the nitro group being branched results in a higher entropy than that of the straight chain isomer. In the one case where branching occurs on the carbon alpha to the nitro-bearing carbon, 1-nitro-2-methyl propane, however, the entropy of new surface formation is less than that of either 1-nitrobutane or 1-nitropropane.

Nitromethane appears to be anomalous in its surface thermodynamics. On the basis of one square cm. of surface, the entropy, enthalpy, and latent heat are much higher than for the other members of the series. If the thermodynamic properties are calculated on a molar basis by assuming spherical molecules and estimating molar surface area (square cm./mole) from

$$\Sigma = N^{1/3} V^{2/3}$$

where Σ is molar surface area, N is Avogadro's number and V is molar volume, the entropy and latent heat of nitromethane fits into the series without apparent anomaly. See the second columns under entropy and latent heat in Table II.

Parachor values are given in Table I. The increase in parachor with chain branching is the opposite of what is observed for hydrocarbons, alcohols, and halo paraffins (*3*). The increase in parachor, a molar volume under the corresponding state of unit surface tension, with chain branching in the highly polar and possibly dimerized nitroparaffins (*2*) may be evidence of a more ordered liquid than expected for the hydrocarbon and haloparaffin liquids.

ACKNOWLEDGMENT

We thank E.E. Toops, J.A. Riddick, and The Commercial Solvents Corp. for providing the nitroparaffin samples.

LITERATURE CITED

(1) Boyd, G.E., Copeland, L.E., *J. Am. Chem. Soc.* **64**, 2540 (1942).

(2) DeMaine, P.A.D., DeMaine, M.M., Goble, A.G., *Trans. Faraday Soc.* **53**, 427 (1957).

(3) Quayle, O.R., *Chem. Rev.* **53**, 439 (1953).

(4) Toops, E.E., *J. Phys. Chem.* **60**, 304 (1956).

(5) Vogel, A.I., *J. Chem. Soc.* **1948**, 1852.

(6) Weissberger, A., ed., "*Techniques of Organic Chemistry,*" Vol. 1, Pt. 1, Chap. XIV by Harkins, W.A. and Alexander, A.E. Interscience, New York, N. Y., 1959.

Southeastern Regional Meeting, ACS, Birmingham, Ala., November 1960. Work supported by the National Science Foundation Grant G-7357.

Thermodynamic Properties of Isobutylene

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EARLIER publications of the thermodynamic properties of isobutylene (2-methyl propene) (*4, 5*) have not only been quite limited in scope but also have involved approximations from using generalized correlations rather than rigorous techniques based on experimental data for this specific compound. Thermodynamic properties were calculated from selected experimental data for isobutylene from the literature. The calculations were based on rigorous thermodynamic relationships employing the Benedict-Webb-Rubin equation of state and were carried out using an electronic digital computer.

Values of pressure, volume, temperature, enthalpy, and entropy are presented for saturated liquid and vapor from 0° F. to the critical temperature, 292.5° F., and for superheated vapor for the region from 70° F. to 500° F. and from 1 atm. to 200 atm.

CHOICE OF DATUM

The datum state for both enthalpy and entropy was taken as identical with that used by the API Research Project 44 (*1*) and the National Bureau of Standards (*8*)—viz., the ideal gas state at absolute zero temperature and 1 atm., so that all values reported here are consistent with the values given in their tables for the ideal gas at 1 atm.

SUPERHEATED VAPOR

The enthalpy, H^0, and entropy, S^0, of the ideal gas at 1 atm. were first calculated for each isotherm by interpolation and extrapolation from the values listed in the tables of API Research Project 44. This was done using the heat capacity equation determined by Spencer (*9*) for the ideal gas.

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$$\text{Molal } C_p^0 = 1.693 + 42.707 \times 10^{-3} T + 12.251 \times 10^{-6} T^2 + 1.3728 \times 10^{-9} T^3 \qquad (1)$$

where $T = {}^\circ$ R.

Calculations were then made along each isotherm from 1 atm. up to vapor pressure for temperatures below the critical and up to 200 atm. for isotherms above the critical, employing the equations

$$p = \frac{RT}{V} + \frac{B_0RT - A_0 - (C_0/T^2)}{V^2} + \frac{(bRT - a)}{V^3} + \frac{a\alpha}{V^6} + \frac{c}{T^2V^3}\left[\left(1 + \frac{\gamma}{V^2}\right) e^{-\frac{\gamma}{V^2}}\right] \qquad (2)$$

$$H = H^0 + pV - RT - \frac{A_0}{V} - \frac{a}{2V^2} + \frac{a\alpha}{5V^5} - \frac{1}{T^2}\left[\frac{3C_0}{V} - \frac{3c}{\gamma} + \left(\frac{3c}{\gamma} + \frac{3c}{2V^2}\right) e^{-\frac{\gamma}{V^2}}\right] \qquad (3)$$

$$S = S^0_{1\text{ atm.}} + R\left[\ln \frac{V}{RT} - \frac{B_0}{V} - \frac{b}{2V^2}\right] - \frac{1}{T^3}\left[\frac{2C_0}{V} - \frac{2c}{\gamma} + \left(\frac{2c}{\gamma} + \frac{c}{V^2}\right) e^{-\frac{\gamma}{V^2}}\right] \qquad (4)$$

Equations 3 and 4 are obtained by applying Equation 2, which is the Benedict-Webb-Rubin equation, in the following rigorous thermodynamic relationships for the isothermal effect of pressure on enthalpy and entropy, respectively,

$$dH = d(pV) + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] dV \qquad (5)$$

$$dS = \left(\frac{\partial p}{\partial T}\right)_V dV \qquad (6)$$

and integrating over the appropriate range of pressure (and hence volume) at constant temperature.

The constants in Equation 2 were determined for isobutylene by Benedict, Webb, and Rubin (*3*) and are (when converted for use with pressure in atm., temperature in ° R., and volume in cu. ft. per lb.)

$B_0 = 0.0331250$

$A_0 = 0.729778$

$C_0 \times 10^{-6} = 0.244887$

$b = 0.00283782$

$a = 0.0393907$

$C \times 10^{-6} = 0.0207284$

$\alpha \times 10^3 = 0.0211973$

$\gamma \times 10^2 = 0.241225$

In comparing pressures calculated from Equation 2 with those experimentally determined by Beattie, Ingersoll, and Stockmayer (*2*), Benedict and coworkers found an average deviation of only 0.29% in calculated pressure over the range of densities from 1 to 7 moles per liter (1.7 times the critical density) and temperatures from 150° to 275° C., indicating that the equation effectively represents the actual behavior of isobutylene.

SATURATED VAPOR

The vapor pressure and saturated vapor volume data presented here are those reported by Hanson (*5*). These values were used in Equations 3 and 4 to determine the enthalpy and entropy of the saturated vapor.

Table I. Thermodynamic Properties of Saturated Isobutylene

(Datum: H and $S = 0$ for ideal gas at 0° R. and 1 atm.)

Temp., ° F.	Pressure, P.S.I.A.	Vol., Cu. Ft./Lb.		H, B.t.u./Lb.		S, B.t.u./Lb., ° R.	
		Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
0	9.40	0.02510	9.10	−72.1	101.6	0.8306	1.2085
10	11.88	0.02535	7.32	−67.4	104.1	0.8420	1.2071
20	14.83	0.02560	5.96	−61.7	107.7	0.8529	1.2060
30	18.33	0.02587	4.89	−56.5	110.8	0.8636	1.2052
40	22.43	0.02614	4.06	−51.3	113.9	0.8741	1.2047
50	27.22	0.02642	3.39	−45.8	117.0	0.8851	1.2045
60	32.74	0.02672	2.85	−40.3	120.1	0.8958	1.2044
70	39.05	0.02702	2.41	−34.8	123.1	0.9065	1.2046
80	46.25	0.02735	2.05	−29.1	126.2	0.9170	1.2048
90	54.42	0.02768	1.76	−23.4	129.3	0.9275	1.2053
100	63.64	0.02803	1.51	−17.9	132.2	0.9375	1.2057
110	73.99	0.02840	1.30	−12.2	135.1	0.9476	1.2062
120	85.58	0.02880	1.13	−6.2	138.1	0.9581	1.2070
130	98.48	0.02921	0.980	0.0	141.0	0.9685	1.2076
140	112.8	0.02965	0.853	+6.3	143.8	0.9789	1.2082
150	128.6	0.03011	0.744	12.8	146.4	0.9898	1.2089
160	146.0	0.03061	0.652	19.4	149.2	1.0001	1.2096
170	165.1	0.03117	0.572	25.9	151.8	1.0104	1.2103
180	186.0	0.03178	0.504	32.6	154.4	1.0208	1.2112
190	208.7	0.03245	0.444	39.4	156.9	1.0309	1.2119
200	233.4	0.03319	0.392	46.4	159.2	1.0416	1.2126
210	260.1	0.03400	0.346	53.7	161.5	1.0521	1.2131
220	289.0	0.03487	0.305	61.1	163.5	1.0629	1.2136
230	320.3	0.03587	0.268	68.7	165.1	1.0739	1.2137
240	354.1	0.03702	0.236	77.1	166.7	1.0857	1.2138
250	390.4	0.0385	0.204	85.7	167.4	1.0976	1.2127
260	429.6	0.0404	0.173	94.6	167.1	1.1097	1.2104
270	471.8	0.0430	0.145	104.6	165.9	1.1231	1.2071
280	517.4	0.0467	0.119	116.3	163.4	1.1384	1.2021
290	567.0	0.0543	0.0907	132.1	156.8	1.1591	1.1920
292.5	580.2	0.0681	0.0681	144.0	144.0	1.1747	1.1747

Table II. Thermodynamic Properties of Superheated Isobutylene

(Datum: H and $S = 0$ for ideal gas at 0° R. and 1 atm.)

P, Atm.		Temperature, ° F. 70	100	130	160	190	220	250	300	350	400	450	500
1 (19.58° F.)	*H*	126.40	138.05	150.25	162.82	175.96	189.48	203.28	227.41	252.82	279.21	306.78	335.34
	S	1.2433	1.2650	1.2862	1.3071	1.3277	1.3480	1.3480	1.4011	1.4335	1.4652	1.4962	1.5268
	V	6.6955	7.1106	7.5216	7.9292	8.3341	8.7370	9.1381	9.8037	10.466	11.127	11.785	12.443
2 (54.1° F.)	*H*	124.37	136.31	148.75	161.50	174.81	188.45	202.35	226.63	252.14	278.62	306.26	334.87
	S	1.2160	1.2382	1.2559	1.2810	1.3019	1.3224	1.3427	1.3759	1.4083	1.4401	1.4713	1.5019
	V	3.2379	3.4610	3.6787	3.8926	4.1069	4.3144	4.5203	4.8604	5.1977	5.5329	5.8664	6.1986
5 (109.6° F.)	*H*			143.86	157.30	171.11	185.18	199.43	224.17	250.05	276.83	304.69	333.48
	S			1.2214	1.2437	1.2654	1.2865	1.3073	1.3411	1.3740	1.4062	1.4376	1.4684
	V			1.3670	1.4676	1.5627	1.6550	1.7451	1.8915	2.0345	2.1768	2.3150	2.4520
10 (160.5° F.)	*H*				148.97	164.13	179.16	194.17	219.87	246.41	273.68	301.96	331.09
	S				1.2091	1.2329	1.2555	1.2774	1.3125	1.3463	1.3790	1.4109	1.4421
	V				0.6453	0.7073	0.7673	0.8165	0.9006	0.9794	1.0554	1.1294	1.2019
15 (194.8° F.)	*H*						172.06	188.19	215.14	242.53	270.43	299.16	328.64
	S						1.2332	1.2567	1.2935	1.3284	1.3619	1.3943	1.4258
	V						0.4594	0.5026	0.5673	0.6261	0.6818	0.7344	0.7854
20 (221.7° F.)	*H*							181.10	209.90	238.39	266.98	296.26	326.13
	S							1.2388	1.2781	1.3144	1.3487	1.3818	1.4137
	V							0.3404	0.3985	0.4485	0.4938	0.5367	0.5771
30 (262.7° F.)	*H*								196.86	228.97	259.52	290.08	320.88
	S								1.2502	1.2911	1.3278	1.3623	1.3953
	V								0.2225	0.2680	0.3048	0.3379	0.3683
40	*H*								171.83	217.15	251.04	283.37	315.35
	S								1.2113	1.2693	1.3100	1.3464	1.3807
	V								0.1110	0.1733	0.2089	0.2380	0.2639
50	*H*								125.07	200.67	241.22	276.11	309.49
	S								1.1477	1.2442	1.2929	1.3323	1.3680
	V								0.0450	0.1110	0.1500	0.1779	0.2012
60	*H*								120.23	179.57	229.89	268.21	303.38
	S								1.1398	1.2152	1.2757	1.3190	1.3566
	V								0.0416	0.0705	0.1104	0.1378	0.1597
80	*H*								116.08	158.82	207.80	251.81	290.82
	S								1.1314	1.1858	1.2446	1.2943	1.3361
	V								0.0387	0.0481	0.0680	0.0902	0.1094
100	*H*								114.09	152.16	194.80	238.29	279.15
	S								1.1261	1.1746	1.2257	1.2748	1.3185
	V								0.0371	0.0428	0.0530	0.0673	0.0821
150	*H*								112.11	146.37	182.72	221.12	260.31
	S								1.1171	1.1607	1.2043	1.2477	1.2896
	V								0.0348	0.0379	0.0422	0.0481	0.0552
200	*H*								111.96	144.81	179.00	214.84	251.84
	S								1.1108	1.1526	1.1937	1.2341	1.2737
	V								0.0335	0.0357	0.0386	0.0421	0.0462

SATURATED LIQUID

Both the saturated liquid volume and latent heat of vaporization data used here were also taken from Hanson's work (*5*). Enthalpies and entropies of the saturated liquid were calculated directly from the saturated vapor values by appropriate use of these latent heat data.

RESULTS

The results of the calculations described above are presented in Table I for the saturated liquid and vapor, Table II for the superheated vapor, and Figure 1 showing the pressure-enthalpy diagram for both regions. These values of thermodynamic properties are believed reliable because of the very satisfactory fit of Equation 2 to the experimental P-V-T data, the reliability of the other data used, and the rigorous calculational procedures employed.

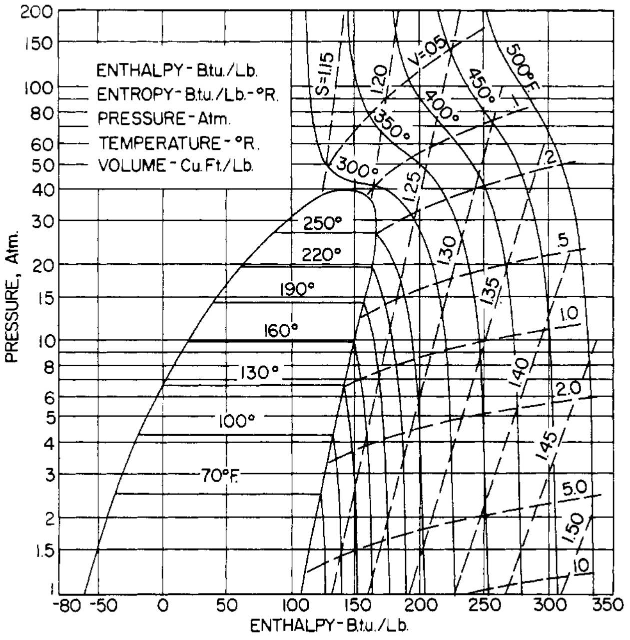

Figure 1. Pressure-enthalpy diagram for isobutylene

The internal consistency of the calculated properties was checked by testing with the following rigorous thermodynamic relationships:

$$\left(\frac{\partial \ln p}{\partial H}\right)_s = \frac{1}{pV} \qquad (7)$$

$$\left(\frac{\partial H}{\partial S}\right)_p = T \qquad (8)$$

The agreement was found to be very good even in the area of maximum density.

This project also provided occasion to evaluate the performance of the original Martin-Hou equation of state (*6*) in predicting pressures for isobutylene over a wide range of density and temperature. The constants for the equation were calculated as prescribed from the experimental critical properties (including the recommended trail adjustment of the value for critical volume) and a single experimental vapor pressure point, in this case the normal boiling point. By comparing calculated pressures with the experimental values of Beattie, Ingersoll, and Stockmayer (*2*), the equation was found to give reliable predictions with less than 1% error up to about the critical density. Above the critical density, however, along all isotherms explored, the error increased rather rapidly, several per cent being common even below the recommended limit of applicability—viz., a reduced density of 1.5. Above this density, errors soon become very large.

Both along the isometrics and the isotherms, the error oscillates from positive to negative with the amplitude of these oscillations increasing rapidly above the critical density. Martin, Kapoor, and de Nevers (*7*) have recognized these characteristics of the original equation and recommend an expansion of this equation to obtain some improvement. The new expanded equation was not evaluated for isobutylene in the present work.

The saturated vapor and liquid values are completely consistent with API 44 data for vapor pressure and heat of vaporization, since our values are based on Hanson's values (*5*) for the saturated phases, which in turn were based on API 44 data over the range for which such exists. The compressed liquid region was not included because of lack of sufficient data and because of the negligible interest in this region compared with those covered.

NOMENCLATURE

$A_0, B_0, C_0, a, b, c, \alpha, \gamma$ = constants for equation of state
C_p = isobaric specific heat, B.t.u./lb., ° R.
H = enthalpy, B.t.u./lb.
p = pressure, atm.
R = gas constant, 0.0130147 atm. cu. ft./lb., ° R.
S = entropy, B.t.u./lb., ° R.
T = temperature, ° R.
V = volume, cu. ft.

Superscript

0 = ideal gas state

LITERATURE CITED

(1) Am. Petrol. Inst. Research Project 44, Vol. 1, Tables 8t and 8u-E (Part I), Carnegie Inst. of Technol., Pittsburgh, Pa., 1952.
(2) Beattie, J.A., Ingersoll, H.G., Stockmayer, W.H., *J. Am. Chem. Soc.* **64**, 548 (1942).
(3) Benedict, M., Webb, G.B., Rubin, L.C., *Chem. Eng. Progr.* **47**, 419 (1951).
(4) Edmister, W.C., *Petroleum Refiner* **28**, No. 3, 139 (1949).
(5) Hanson, G.H., *Trans. A.I.Ch.E.* **42**, 959 (1946).
(6) Martin, J.J., Hou, Y.C., *A.I.Ch.E. Journal* **1**, 142 (1955).
(7) Martin, J.J., Kapoor, R.M., de Nevers, N., *A.I.Ch.E. Journal* **5**, 159 (1959).
(8) *Natl. Bur. Standards (U. S.) Circ.* No. **C461**, 1947.
(9) Spencer, H.M., *Ind. Eng. Chem.* **40**, 2152 (1948).

RECEIVED for review November 13, 1961. Accepted April 3, 1962.