THERMODYNAMIC PROPERTIES OF 1-BUTENE

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The thermodynamic properties of 1-butene have been calculated over a temperature range of 32° to 480°F. and at pressures up to 1,000 lb./sq. in. abs. These properties were determined from vapor-pressure, volumetric, heat-capacity, and latent-heat of vaporization data through the application of rigorous thermodynamic relationships. The calculated data have been found to be internally consistent. The enthalpy values are believed to be accurate to within ±0.5 B.t.u./lb. and the entropy values to ±0.0005 B.t.u./(lb.) (°R.).

Thermodynamic data are available for a number of paraffinic compounds but are limited to ethylene (*16*) and propene(*10*) in the olefinic series. It is the purpose of this paper to present thermodynamic data for 1-butene, one of the C_4H_8 olefins, important as a compound resulting from the dehydrogenation of *n*-butane, a step in the manufacture of 1, 3-butadiene.

AVAILABLE DATA

Volumetric data for 1-butene have been measured by three groups of investigators. The earliest work, that of Roper(*13*), covers the temperature range of—22° to +140°F. with the upper pressure limit of 16.5 lb./sq.in. abs. These data are correlated by an equation of state in the virial form

$$PV_M = RT + \frac{\beta}{V_M} \qquad (1)$$

where β is the second virial coefficient and a function of temperature only. Roper expressed this function as

$$\beta = f + \frac{g}{T} + \frac{b}{T^2} \qquad (2)$$

where *f*, *g*, and *h*, are constants. A more extensive investigation of the volumetric behavior was made by Olds, Sage, and Lacey(*12*), whose *investigation* covered the temperature range of 100° to 340°F. at pressures up to 10,000 lb./sq.in. abs. Liquid as well as vapor volumetric data are reported, including data for the liquid at the bubble point and the vapor at the dew point.

Beattie and Marple(*8, 9*) made two investigations of the behavior of 1-butene. The initial report(*8*) gives orthobaric liquid densities from 50° to 125°C. and the critical properties. The second investigation of Beattie and Marple(*9*) reports volumetric data from 150° to 250°C. and from densities of 1 to 8 moles/liter. The results, up to densities of 4 moles/liter, were fitted to the Beattie-Bridgman equation of state, and the constants are given.

Difficulties due to the polymerization of the 1-butene are reported by Olds, Sage, and Lacey(*12*) and Beattie and Marple(*9*). The former report that their sample apparently deteriorated after several hours' exposure to a temperature of 340° F., and the latter report slow polymerization at 200°C. (392°F.) and rapid deterioration at 250°C. (482°F.) The phenomenon limits somewhat the accuracy of the results at the higher temperatures.

Since there is very little overlap in the various sets of volumetric data, comparison of the results is impossible over most of the temperature and pressure range. Some comparison can be made of the data of Olds, Sage, and Lacey(*12*) with those of Beattie and Marple (*9*), but a double interpolation is necessary. This shows good agreement between the sets of data. Also, since the Beattie-Bridgman equation of state was fitted to the data of Beattie and Marple, volumetric data may be calculated at even values of temperature and pressure and compared with those of Olds, Sage and Lacey. Again this shows good agreement between the two sets of volumetric data over the limited range for which comparison is possible. Volumetric data for the saturated liquid from 30° to 77°F. have been reported (*1*).

Several studies have been made of the vapor pressure-temperature relationship of 1-butene. Lamb and Roper(*11*) report data up to 32°F.; Olds, Sage and Lacey(*12*), data from 132.7°F. to the critical point; Beattie and Marple(*8*), data from -75° to 125°C.; and the A.P.I. Research Project 44(*2*) from 30° to 55°F. Olds, Sage, and Lacey fitted an equation,

$$\log P \text{ (lb./sq. in. abs.)} = 6.18466 - \frac{2285.22}{T} - 0.000546337T$$

to their results. Beattie and Marple fitted the equation

$$\log P \text{ (atm.)} = 5.196066 - \frac{1298.1722}{T\ (^\circ\text{K.})} - 0.001248297T$$

to their data. A.P.I. 44 gives the constants for the Antoine equation for the range of data reported. As can be seen, the vapor pressure-temperature relationship has been well described. With the exception of the temperature range of 122° to 167°F. (50° to 75°C.), the data of Olds, Sage, and Lacey and of Beattie and Marple are in excellent agreement. In this temperature range, the vapor pressures determined by Olds, Sage, and Lacey are lower than those reported by Beattie and Marple by 1/2 to 1/4%. The data of Lamb and Roper and Beattie and Marple are in excellent agreement.

There is some question about the critical properties of 1-butene. Olds, Sage, and Lacey(*12*) report conditions at the critical as $t_c =$ 297°F., $P_c = 588$ lb./sq.in. abs., and $V_c = 3.85$ cu.ft./lb. mole; Beattie and Marple(*8*) report $t_c = 295.6$°F. (146.4°C.), $P = 583$ lb./sq.in. abs. (39.7 atm.), and $V_c = 3.67$ cu.ft./lb. mole (0.241 liter/mole). These latter values have apparently been accepted by the A.P.I. project(*3*) and have been used for this work.

Thermal data available include isobaric heat capacities of the liquid at the bubble point, measured by Schlinger and Sage(*15*); latent heat of vaporization information at the normal boiling point, 20.73° F., and 77°F., reported by A.P.I. 44 (*4*); and heat capacities of the ideal gas at unit fugacity, reported by A.P.I. 44(*5*). These latest listed data were used to calculate enthalpies and entropies of the ideal gas at unit fugacity up to 2,200°F. Additional constants used in the calculations were, molecular weight of 1-butene, 56.104; gas-law constant,*R*, 10.730(lb./sq.in. abs.) (cu. ft./lb. mole) (°R.); ice point, 491.69°R.

METHOD OF CALCULATIONS

The specific volume of the saturated liquid over the complete range of temperatures, from the literature sources cited, were plotted against temperature on a largescale graph and values at even 10°F. increments read; these values are reported in Table 1. The specific volumes of the saturated vapor were, in the main, obtained directly from the literature references given above. At temperatures below 100°F., however, values were obtained by use of the Clapeyron equation, since accurate latent-heat-of-vaporization and vapor-pressure data were available below this temperature. The residual volumes, α's, were determined and smoothed on a plot of α vs. temperature. The specific volume data of the saturated vapor are reported in Table 1.

The specific volume data of the superheated vapor were obtained from the references cited above. The Beattie-Bridgman equation, with constants reported by Beattie and Marple(*9*), was used to determine the data above 340°F. and pressure above 500 lb./sq.in. abs. The volumetric data were smoothed with the aid of large-scale plots of α vs. temperature with pressure parameters.

A region for which data were not available lay above the 340°F. isotherm and between the 14.7 and 500 lb./sq.in. abs. isobars. To complete the data, the Berthelot equation of state was used to calculate the volumetric data below 100 lb./sq.in. abs. It was felt this could be done without error, since the equation was tested at lower temperatures than 340°F. and below 100 lb./sq.in. abs. pressure, and excellent agreement with the experimental data was obtained. A plot of α vs. pressure with temperature parameters was then drawn. The isotherms above 340°F. were completed without difficulty, for the residuals changed very little up to 500 lb./sq. in. abs. at the high temperature involved. Also, the interpolation was facilitated by use of the completed isotherm at 340°F. as a guide.

Fugacity. The fugacity of the saturated and superheated vapor was determined from the graphical integration of a plot of α at constant temperature vs. pressure or mathematically,

$$\ln \frac{f}{P} = -\frac{1}{RT} \int_0^P \alpha \, dP \tag{3}$$

The results of this operation are reported in Tables 1 and 2. The fugacity data up to temperatures of 340°F. have been reported by Sage and Lacey(*14*); their values agree very well with those reported in this work, as may be expected, since the same set of volumetric data was used in both cases.

Selection of the Datum Plane. The enthalpy and entropy of the saturated liquid at 32°F. were arbitrarily set equal to zero. This required that the enthalpy and entropy data for 1-butene in the ideal gas state, unit fugacity, reported in A.P.I. 44(*6, 7*) be changed to the datum plane used in this work.

Latent Heat of Vaporization. With the exception of the two values given in A.P.I. 44(*4*), all the latent-heat-of-vaporization data were calculated by the Calpeyron equation,

$$\frac{dP}{dT} = \frac{\Delta H_V}{T \Delta V} \tag{4}$$

Vapor-pressure and volumetric data were obtained from literature sources cited above.

Saturated Liquid and Vapor Phases. The heat capacity data of liquid 1-butene at its bubble point reported by Schlinger and Sage(*15*) enabled the evaluation of the enthalpy and entropy of the saturated liquid phase up to 220°F. Above this temperature these properties were determined by subtracting the enthalpy or entropy of vaporization from their respective values in the saturated vapor phase; this was necessary since there were no heat-capacity data above 220°F. The thermodynamic properties of the saturated vapor phase below 220°F. were obtained by adding the enthalpy or entropy of vaporization to their respective values in the saturated liquid phase. Above 220°F. the isobars on enthalpy-temperature and temperature-entropy plots were extrapo-

TABLE 1.—THERMODYNAMIC PROPERTIES OF SATURATED 1-BUTENE

			Volume		Enthalpy			Entropy		
Temperature, °F.	Pressure lb./sq. in., abs.	Fugacity/pressure, f/P	Liquid, cu. ft./lb.	Vapor, cu. ft./lb.	Liquid, B.t.u./lb.	Vaporization, B.t.u./lb.	Vapor, B.t.u./lb.	Liquid, B.t.u. (lb.) (°R.)	Vaporization, B.t.u./(lb.) (°R.)	Vapor, B.t.u./(lb.) (°R.)
32	18.64	0.961	0.02588	4.79	0.0	166.1	166.1	0.0000	0.3378	0.3378
40	21.91	0.954	0.02610	4.19	3.4	164.9	168.3	0.0068	0.3300	0.3368
50	26.60	0.944	0.02638	3.52	8.4	163.0	171.4	0.0167	0.3198	0.3365
60	32.0	0.935	0.02667	2.89	13.6	160.8	174.4	0.0268	0.3094	0.3365
70	38.2	0.926	0.02698	2.41	19.2	158.3	177.5	0.0375	0.2988	0.3365
80	45.2	0.917	0.02730	2.25	25.4	155.1	180.5	0.0491	0.2874	0.3365
90	53.1	0.909	0.02770	1.76	31.2	152.5	183.7	0.0597	0.2774	0.3371
100	62.5	0.900	0.02811	1.52	37.0	149.7	186.7	0.0702	0.2675	0.3377
110	72.1	0.890	0.02852	1.33	42.9	146.7	189.6	0.0806	0.2575	0.3381
120	83.5	0.881	0.02898	1.16	48.7	143.8	192.5	0.0907	0.2481	0.3388
130	96.3	0.872	0.02943	1.01	54.4	140.8	195.2	0.1007	0.2388	0.3395
140	110.2	0.862	0.02992	0.875	60.5	138.0	198.5	0.1107	0.2301	0.3408
150	125.5	0.852	0.03042	0.768	66.6	134.9	201.5	0.1207	0.2213	0.3420
160	142.4	0.843	0.03091	0.676	72.7	131.7	204.4	0.1307	0.2125	0.3432
170	161.3	0.831	0.03145	0.595	79.0	128.5	207.5	0.1409	0.2041	0.3450
180	182.0	0.820	0.03202	0.524	85.5	124.9	210.4	0.1511	0.1952	0.3463
190	204.7	0.807	0.03261	0.463	92.2	120.9	213.1	0.1615	0.1861	0.3476
200	228.6	0.795	0.03328	0.409	99.1	116.8	215.9	0.1721	0.1771	0.3492
210	254.6	0.783	0.03399	0.364	106.4	112.2	218.6	.01831	0.1675	0.3506
220	282.8	0.770	0.03477	0.324	114.1	107.1	221.2	0.1944	0.1576	0.3520
230	313.4	0.758	0.03567	0.286	122.0	101.4	223.4	0.2059	0.1470	0.3529
240	346.4	0.744	0.03671	0.251	130.0	95.2	225.2	0.2174	0.1361	0.3535
250	382.5	0.731	0.03800	0.219	138.4	88.3	226.7	0.2293	0.1244	0.3537
260	421.3	0.717	0.03962	0.189	147.1	79.4	226.5	0.2415	0.1103	0.3518
270	462.2	0.703	0.04180	0.161	158.5	67.9	226.4	0.2572	0.0931	0.3503
280	505.0	0.688	0.04488	0.134	173.4	52.0	225.4	0.2748	0.0703	0.3451

Table 2.—Thermodynamic Properties of Superheated 1-Butene

Temperature °F.	Volume cu. ft./lb.	Enthalpy B.t.u./lb.	Entropy B.t.u./(lb.) (°R.)	Fugacity/pressure f/P	Volume cu. ft./lb.	Enthalpy B.t.u./lb.	Entropy B.t.u./(lb.) (°R.)	Fugacity/pressure f/P
		14.696 lb./sq. in. abs. (20.73°)*				25 lb./sq. in. abs. (46.7°)*		
(at. satn.)	......	......	......	......	3.657	170.5	0.3366	0.948
32	6.156	166.7	0.3469	0.964				
40	6.272	169.4	0.3526	0.966				
60	6.557	176.5	0.3665	0.970	3.772	175.3	0.3484	0.952
80	6.830	183.8	0.3803	0.974	3.940	182.6	0.3622	0.956
100	7.110	191.3	0.3940	0.977	4.103	190.2	0.3758	0.960
120	7.384	199.4	0.4077	0.979	4.275	198.4	0.3894	0.964
140	7.657	207.6	0.4213	0.982	4.441	206.7	0.4029	0.969
160	7.928	215.9	0.4347	0.983	4.605	215.0	0.4163	0.971
180	8.199	224.2	0.4480	0.985	4.767	223.4	0.4296	0.975
200	8.468	232.2	0.4613	0.986	4.925	231.5	0.4428	0.977
220	8.737	241.2	0.4745	0.988	5.086	240.5	0.4560	0.980
240	9.006	250.1	0.4876	0.989	5.246	249.4	0.4691	0.982
260	9.274	259.0	0.5005	0.990	5.407	258.4	0.4820	0.983
280	9.541	268.2	0.5134	0.991	5.565	267.6	0.4948	0.984
300	9.807	278.3	0.5263	0.991	5.726	277.7	0.5077	0.985
320	10.08	288.4	0.5390	0.992	5.882	287.9	0.5204	0.987
340	10.34	298.6	0.5517	0.993	6.045	298.1	0.5331	0.988
360	10.59	308.9	0.5643	0.993	6.198	308.4	0.5457	0.989
380	10.86	319.5	0.5769	0.994	6.355	319.0	0.5582	0.990
400	11.12	329.8	0.5893	0.994	6.513	329.6	0.5706	0.991
420	11.38	340.6	0.6017	0.995	6.668	340.2	0.5831	0.992
440	11.65	351.6	0.6141	0.995	6.825	351.3	0.5954	0.992
460	11.91	362.8	0.6263	0.996	6.980	362.4	0.6076	0.993
480	12.17	373.9	0.6384	0.996	7.135	373.5	0.6197	0.993
		50 lb./sq. in. abs. (86.2°)*				75 lb./sq. in. abs. (112.7°)*		
(at satn.)	1.891	182.5	0.3367	0.912	1.280	190.4	0.3383	0.888
100	1.957	187.7	0.3481	0.921				
120	2.049	196.0	0.3620	0.929	1.305	193.0	0.3444	0.894
140	2.140	204.5	0.3758	0.938	1.371	201.7	0.3586	0.907
160	2.229	213.0	0.3894	0.944	1.436	210.5	0.3725	0.916
180	2.308	221.4	0.4029	0.950	1.499	219.1	0.3863	0.926
200	2.402	229.7	0.4163	0.955	1.560	227.5	0.3999	0.932
220	2.488	238.8	0.4296	0.959	1.620	236.2	0.4134	0.939
240	2.571	247.8	0.4428	0.963	1.679	245.9	0.4267	0.944
260	2.653	256.9	0.4559	0.966	1.737	255.1	0.4400	0.949
280	2.737	266.1	0.4689	0.969	1.795	264.2	0.4521	0.953
300	2.819	276.4	0.4818	0.971	1.860	274.8	0.4662	0.956
320	2.901	286.6	0.4947	0.973	1.909	285.1	0.4791	0.960
340	2.981	296.9	0.5074	0.976	1.964	295.5	0.4920	0.964
360	3.063	307.3	0.5201	0.978	2.019	306.0	0.5047	0.966
380	3.143	317.9	0.5327	0.980	2.074	316.7	0.5175	0.969
400	3.225	328.5	0.5452	0.981	2.129	327.3	0.5300	0.972
420	3.306	339.1	0.5577	0.983	2.183	338.1	0.5426	0.974
440	3.386	350.3	0.5700	0.984	2.236	349.3	0.5550	0.976
460	3.464	361.5	0.5823	0.986	2.292	360.5	0.5673	0.978
480	3.544	372.7	0.5945	0.986	2.347	371.9	0.5795	0.979
		100 lb./sq. in. abs. (132.7°)*				150 lb./sq. in. abs. (164.0°)*		
(at satn.)	0.964	196.3	0.3399	0.869	0.642	205.6	0.3438	0.839
140	0.984	198.8	0.3448	0.876				
160	1.038	207.9	0.3592	0.888				
180	1.089	216.7	0.3733	0.901	0.672	212.7	0.3545	0.851
200	1.138	225.3	0.3872	0.911	0.713	220.5	0.3671	0.867
220	1.187	234.2	0.4010	0.919	0.749	229.9	0.3815	0.879
240	1.233	244.0	0.4145	0.926	0.782	240.1	0.3956	0.889
260	1.278	253.3	0.4280	0.932	0.818	249.7	0.4096	0.899
280	1.324	362.5	0.4403	0.938	0.866	259.4	0.4229	0.908
300	1.362	273.2	0.4545	0.943	0.881	270.0	0.4369	0.915
320	1.411	283.6	0.4675	0.947	0.912	280.6	0.4502	0.922
340	1.455	294.1	0.4805	0.953	0.944	291.3	0.4635	0.930
360	1.496	304.7	0.4933	0.956	0.972	302.0	0.4765	0.934
380	1.537	315.5	0.5063	0.959	1.002	313.0	0.4898	0.939
400	1.580	326.1	0.5188	0.962	1.031	323.8	0.5025	0.943
420	1.621	337.0	0.5315	0.965	1.059	334.8	0.5153	0.948
440	1.663	348.3	0.5440	0.967	1.089	346.2	0.5280	0.952
460	1.705	359.6	0.5563	0.971	1.118	357.7	0.5404	0.956
480	1.747	371.0	0.5686	0.973	1.129	369.2	0.5529	0.959
		200 lb./sq. in. abs. (188.0°)*				300 lb./sq. in. abs. (225.8°)*		
(at satn.)	0.4738	212.6	0.3476	0.812	0.2997	222.6	0.3522	0.764
200	0.4965	216.9	0.3530	0.823				
220	0.5278	225.5	0.3654	0.840				
240	0.5556	236.1	0.3803	0.853	0.3206	228.0	0.3591	0.781
260	0.5836	245.9	0.3948	0.867	0.3454	237.6	0.3719	0.801
280	0.6112	255.8	0.4086	0.878	0.3683	248.5	0.3868	0.819
300	0.638	266.7	0.4230	0.888	0.3903	259.4	0.4009	0.834
320	0.664	277.5	0.4368	0.897	0.4121	270.8	0.4158	0.849
340	0.690	288.4	0.4504	0.908	0.4309	282.2	0.4302	0.864

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*Saturation temperature.

TABLE 2.—THERMODYNAMIC PROPERTIES OF SUPERHEATED 1-BUTENE (*continued*)

Temperature, °F.	Volume, cu. ft./lb.	Enthalpy, B.t.u./lb.	Entropy, B.t.u./(lb.) (°R.)	Fugacity, Pressure f/P	Volume, cu. ft./lb.	Enthalpy, B.t.u./lb.	Entropy, B.t.u./(lb.) (°R.)	Fugacity, pressure f/P
	200 lb./sq. in. abs. (188.0°)*				300 lb./sq. in. abs. (225.8°)*			
360	0.712	299.3	0.4637	0.914	0.449	293.6	0.4441	0.872
380	0.733	310.4	0.4772	0.920	0.466	305.1	0.4582	0.881
400	0.758	321.4	0.4901	0.925	0.483	316.5	0.4716	0.889
420	0.781	332.6	0.5031	0.931	0.500	328.0	0.4850	0.897
440	0.803	344.1	0.5160	0.936	0.516	339.9	0.4983	0.904
460	0.827	355.7	0.5285	0.942	0.532	351.7	0.5111	0.912
480	0.848	367.4	0.5412	0.946	0.549	363.8	0.5241	0.920
	400 lb./sq. in. abs. (254.8°)*				500 lb./sq. in. abs. (278.6°)*			
(at satn.)	0.2042	226.5	0.3524	0.726	0.1367	226.0	0.3460	0.691
260	0.2133	228.9	3.3551	0.734				
280	0.2388	238.8	0.3674	0.759	0.1408	226.4	0.3471	0.694
300	0.2596	249.9	0.3816	0.779	0.1755	238.5	0.3630	0.722
320	0.2791	262.6	0.3971	0.800	0.1982	252.1	0.3799	0.749
340	0.2974	275.0	0.4127	0.821	0.2154	266.1	0.3968	0.776
360	0.315	287.2	0.4278	0.832	0.2317	279.7	0.4125	0.791
380	0.329	299.4	0.4427	0.844	0.2461	293.0	0.4287	0.807
400	0.344	311.2	0.4567	0.853	0.2595	305.2	0.4434	0.820
420	0.357	323.0	0.4705	0.864	0.2726	317.3	0.4576	0.835
440	0.371	335.3	0.4842	0.874	0.2848	330.1	0.4715	0.847
460	0.385	347.5	0.4972	0.885	0.2967	342.7	0.4848	0.859
480	0.399	359.9	0.5105	0.895	0.3090	355.4	0.4985	0.871
	600 lb./sq. in. abs.				700 lb./sq. in. abs.			
320	0.1354	240.2	0.3611	0.698	0.0857	222.4	0.3335	0.642
340	0.1571	256.5	0.3811	0.731	0.1098	242.0	0.3581	0.683
360	0.175	270.9	0.3972	0.749	0.1311	260.5	0.3811	0.707
380	0.189	285.6	0.4152	0.769	0.1475	277.1	0.4015	0.732
400	0.202	298.5	0.4305	0.786	0.1617	291.1	0.4177	0.752
420	0.214	311.0	0.4448	0.803	0.1724	303.6	0.4322	0.772
440	0.225	324.2	0.4600	0.817	0.1827	318.3	0.4483	0.789
460	0.236	337.5	0.4737	0.832	0.1931	331.9	0.4635	0.805
480	0.246	350.5	0.4877	0.846	0.2031	345.3	0.4779	0.821
	800 lb./sq. in. abs.				900 lb./sq. in. abs.			
340	0.0752	226.8	0.3373	0.634	0.0569	211.7	0.3182	0.588
360	0.0969	248.3	0.3638	0.665	0.0748	235.8	0.3474	0.624
380	0.1144	267.1	0.3871	0.695	0.0900	256.9	0.3728	0.658
400	0.1286	283.0	0.4050	0.718	0.1042	274.6	0.3928	0.682
420	0.1409	297.2	0.4222	0.741	0.1167	290.0	0.4115	0.706
440	0.1516	312.1	0.4392	0.760	0.1271	305.6	0.4295	0.730
460	0.1617	326.1	0.4540	0.779	0.1370	320.0	0.4448	0.753
480	0.1711	339.8	0.4689	0.797	0.1459	334.0	0.4603	0.773
	1,000 lb./sq. in. abs.							
340	0.0500	199.5	0.3033	0.548				
360	0.0625	225.4	0.3340	0.587				
380	0.0748	247.9	0.3605	0.623				
400	0.0867	266.7	0.3828	0.650				
420	0.0981	282.8	0.4011	0.678				
440	0.1085	298.9	0.4198	0.704				
460	0.1176	313.7	0.4355	0.728				
480	0.1264	328.0	0.4515	0.750				

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* Saturation temperature.

lated to the vaporization temperature. The enthalpy and entropy were then obtained directly from the plots. In all cases the extrapolations were over short ranges of temperature, and the final results were smoothed on an enthalpy-entropy plot. Table 1 lists the properties of the saturated liquid and vapor phases.

Entropy and Enthalpy. The change of entropy with pressure under isothermal conditions was determined through the use of the equation

$$M\,(S_P - S^o)_T = -\int_{P^o}^{P} \frac{R}{P}\,dP + \int_{P^o}^{P} \left(-\frac{\partial \alpha}{\partial T}\right)_P dP \qquad (5)$$

the second term in the right-hand member of the equation being determined by graphical integration. The changes calculated from this equation were then added to the entropy of the ideal gas at the same temperature. The change in enthalpy of the superheated vapor with pressure under isothermal conditions was determined by use of the equation

$$M\,(H_P - H^o)_T = -\int_{P^o}^{P} \left[\alpha - T\left(\frac{\partial \alpha}{\partial T}\right)_P\right] dP \qquad (6)$$

In this case the entire right-hand member of the equation was evaluated by graphical integration. The changes in enthalpy thus calculated were then added to the enthalpy of the ideal gas at the same temperature, and the results were plotted on a large-scale graph as

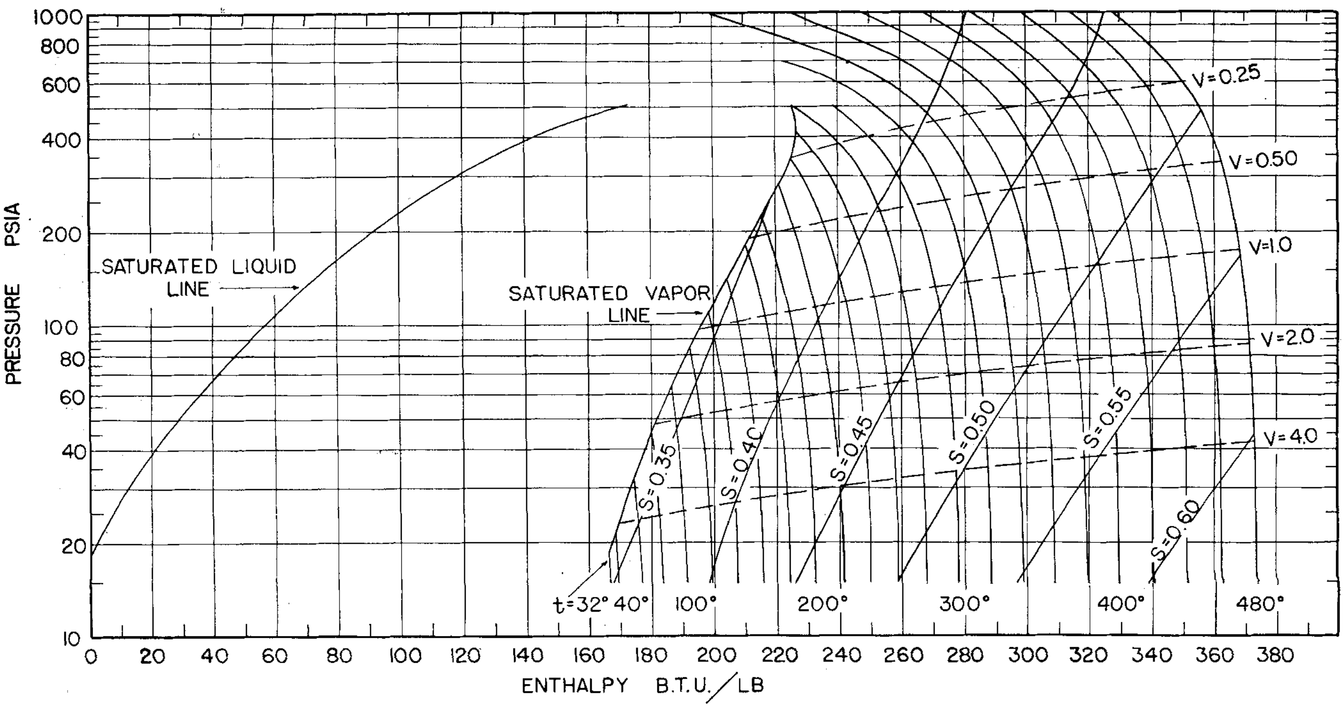

FIG. 1. PRESSURE-ENTHALPY DIAGRAM FOR 1-BUTENE.

temperature-entropy, enthalpy-temperature, and enthalpy-entropy and smoothed. The final results are presented in tabular form in Table 2. The complete results, for both saturated and superheated conditions, are presented in graphical form in Figure 1.

INTERNAL CONSISTENCY OF THE RESULTS

One method to check the internal consistency of thermodynamic data of this type is through the use of the equation:

$$dH = TdS + VdP \qquad (7)$$

which is a statement of the first two laws of thermodynamics. Setting the value of the entropy at a constant reduces the equation to

$$dH = VdP \qquad (8)$$

Multiplying the right-hand member by P/P and integrating results in the equation

$$H_2 - H_1 = PV\int_{P_1}^{P_2} d\ln P \qquad (9)$$

The right-hand member can then be evaluated by graphical integration and compared with enthalpy differences obtained from the calculated data. Such consistency checks were made on the thermodynamic data presented in this paper, and good agreement was obtained in all instances.

Since there are not enough thermal data to check the results by an independent method, the accuracy of the data presented here cannot be stated with certainty. However, it is believed that the enthalpy values are accurate within ±0.5 B.t.u./lb. and the entropy values, within ±0.0005 B.t.u./(lb.)(°R).

CONCLUSIONS

The thermodynamic properties of 1-butene, using fundamental relationships, have been calculated over the temperature range 32° to 480°F. and up to pressures of 1,000 lb./sq.in. abs. The data have been found to be internally consistent and are presented in graphical and tabular form.

NOTATION

H = enthalpy, B.t.u./lb.
M = molecular weight
P = pressure, lb./sq.in. abs., unless otherwise specified
R = gas-law constant
S = entropy, B.t.u./lb.
T = absolute temperature, °R. unless specified as °K.
V = specific volume, cu.ft./lb.
f = fugacity, same units as pressure
t = temperature, °F.
α = residual volume, cu.ft./lb. mole, $\alpha = \frac{RT}{P} - V_M$
β = second virial coefficient, defined in Equation (1)

Subscripts

c = critical property
M = molal quantity
V = vaporization

Superscripts

o = property in ideal gas state at unit fugacity

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