Thermodynamic Properties of Tertiary Butyl Alcohol

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By use of C_p values from the literature and experimentally determined vapor-pressure–temperature and pressure-volume-temperature relationships, a thermodynamic network has been established for tertiary butyl alcohol in the range of 78° to 500°F. and 14.7 to 700 lb./sq. in. abs. The results include tabulated values of p, v, T, H, S, f, and Z, as well as the vapor-pressure–temperature curve, the critical properties, and constants for the Beattie-Bridgeman equation.

The original pressure data were accurate to within 0.14% in the high range and to within 4% in the low range. The limits on the experimental volume data were 0.07% for large vapor volumes and 2% for liquid volumes. The temperature was determined to within 0.1°F., or less than 0.02% of the absolute temperature.

Experimentally determined vapor pressures were found to be lower than those reported in the literature in the range above 1 atm. Values previously reported were obtained by extrapolation of a vapor-pressure–temperature relation developed for use at subatmospheric pressures. For pressures below 1 atm. the experimental values agreed with the reported values.

The equipment used was modeled after that of Kay (*5*, *6*, *7*). The fluid was confined over mercury in a calibrated thick-walled glass capillary tube. Temperature control was provided by refluxing under controlled pressure one of a series of pure organic liquids around the tube.

Temperatures were measured by means of a copper-constantan thermocouple and a precision potentiometer calibrated against a National Bureau of Standards thermometer. A Heise precision Bourdon-tube pressure gauge, calibrated by the manufacturer, was used for pressure measurements. Volumes were determined by the use of a cathetometer. The critical temperature was determined by the disappearance of the meniscus and of critical opalescence.

The operation of the apparatus used for obtaining the original data was checked by determining the pressure-volume-temperature and vapor-pressure–temperature relationship for water at several temperatures. Tertiary butyl alcohol was chosen for this study because it is used widely enough in industry, as both a solvent and an intermediate, to make a study of its properties worth while. In addition, from the standpoint of the initial testing of a new experimental setup, it was desirable to have a compound with a melting point above room temperature at normal atmospheric pressure, in order to establish this as the zero point for both enthalpy and entropy. Also, it was possible to reach the critical point in the glass apparatus and desirable to be able to observe critical phenomena visually.

The sample of tertiary butyl alcohol was over 99% pure as received. This was distilled and a center cut taken which was then dried over anhydrous calcium sulfate. The dried material was fractionally crystallized. The freezing point of the final sample indicated greater than 99.8% purity and the refractive index indicated 100% purity.

CALCULATION METHODS

By the methods described in the original article (*1*) the constants for the Beattie-Bridgeman equation were deter-

Equations used to calculate enthalpy, entropy, and fugacity, equation-of-state calculations, and collected data on properties of tertiary butyl alcohol are on file as document 5058 with the American Documentation Institute, Auxiliary Publications Project, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm. The collected data from literature sources include vapor pressures, heat of fusion, heat of vaporization, heat capacities, densities, coefficients of expansion, viscosity, surface tension, refractive index, parachor, standard enthalpy and free energy of formation, and some properties of mixtures of tertiary butyl alcohol and water.

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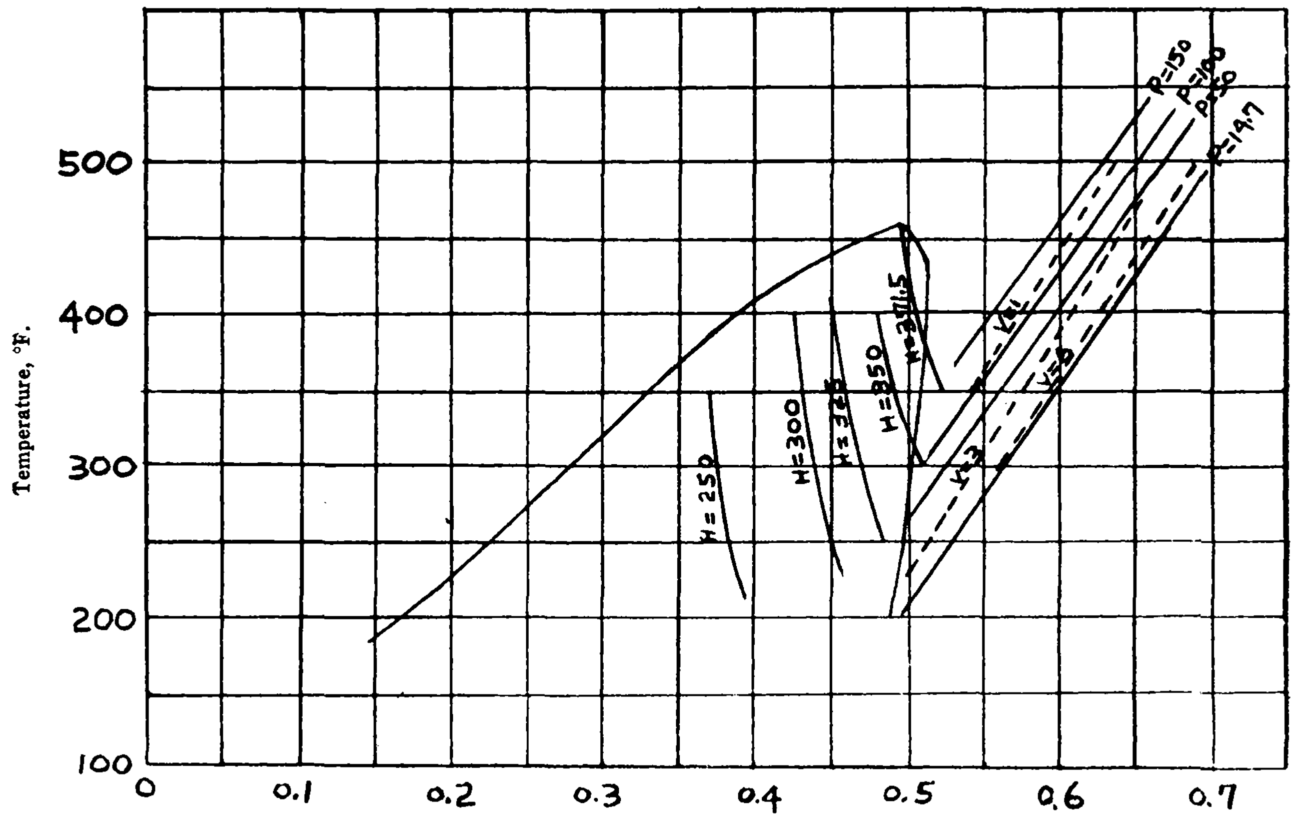

Entropy, B.t.u./lb.

Temperature-entropy diagram.

TABLE 1. THERMODYNAMIC PROPERTIES OF SATURATED TERTIARY BUTYL ALCOHOL

Temperature, °F.	Pressure, lb./sq. in abs.	Volume, cu. ft./lb. Liquid	Vapor	Enthalpy,* B.t.u./lb. Liquid	Vapor	Entropy,* B.t.u./(lb.)(°R.) Liquid	Vapor
182	14.7	0.021	6.12	85.5	304.5	0.147	0.488
200	21.6	0.022	4.22	99.4	311.4	0.168	0.489
225	33.0	0.023	2.79	119.0	322.0	0.197	0.493
250	50.7	0.024	1.762	139.7	329.7	0.226	0.494
275	74.1	0.025	1.223	158.5	339.5	0.253	0.499
300	106.5	0.026	0.845	178.5	348.5	0.278	0.502
325	148.9	0.027	0.584	200.0	356.0	0.307	0.506
350	202.3	0.028	0.413	217.3	361.3	0.331	0.509
375	270.2	0.031	0.314	240.4	371.9	0.357	0.514
400	354.4	0.035	0.223	268.3	378.5	0.387	0.515
425	452.3	0.039	0.151	297.3	377.9	0.422	0.513
450	577.0	0.047	0.087	353.8	375.9	0.476	0.500
456.3	613.8	0.062	0.062	371.5	371.5	0.496	0.496

*Based on $H = 0$ and $S = 0$ for liquid at 1-atm. pressure and 78°F.

TABLE 2. THERMODYNAMIC PROPERTIES OF SUPERHEATED TERTIARY BUTYL ALCOHOL

Temperature, °F.	Pressure, lb./sq. in. abs.	Volume, cu. ft./lb.	Compressibility factor	Enthalpy,* B.t.u./lb.	Entropy,* B.t.u./(lb.)(°R.)	Fugacity, lb./sq. in abs.
200	14.7	6.25	—	312.2	0.499	
225	14.7	6.50	—	324.4	0.517	
	20.0	4.75	0.955	324.0	0.508	19.0
	30.0	3.06	0.929	322.4	0.496	28.0
250	14.7	6.75	—	335.0	0.533	
	20.0	4.95	0.959	334.6	0.524	19.0
	30.0	3.21	0.938	333.3	0.512	28.0
	40.0	2.35	0.916	332.0	0.503	36.2
275	14.7	7.0	—	347.0	0.550	
	20.0	5.13	0.964	346.8	0.542	19.0
	30.0	3.37	0.946	345.7	0.530	28.0
	40.0	2.44	0.925	344.3	0.521	36.2
	50.0	1.93	0.904	343.0	0.514	45.0
300	14.7	7.25	—	359.3	0.566	
	20.0	5.33	0.966	359.0	0.558	19.0
	30.0	3.47	0.950	358.1	0.546	28.0
	40.0	2.57	0.934	357.0	0.536	36.2
	50.0	2.01	0.917	355.7	0.529	45.0
	75.0	1.28	0.866	352.6	0.516	66.0
325	14.7	7.50	—	372.0	0.583	
	20.0	5.53	0.971	371.5	0.575	20.0
	30.0	3.60	0.956	370.5	0.563	29.0
	40.0	2.67	0.940	370.0	0.554	38.0
	50.0	2.10	0.924	369.5	0.547	47.0
	75.0	1.34	0.884	365.3	0.533	67.5
	100.0	0.96	0.844	362.4	0.523	86.5
350	14.7	7.75	—	384.9	0.599	
	20.0	5.75	0.973	384.3	0.590	20.0
	30.0	3.75	0.961	383.7	0.579	29.0
	40.0	2.78	0.948	382.9	0.570	38.0
	50.0	2.21	0.933	381.9	0.563	47.0
	75.0	1.39	0.893	379.0	0.550	67.5
	100.0	1.01	0.859	376.3	0.540	87.2
	150.0	0.60	0.777	370.0	0.525	122.0
375	14.7	8.0	—	398.2	0.615	
	20.0	5.90	0.976	398.0	0.607	20.0
	30.0	3.87	0.964	397.0	0.595	29.0
	40.0	2.88	0.952	396.2	0.586	38.0
	50.0	2.27	0.939	395.5	0.579	47.0
	75.0	1.46	0.906	392.7	0.566	68.0
	100.0	1.05	0.874	390.2	0.557	88.1
	150.0	0.65	0.807	384.7	0.542	125.0
	200.0	0.46	0.750	378.5	0.528	156.0

mined, use being made of the experimental pressure-volume-temperature data. The constants were adjusted until the pressure calculated by the equation agreed with the measured pressure to within experimental accuracy.

The thermodynamic properties were calculated from these data, the Beattie-Bridgeman equation, and heat-capacity data available in the literature (*2, 10, 11*), by use of standard thermodynamic equations (*3*).

The critical pressure was obtained by extrapolation of the vapor-pressure equation to the critical temperature. The critical volume was determined by the method of rectilinear diameters. These methods are all described in detail by Kobe and Lynn (*8*).

RESULTS AND DISCUSSION

Tables 1 and 2 summarize the properties of saturated and superheated tertiary butyl alcohol. The enthalpy and entropy of tertiary butyl alcohol at its freezing point (78°F.) and atmospheric pressure were taken as zero. The vapor-pressure equation determined from experimental data was

$$\ln p = 39.7545 - 10456/T - 3.215 \ln T$$

The constants for the Beattie-Bridgeman equation appear in Table 3.

The critical temperature, 456.3°F., agrees well with the reported value of 455°F. (*9*). The critical volume was found to be 0.062 cu. ft./lb. The experimentally determined vapor pressures in the range above 1 atm. were found to be lower than those reported in the literature (*4*). No record of experimental work in this range could be found, and it is believed that the reported values were obtained by extrapolation of the vapor-pressure–temperature relationship developed for use at subatmospheric pressure. The same applies to the critical pressure, no record of experimental determination having been found. Thus the critical pressure, as determined in this study, is 613.8 lb./sq. in., the literature value being 720 lb./sq. in.

The figure shows a temperature-entropy diagram for this system which differs from that usually illustrated in thermodynamic tests in that the saturated-vapor line curves back on itself. However, this behavior has been reported for other compounds, particularly those in the butane family.

The original pressure data were accurate to within 0.14% in the high range and to within 4% in the low range. The limits on the experimental volume data were 0.7% for large vapor volumes and 2% for liquid volumes. The temperature was determined to within 0.1°F., which amounted to less than 0.02% of the absolute temperature. The results of

Table 2—(Continued).

Thermodynamic Properties of Superheated Tertiary Butyl Alcohol

Temperature, °F.	Pressure, lb./sq. in abs.	Volume, cu. ft./lb.	Compressibility factor	Enthalpy,* B.t.u./lb.	Entropy,* B.t.u./(lb.)(°R.)	Fugacity, lb./sq. in. abs.
400	14.7	8.25	—	412.9	0.631	
	20.0	6.11	0.978	412.6	0.623	20.0
	30.0	4.00	0.966	411.9	0.611	29.0
	40.0	2.97	0.956	411.0	0.603	38.0
	50.0	2.38	0.944	410.1	0.596	47.5
	75.0	1.52	0.915	408.1	0.583	69.2
	100.0	1.10	0.886	405.2	0.574	89.5
	150.0	0.69	0.829	400.8	0.558	127.2
	200.0	0.48	0.778	395.5	0.547	160.5
425	14.7	8.50	—	426.0	0.647	
	20.0	6.28	0.979	425.8	0.638	20.0
	30.0	4.19	0.970	425.0	0.627	29.0
	40.0	3.10	0.961	424.0	0.619	38.0
	50.0	2.45	0.951	423.2	0.612	47.5
	75.0	1.58	0.923	420.8	0.600	69.8
	100.0	1.15	0.897	419.0	0.590	90.0
	150.0	0.72	0.844	415.0	0.576	129.0
	200.0	0.52	0.800	410.1	0.564	163.5
	250.0	0.40	0.766	406.0	0.554	195.0
	300.0	0.32	0.739	402.0	0.546	225.0
	350.0	0.26	0.717	397.6	0.538	252.0
450	14.7	8.75	—	440.3	0.663	
	20.0	6.48	0.982	440.2	0.655	20.0
	30.0	4.26	0.974	439.8	0.643	29.0
	40.0	3.19	0.965	438.8	0.634	38.0
	50.0	2.51	0.955	438.0	0.628	47.5
	75.0	1.64	0.929	436.0	0.616	69.8
	100.0	1.20	0.904	434.0	0.606	91.0
	150.0	0.75	0.862	429.8	0.592	130.0
	200.0	0.55	0.821	425.6	0.582	166.0
	250.0	0.42	0.788	421.6	0.572	199.8
	300.0	0.34	0.758	417.5	0.563	232.0
	350.0	0.28	0.731	413.5	0.556	265.0
475	14.7	9.0	—	455.0	0.679	
	20.0	6.66	0.984	455.0	0.671	20.0
	30.0	4.40	0.976	454.2	0.659	29.0
	40.0	3.28	0.967	453.6	0.650	38.0
	50.0	2.59	0.959	453.0	0.644	47.5
	75.0	1.70	0.936	451.3	0.632	69.8
	100.0	1.23	0.913	449.2	0.623	91.5
	150.0	0.79	0.870	445.1	0.609	132.5
	200.0	0.58	0.839	441.5	0.597	169.5
	250.0	0.44	0.808	437.8	0.588	203.5
	300.0	0.36	0.782	434.0	0.582	237.0
	350.0	0.30	0.761	429.6	0.576	271.0
	400.0	0.25	0.739	427.0	0.569	301.0
500	14.7	9.25	—	470.1	0.695	
	20.0	6.95	0.987	470.0	0.687	20.0
	30.0	4.53	0.979	469.3	0.675	29.0
	40.0	3.37	0.971	468.9	0.667	38.0
	50.0	2.68	0.963	468.0	0.661	47.5
	75.0	1.76	0.944	466.3	0.648	70.5
	100.0	1.28	0.925	464.0	0.639	93.0
	150.0	0.82	0.886	461.8	0.626	134.5
	200.0	0.59	0.851	457.5	0.616	172.5
	250.0	0.46	0.824	453.9	0.607	207.5
	300.0	0.38	0.805	450.6	0.600	240.0
	350.0	0.32	0.788	447.4	0.594	274.5
	400.0	0.27	0.769	444.2	0.587	308.5

*Based on $H = 0$ and $S = 0$ for liquid at 1 atm. pressure and 78°F.

check runs in the apparatus using water showed an average volumetric deviation of 0.63% from the accepted value.

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Table 3. Constants for the Beattie-Bridgeman Equation

$$p = \frac{RT}{v^2}\left[1 - \frac{c}{vT^3}\right]$$

$$[v + B_0(1 - b/v)] - (A_0/v^2)(1 - a/v)$$

$a = 0.145$

$A_0 = 20$

$b = 0.081$

$B_0 = 0.070$

$c = 3 \times 10^7$

NOTATION

- a = constant in the Beattie-Bridgeman equation, cu. ft./lb.
- A_0 = constant in the Beattie-Bridgeman equation, (lb./sq. in. abs.)(cu. ft./lb.)^2
- b = constant in the Beattie-Bridgeman equation, cu. ft./lb.
- B_0 = constant in the Beattie-Bridgeman equation, cu. ft./lb.
- c = constant in the Beattie-Bridgeman equation, (cu. ft./lb.)/°R.^{3}
- f fugacity, lb./sq. in. abs.
- H = enthalpy, B.t.u./lb.
- p = pressure, lb./sq. in. abs.
- R = gas constant, (lb./sq. in. abs.)(cu. ft./lb.)/°R. (= 0.1448)
- S = entropy, B.t.u./(lb.)(°R.)
- T = temperature, °R.
- v = volume, cu. ft./lb.
- Z = compressibility factor

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