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Liquid Heat Capacity of *tert*-Butyl Alcohol, Isobutyl Alcohol, and Isopropyl Alcohol at High Temperature

Steven P. Hoffman, Juan Luis San José, and Robert C. Reid*

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Liquid isobaric heat capacities of *tert*-butyl alcohol, isobutyl alcohol, and isopropyl alcohol were measured in a flow calorimeter at temperatures ranging between the normal boiling point and a reduced temperature of 0.93–0.97. Pressures up to the critical pressure were studied. Heat capacities were found to increase with temperature but, for the alcohols studied, inflection points were found at temperatures of about $T_r = 0.65$ and 0.85; within this reduced temperature range the C_p–T curve was concave to the temperature axis. This behavior has not been observed in nonpolar compounds such as hydrocarbons or is it noted for liquid water or ammonia.

In a recent paper (*14*), isobaric liquid heat capacities were reported for several hydrocarbons and 1-butanol at temperatures above the normal boiling point. The data for 1-butanol were found to differ qualitatively from those for hydrocarbons in that an inflection point was noted when graphing C_p as a function of temperature. To investigate this phenomenon further, additional experiments have been carried out with three other alcohols and the results are reported in this paper. Data were obtained in the same closed-loop flow calorimeter described earlier (*14*) but the heater was replaced with one having an increased heat transfer area since the alcohols to be studied were expected to have quite large heat capacities, especially at high reduced temperatures. Experimental details are given elsewhere (*7*) and the method of calculating heat capacities from experimental data has been outlined (*14*).

Results

Isobutyl Alcohol. The pressure–temperature field studied is shown in Figure 1. Data were collected at each isobar (12.6, 26.8, and 41.9 bar), and measurements made both for ascending and descending temperatures. The highest reduced temperature attained was 0.93 (234 °C).

The vapor pressure curve of Ambrose and Townsend (*1*) is also shown in Figure 1.

Heat capacities as a funciton of temperature are given in Figure 2 along with the low-temperature results of Counsell et al. (*4*). At low temperatures (20–75 °C), C_p increases with temperature with a positive second derivative. This behavior is similar to that found for hydrocarbons (*14*). At higher temperatures, the C_p–T curves become concave with respect to the temperature axis, but, eventually, there is a second inflection point ($T_r \sim 0.85$) and C_p then increases rapidly as the critical point is approached.

At temperatures below the normal boiling point (108 °C; $T_r = 0.7$), C_p is nearly independent of pressure. At higher temperatures, an increase in pressure reduces C_p in a manner significantly more pronounced than found in hydrocarbon systems.

The dashed line in Figure 2 represents the saturated liquid. This boundary was obtained by cross-plotting C_p as a function of pressure as shown in Figure 3. Isothermal data were then extrapolated to the vapor pressure corresponding to the appropriate temperature.

Smoothed isobaric liquid heat capacities are given in Table I. The uncertainty is believed to be less than 1%.

tert-Butyl Alcohol. Measurements were made at five different isobars (8.4, 12.7, 18.5, 31.8, and 39.5 bar) over a temperature range of 30–219 °C (T_r from 0.6 to 0.97). Experimental results are shown in Figure 4. Agreement with the low-temperature data of Oetting (*10*) is excellent; the maximum deviation is +0.3% at 58 °C.

Over the temperature range of 30–150 °C ($T_r = 0.6$ to $T_r = 0.84$), the C_p vs. T curve is concave to the temperature axis, a behavior similar to that observed for isobutyl alcohol over the same reduced temperature region. The low-temperature inflection point (if there is one) is difficult to locate. Under atmospheric pressure, *tert*-butyl alcohol is a liquid over a very small temperature range ($T_{mp} = 25.5$ °C and $T_b = 82.9$ °C). Oetting made heat capacity measurements of the solid down to 15 K and these results are shown in Figure 5. Solid *tert*-butyl alcohol can exist in two different crystalline forms denoted as crystal I and II. From 110 to 286 K ($T_r = 0.22$ to $T_r = 0.57$) the C_p vs. T curve for crystal II is concave upward, a behavior similar to that observed for hydrocarbons and other polar compounds below their normal boiling points. At 286.14 K a discontinuity occurs in the C_p vs. T curve and the crystal I structure exists from 286.14 to 298.97 K ($T_r = 0.57$ to $T_r = 0.59$). Above this temperature *tert*-butyl alcohol is a liquid and the C_p–T curve is concave to the temperature axis. Note that C_p for crystal II can be extrapolated to $T_r = 0.59$ and joins smoothly with the curve for C_p of

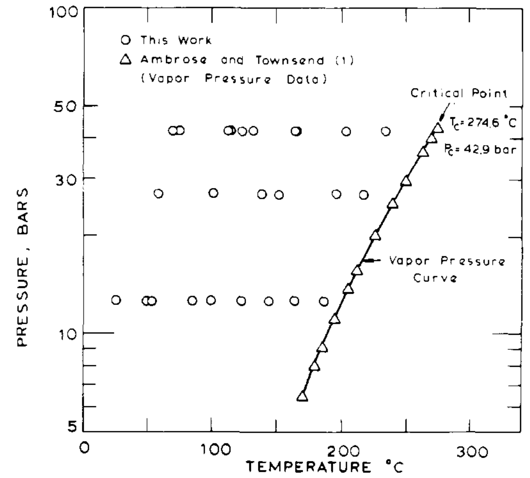

Figure 1. Range of experimental data gathered for isobutyl alcohol.

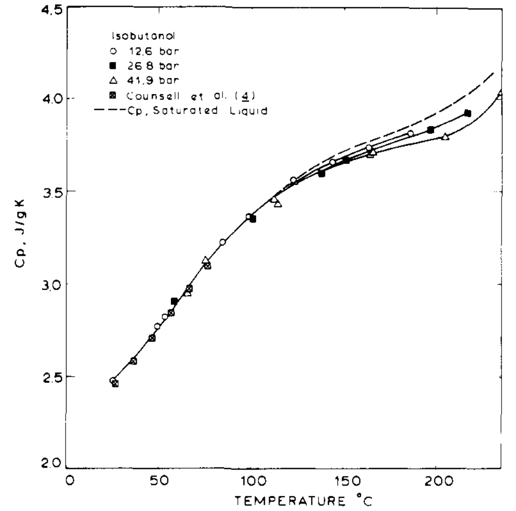

Figure 2. Experimental values of C_p for isobutyl alcohol.

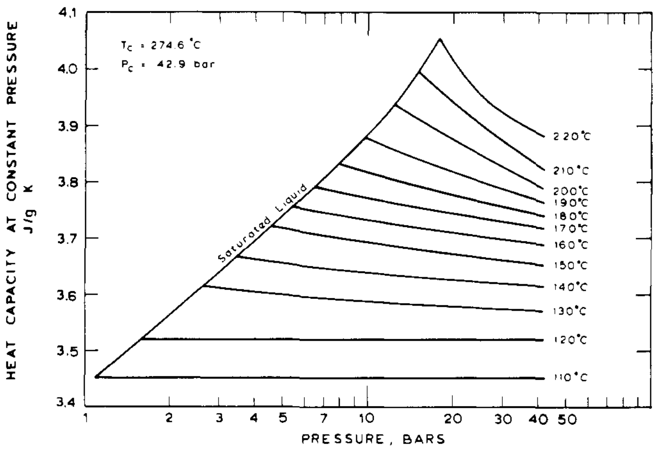

Figure 3. Isobaric liquid heat capacity of isobutyl alcohol.

the liquid. Between $T_r = 0.57$ and $T_r = 0.59$ an inflection point would presumably occur but for the solid-state transition at $T_r = 0.57$.

The effect of pressure on C_p for *tert*-butyl alcohol can be clearly seen in Figure 4. This separation of the different isobars for low reduced pressure ($P_r < 0.8$) is much more pronounced than observed previously for either isobutyl alcohol or hydrocarbons. At high reduced pressure ($P_r > 0.8$) a clear distinction cannot be made between the different isobars. This is evidenced here by a single curve drawn through the data gathered at 31.8 and 39.5 bar. At this time, no attempt has been made to explain these experimentally observed results using thermodynamics.

Table I. Smoothed Heat Capacity of Isobutyl Alcohol, J/(g K)

Temp, °C	C_p on satn curve	Pressure, bar 10	15	20	25	30	40
110	3.45	3.45	3.45	3.45	3.45	3.45	3.45
120	3.52	3.52	3.52	3.52	3.52	3.52	3.52
130	3.61	3.59	3.58	3.58	3.58	3.57	3.57
140	3.67	3.64	3.63	3.63	3.62	3.62	3.62
150	3.72	3.69	3.68	3.67	3.67	3.66	3.65
160	3.76	3.73	3.72	3.71	3.70	3.70	3.69
170	3.79	3.77	3.76	3.75	3.74	3.73	3.72
180	3.83	3.82	3.79	3.78	3.77	3.76	3.74
190	3.88	3.88	3.84	3.82	3.80	3.79	3.77
200	3.94		3.91	3.88	3.85	3.83	3.79
210	3.99		3.99	3.94	3.90	3.87	3.83
220	4.05			4.01	3.96	3.92	3.89

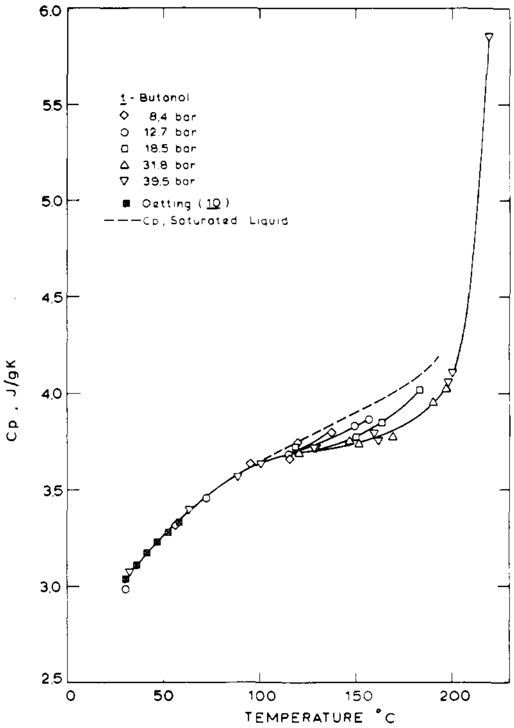

Figure 4. Experimental values of C_p for *tert*-butyl alcohol.

As temperature is increased above 200 °C ($T_r = 0.93$) a very sharp increase in C_p is observed. This is consistent with the fact that C_p is undefined at the critical temperature ($T_c = 233.0$ °C for *tert*-butyl alcohol).

Figure 6 shows the results of C_p plotted as a function of pressure. The strong pressure dependence of C_p at high reduced temperature can readily be observed. Another interesting observation is that along the saturated liquid curve, the intersections of the isotherms are about evenly spaced. However, at high reduced pressures over a temperature range of 110–160 °C, the isotherms are very close together. This denotes the region over which a temperature increase causes a very small increase in C_p.

Smoothed isobaric liquid heat capacity values for *tert*-butyl alcohol are shown in Table II.

Isopropyl Alcohol. Isopropyl alcohol is the only alcohol for which saturated liquid heat capacities have been reported above a reduced temperature of 0.75. Ginnings and Corruccini (*6*)

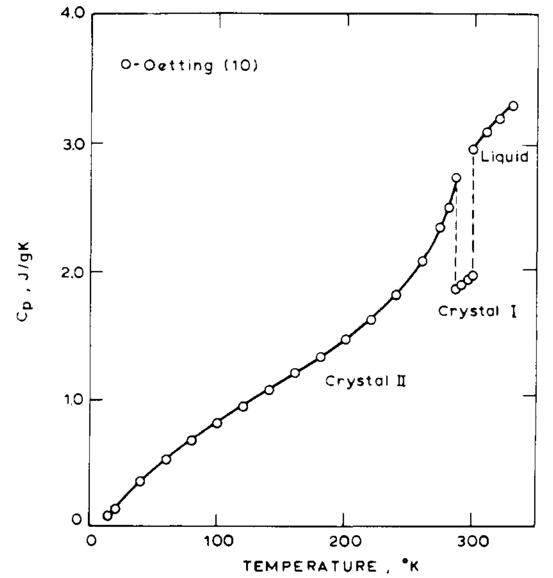

Figure 5. C_p values of Oetting (*10*) for solid and liquid *tert*-butyl alcohol.

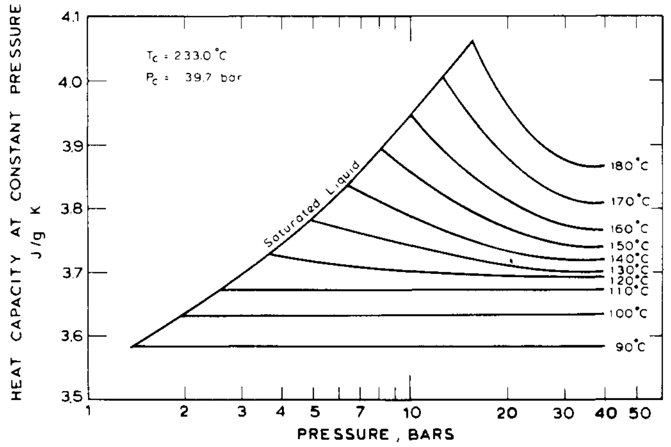

Figure 6. Isobaric liquid heat capacity of *tert*-butyl alcohol.

Table II. Smoothed Heat Capacity of *tert*-Butyl Alcohol, J/(g K)

Temp, °C	C_p on satn curve	Pressure, bar 10	15	20	25	30	35
80	3.52	3.52	3.52	3.52	3.52	3.52	3.52
90	3.58	3.58	3.58	3.58	3.58	3.58	3.58
100	3.63	3.63	3.63	3.63	3.63	3.63	3.63
110	3.67	3.67	3.67	3.67	3.67	3.67	3.67
120	3.73	3.70	3.70	3.69	3.69	3.69	3.69
130	3.78	3.74	3.72	3.71	3.71	3.70	3.70
140	3.84	3.79	3.75	3.74	3.73	3.72	3.72
150	3.89	3.86	3.80	3.77	3.75	3.74	3.74
160	3.95		3.86	3.81	3.79	3.77	3.77
170	4.00		3.95	3.88	3.84	3.82	3.81
180	4.06			3.96	3.90	3.88	3.87

measured $C_{s\sigma}$ for isopropyl alcohol over a temperature range of 0–200 °C ($T_r = 0.54$ to $T_r = 0.93$).

To study further the behavior of C_p as a function of temperature and pressure for alcohols, experimental data were obtained on isopropyl alcohol on three isobars (15.4, 26.6, and 41.6 bar) and at temperatures of 27–208 °C. C_p is plotted as a function of temperature in Figure 7; the data of Ginnings and Corruccini are also shown. The agreement between the data over the low-temperature region of the curve is very good, with a maximum deviation of +2.0% at $T = 80$ °C. At temperatures greater than 100 °C, a correction was required to convert the $C_{s\sigma}$ data of Ginnings and Corruccini to C_p. ($C_{s\sigma}$ is always less than C_p at $T_r > 0.8$.) This correction can be made using P-V-T data. However, such data for liquid isopropyl alcohol could not be found in the literature. San José and Reid (*15*) suggest the following approximate correlation to correct $C_{s\sigma}$ to C_p for liquids above $T_r = 0.8$, i.e., at $1.0 > T_r \geq 0.8$

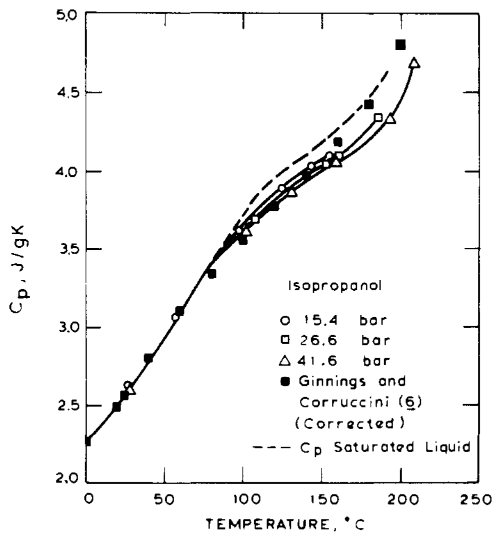

Figure 7. Experimental values of C_p for isopropyl alcohol.

Table III. Conversion of $C_{s\sigma}$ Values of Ginnings and Corruccini to C_p for Isopropyl Alcohol, Using Eq 1 [a]

T, °C	T_r	α	$C_{s\sigma}$, J/(g K)	C_p, J/(g K)
120	0.77	0.209	3.740	3.769
140	0.81	0.322	3.928	3.973
160	0.85	0.539	4.112	4.187
180	0.89	1.056	4.284	4.430
200	0.93	2.606	4.443	4.803

[a] Note: T_c = 235.1 °C, ω = 0.666, R = 0.1384 J/(g K).

Table IV. Smoothed Heat Capacity of Isopropyl Alcohol, J/(g K)

Temp, °C	C_p on satn curve	Pressure, bar 10	15	20	25	30	40
80	3.40	3.40	3.40	3.40	3.40	3.40	3.40
90	3.57	3.52	3.51	3.51	3.51	3.50	3.50
100	3.71	3.66	3.64	3.63	3.62	3.61	3.59
110	3.84	3.78	3.75	3.73	3.71	3.70	3.68
120	3.95	3.89	3.85	3.83	3.81	3.80	3.77
130	4.03	3.97	3.93	3.91	3.89	3.88	3.85
140	4.10	4.05	4.01	3.98	3.96	3.95	3.93
150	4.18	4.17	4.09	4.05	4.03	4.01	4.00
160	4.27		4.18	4.12	4.09	4.07	4.06
170	4.37		4.34	4.24	4.19	4.16	4.13
180	4.47			4.39	4.30	4.25	4.21
190	4.60				4.44	4.37	4.31

$$\alpha = (C_p - C_{s\sigma})/R = (1 + \omega)^{0.85} \exp(-0.7074 - 31.014T_r + 34.36T_r^2) + \exp(8.655T_r - 8.385) \quad (1)$$

Equation 1 is believed reliable to within 3–5% over the high-temperature region.

Values used for the correction factor, α, along with the corrected isopropyl alcohol data of Ginnings and Corruccini are given in Table III. The acentric factor was obtained from the vapor pressure data of Ambrose and Townsend (*1*).

Over the temperature range from 80 to 200 °C the experimental C_p curve for the saturated liquid has an average deviation

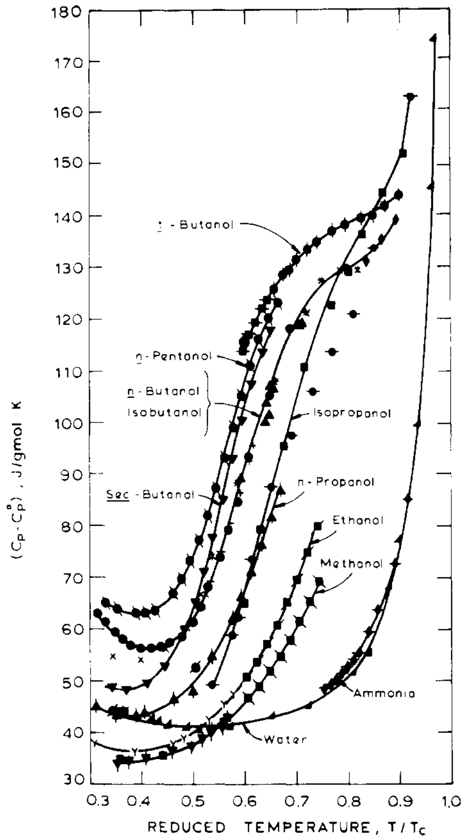

Figure 8. Heat capacity of polar compounds vs. reduced temperature.

of +2.4% from the corrected $C_{s\sigma}$ values of Ginnings and Corruccini with the maximum deviation of 4.5% occurring at 120 °C. This is satisfactory agreement considering the approximate nature of the correction.

The general shape of the C_p vs. T curve is similar to that observed for isobutyl alcohol and *tert*-butyl alcohol. From 0 to 60 °C the behavior resembles that of hydrocarbons, isobutyl alcohol, and *n*-butyl alcohol over the same reduced temperature range. At 60 °C ($T_r = 0.66$) there is an inflection point and the curve becomes concave to the temperature axis as temperature is increased. This trend continues until a temperature of 155 °C ($T_r = 0.84$) is approached, where a second inflection point occurs. With a further increase in temperature C_p rises rapidly as the critical temperature, $T_c = 235.1$ °C, is approached. This curvature is confirmed by the data of Ginnings and Corruccini which shows a similar trend for the C_p vs. T curve.

Smoothed heat capacity values for isopropyl alcohol are listed in Table IV.

C_p for Polar Compounds. From data collected by San José (*13*) and in the present study, Figure 8 was drawn. Here, the difference, $C_p - C_p^\circ$, is plotted against reduced temperature for nine alcohols, liquid ammonia, and water. C_p refers to the saturated liquid heat capacity and C_p° is the ideal-gas heat capacity at the same temperature. The symbols are defined in Table V. The following comments seem appropriate: at a given reduced temperature, $C_p - C_p^\circ$ increases with the molecular weight of the alcohol, with the exception of *n*-pentyl alcohol; at a fixed carbon number, $C_p - C_p^\circ$ increases in the order tertiary > secondary > iso ~ primary; alcohols, but neither ammonia nor water, show inflection points in a ($C_p - C_p^\circ$)-T_r plot; $C_p - C_p^\circ$ for alcohols usually exhibits a minimum in the reduced temperature range of 0.37–0.44.

Table V. Symbols for Figure 8

Methanol
▼ Kelly (*9*)
■ Parks (*11*)
■ Fiock et al. (*5*)
Ethanol
Y Parks (*11*)
■ Fiock et al. (*5*)
n-Propyl Alcohol
● Parks and Huffman (*12*)
▲ Counsell et al. (*4*)
Isopropyl Alcohol
● Ginnings and Corruccini (*6*)
■ This Work
n-Butyl Alcohol
X Parks (*11*)
\+ Williams and Daniels (*17*)
✱ Stephens and Tamplin (*16*)
▲ San José (*13*)

Isobutyl Alcohol
● Counsell et al. (*4*)
♦ This Work
sec-Butyl Alcohol
▼ Andon et al. (*2*)
n-Pentyl Alcohol
● Counsell et al. (*4*)
tert-Butyl Alcohol
■ Oetting (*10*)
● This Work
Water
▶ Keenen et al. (*8*)
Ammonia
♦ Babcock (*3*)

Glossary

C_p	isobaric heat capacity $[(\partial H/\partial T)_p]$, J/(g K) (J/(g-mol K))
C_p°	ideal gas heat capacity, J/(g K) (J/(g-mol K))
$C_{s\sigma}$	saturated heat capacity $[T(dS/dT)_{sat}]$, J/(g K) (J/(g-mol K))
P	pressure, bar
P_c	critical pressure, bar
P_r	reduced pressure (P/P_c), dimensionless
R	gas constant, J/(g K)
T	temperature, °C or K
T_b	boiling temperature, °C
T_c	critical temperature, °C
T_{mp}	melting temperature, °C
T_r	reduced temperature (T/T_c), dimensionless

Greek Letters

α	correction factor relating C_p and $C_{s\sigma}$ (eq 1), dimensionless
ω	Pitzer acentric factor, dimensionless

Subscripts

sat	along the saturation envelope

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