

## Reviews

### Vapor-Liquid Critical Properties of Elements and Compounds. 4. Aliphatic Alkanols

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This is part 4 of a series of contributions by the critical properties group of the IUPAC Commission I.2 on Thermodynamics, Subcommittee on Thermodynamic Data. It presents all known experimental data for the critical constants of aliphatic alkanols up to C<sub>12</sub>. Recommended critical constants are given together with their uncertainties, which increase for the more unstable higher alkanols. The critical temperatures have been converted to ITS-90.

#### Introduction

Part 1 [95-amb/you] was an introductory survey which included a detailed discussion of the various experimental methods used to determine critical temperatures, pressures, and volumes. Part 2 [95-amb/tso] presented experimental and evaluated data for *n*-alkanes while part 3 [95-tso/amb] presented experimental and evaluated data for aromatic hydrocarbons. The method of presentation and evaluation of the experimental data follow the guidelines of Ambrose *et al.* in parts 1 and 2 of this series. The recommended values are given in Table 1, while all known experimental values have been collected in Table 2. The references follow the recommended format (year-first three letters of first author/first three letters of second author, and, where required, a sequence number).

The lower members of the alkanol series have received the most attention in the literature because of their industrial importance, thermal stability, and moderate critical temperatures. Measurements on the higher members of the series have been made only in the last few decades.

Ethanol played an important role in the discovery of the existence of the gas-liquid critical point [1822-del]. Prior to 1900, an impressive number of measurements of physical properties of alkanols were performed by Ramsay and Young [1886-ram/you, 1887-ram/you, 1889-ram/you], who reported accurate values of the thermal properties and critical states of a wide variety of substances, including alkanols. A summary of their work, with slightly revised values in some cases, was published by Young [10-you].

Most measurements of critical temperatures and pressures of the alkanols reported in the literature were obtained with an apparatus similar to that developed by Andrews [1869-and], and later refined by Ramsay and Young, and Kay and co-workers [53-kay/ram]. This apparatus, which is frequently referred to as a Kay tube or Cailletet tube [1869-cai], is generally used not only for the measurements of critical properties but also for the determination of vapor pressures at elevated temperatures. The sample is generally confined over mercury, or sometimes gallium [80-kay/pak], in a long cylindrical glass tube and

is pressurized by the action of a compressed gas on the confining liquid. The sample is usually heated rather slowly in order to maintain thermal equilibrium, slow heating and fine temperature control being required to obtain high precision. However, in the case of thermally unstable substances, the extended exposure to high temperatures leads to excessive amounts of reaction products which may falsify the results and even make the determination of the critical properties impossible.

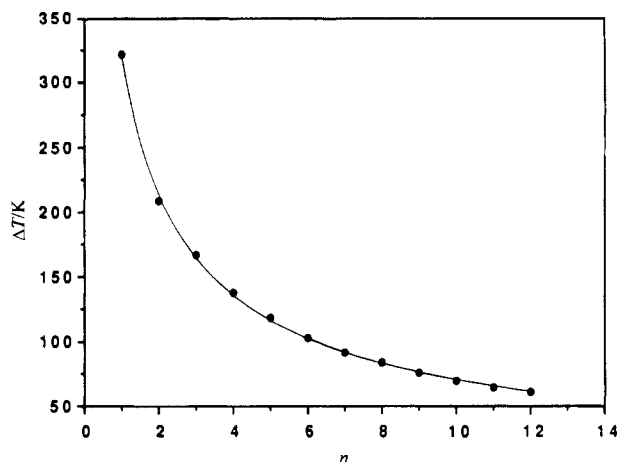
The critical properties of alkanols have also been obtained using the sealed tube (or sealed ampule) method which allows the measurement of the critical temperature and, under certain conditions, also the critical density. In this method, first used by Cagniard de la Tour in 1822 [1822-del], the substance under study is enclosed in a glass tube which is sealed at both ends. The tube is loaded with a mass of substance corresponding approximately to the amount required to obtain the critical density and is then heated to the critical temperature of the substance. Rapid heating can be applied to minimize the amount of decomposition occurring during the heating phase if the substance is thermally unstable at its critical point.

Most critical properties of the alkanols reported in the literature were obtained using the two methods described above. Thus, only a few examples of important contributions with these methods are given below, and other techniques are described in more detail.

Ambrose *et al.* [74-amb/bro] reported that 1-octanol "decomposed rapidly at 650 K". Moreover, they were unable to obtain a value for the critical temperature or pressure of 1-decanol because of its rapid decomposition at elevated temperatures. The critical pressure of 1-octanol was measured in a Kay tube apparatus, but a relatively large uncertainty (0.1 MPa) was assigned by Ambrose to the value obtained because of thermal decomposition. The critical temperature of 1-octanol was measured in a sealed glass ampule using a rapid heater that allowed the critical point to be reached "within 10 min in favorable circumstances" [60-amb/cox].

Nozdrev [56-noz] obtained the critical temperatures of methanol, ethanol, and 2-methyl-1-propanol by measuring ultrasonic velocities at different temperatures along the saturation curve. The critical point was obtained by locating the temperature (and corresponding pressure) of minimum ultrasonic velocity.

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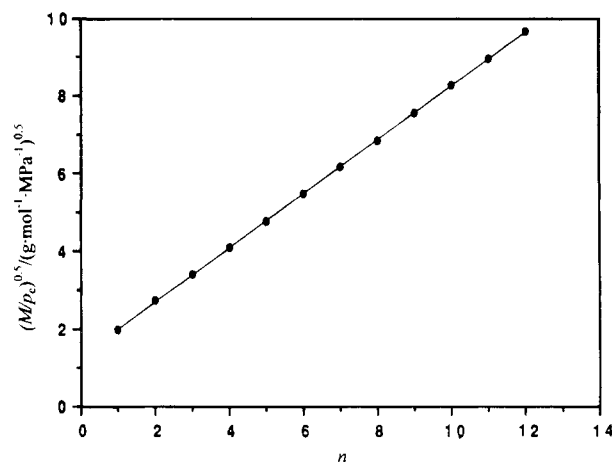


**Figure 1.** Difference in the critical temperature of corresponding 1-alkanols and *n*-alkanes ( $\Delta T = T_c(1\text{-alkanol}) - T_c(n\text{-alkane})$ ) versus the carbon number *n*.

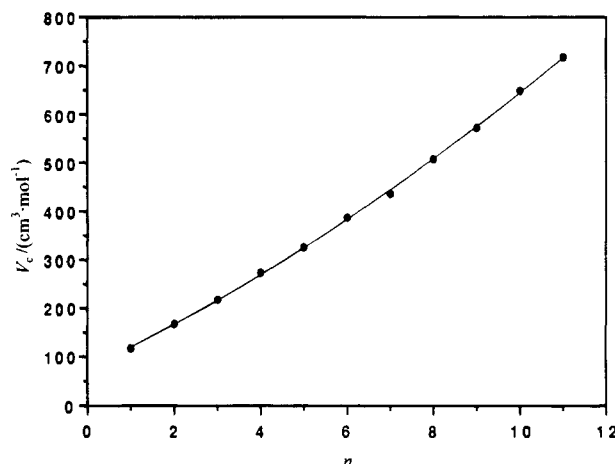
Observation of the heating and cooling curves of a substance enclosed in an autoclave was used by Glaser and Rüländ [57-gla/rue] to obtain the critical temperatures and pressures of a large number of compounds, including cyclohexanol. However, the substances under study were kept at high temperatures for "7 to 8 hours" during the experiment. This would undoubtedly have resulted in extensive decomposition in the case of thermally unstable substances. As a result, their method is not very accurate and it is believed that their reported critical properties for cyclohexanol are most likely incorrect.

Efremov [66-efr] measured the critical temperatures and densities of 1-alkanols from methanol through 1-decanol in a sealed ampule apparatus. The critical densities were determined from coexisting vapor and liquid densities on the saturation curve using the "law" of rectilinear diameters [1888-cai/col]. The critical pressures reported by Efremov were calculated from an empirical equation using the measured values of the critical temperatures and densities. These pressures were therefore not considered further in the present work. The critical temperatures reported by Efremov for the lower members of the 1-alkanol series are close to those reported by other researchers; however, the values for 1-octanol through 1-decanol appear to be too high (by about 6 to 20 K). In addition, the critical temperature of 1-octanol seems to be misprinted in Table 2 of Efremov's paper. The value reported there (668 K) differs from that deduced from his Table 1 (658 K) which appears to be the more likely value. Efremov apparently did not observe any decomposition of these substances at the elevated temperatures used in his study. However, it should be added that such decomposition would lead to lower apparent critical temperatures rather than to the higher than actual values reported by Efremov.

Smith *et al.* [86-smi/ans] and later Anselme and Teja [88-ans/tej] used a modified sealed ampule technique with a rapid heating device to measure the critical temperatures and densities of isomeric alkanols from pentanol through decanol. In their apparatus, the critical point could be reached within 3 min from the start of the experiment. The temperature of the sample during the experiment and also the temperatures of successive meniscus disappearances and reappearances were recorded. A thermal stability test of each substance and a record of temperature as a function of time allowed them to extrapolate back to the critical temperature of the original, pure sample. The critical density was obtained from an experiment where the meniscus disappearances and reappearances were exactly at the half volume position in the ampule.



**Figure 2.** Ratio  $(M/\rho_c)^{0.5}$  for 1-alkanols versus the carbon number *n*.



**Figure 3.** Critical volume of the 1-alkanols versus the carbon number *n*.

In a modification of the work of Roes [36-roe], Rosenthal and Teja [89-ros/tej] used a flow technique to measure the critical temperatures and pressures of 1-alkanols from ethanol through 1-dodecanol and 2-alkanols from 2-propanol through 2-decanol. In their apparatus, the substance was pumped, under pressure, through a view cell which was located in a furnace. By properly adjusting the furnace temperature, flow pressure, and flow rate, the critical point could be reached inside the view cell (observed by opalescence). Residence times of the substance in the heated zone were between 10 and 20 s, thus minimizing the amount of reaction products formed. Measured values of critical temperature and pressure at different residence times (obtained by changing the furnace temperature and flow rate) were used to extrapolate to the "pure" substance at zero residence time.

Lydersen and Tsochev [90-lyd/tso] used a technique that exploits the change in volume of condensation and vaporization as the critical point is approached. This technique was also used to determine the critical temperatures and pressures of seven isomeric alkanols from methanol through butanol.

Quadri *et al.* [91-qua/khi] modified the Kay-type apparatus to allow for rapid heating of the sample to its critical point. Rapid heating was achieved by inserting the observation tube, surrounded by a metal heating block, into a preheated furnace. They were able to measure the critical temperatures and pressures of 1-hexanol through 1-decanol and several of the isomers. No allowance, however, was made for any decomposition of the sample, and their reported critical temperatures and pressures

Table 1. Recommended Values of Critical Properties of Aliphatic Alkanols

	molar mass $M/\text{g}\cdot\text{mol}^{-1}$	$T_c/\text{K}^a$	( $\pm$ )	$p_c/\text{MPa}$	( $\pm$ )	$\rho_c/\text{g}\cdot\text{cm}^{-3}$	( $\pm$ )	$V_c/\text{cm}^3\cdot\text{mol}^{-1}$	$Z_c^b$
methanol	32.042	512.5	(0.2)	8.084	(0.02)	0.273	(0.002)	117	0.223
ethanol	46.069	514.0	(0.2)	6.137	(0.02)	0.275	(0.002)	168	0.241
1-propanol	60.096	536.8	(0.3)	5.169	(0.02)	0.276	(0.003)	218	0.252
2-propanol	60.096	508.3	(0.3)	4.764	(0.02)	0.271	(0.004)	222	0.250
2-propen-1-ol	58.080	545.1							
1-butanol	74.123	563.0	(0.3)	4.414	(0.02)	0.271	(0.003)	274	0.258
2-butanol	74.123	536.2	(0.3)	4.202	(0.02)	0.276	(0.004)	269	0.253
2-methyl-1-propanol	74.123	547.8	(0.3)	4.295	(0.02)	0.271	(0.005)	274	0.258
2-methyl-2-propanol	74.123	506.2	(0.3)	3.972	(0.02)	0.270	(0.005)	275	0.259
1-pentanol	88.150	588.1	(0.5)	3.897	(0.02)	0.270	(0.003)	326	0.260
2-pentanol	88.150	560.3	(0.5)	3.675	(0.02)	0.268	(0.015)	329	0.259
3-pentanol	88.150	559.6	(0.5)			0.271	(0.015)	325	
2-methyl-1-butanol	88.150	575.4	(0.5)	3.94	(0.02)				
3-methyl-1-butanol	88.150	577.2	(0.5)	3.93	(0.02)				
2-methyl-2-butanol	88.150	543.7	(0.5)	3.71	(0.02)				
3-methyl-2-butanol	88.150	556.1	(0.5)	3.87	(0.02)				
cyclopentanol	86.134	619.5	(1)	4.9	(0.1)				
1-hexanol	102.177	610.3	(0.5)	3.417	(0.02)	0.264	(0.005)	387	0.261
2-hexanol	102.177	585.9	(0.5)	3.31	(0.02)	0.266	(0.005)	384	0.261
3-hexanol	102.177	582.4	(0.5)	3.36	(0.02)	0.267	(0.005)	383	0.266
2-methyl-1-pentanol	102.177	604.4	(0.5)	3.45	(0.02)				
4-methyl-1-pentanol	102.177	603.5	(0.7)						
2-methyl-2-pentanol	102.177	559.5	(0.7)						
4-methyl-2-pentanol	102.177	574.4	(0.5)						
2-methyl-3-pentanol	102.177	576.0	(0.5)	3.46	(0.02)				
3-methyl-3-pentanol	102.177	575.6	(0.6)	3.52	(0.02)				
cyclohexanol	100.161	650.1	(2)	4.26	(0.05)				
1-heptanol	116.203	632.6	(0.5)	3.058	(0.02)	0.267	(0.005)	435	0.253
2-heptanol	116.203	608.3	(0.6)	3.021	(0.02)	0.263	(0.015)	442	0.264
3-heptanol	116.203	605.4	(0.5)			0.268	(0.015)	434	
4-heptanol	116.203	602.6	(0.5)			0.269	(0.015)	432	
1-octanol	130.230	652.5	(0.5)	2.777	(0.03)	0.262	(0.005)	497	0.254
2-octanol	130.230	629.6	(0.5)	2.754	(0.05)	0.251	(0.005)	519	0.273
3-octanol	130.230	628.5	(0.5)			0.253	(0.005)	515	
4-octanol	130.230	625.1	(0.5)			0.253	(0.005)	515	
2-ethyl-1-hexanol	130.230	640.6	(1)	2.8	(0.1)				
4-methyl-3-heptanol	130.230	623.5	(0.5)						
5-methyl-3-heptanol	130.230	621.2	(0.5)						
1-nonanol	144.257	670.7	(1)	2.528	(0.05)	0.252	(0.005)	572	0.260
2-nonanol	144.257	649.6	(1)	2.53	(0.05)	0.251	(0.005)	575	0.269
3-nonanol	144.257	648.0	(1)			0.250	(0.005)	577	
4-nonanol	144.257	645.1	(1)			0.251	(0.005)	575	
1-decanol	158.284	687.3	(1)	2.315	(0.05)	0.244	(0.005)	649	0.263
2-decanol	158.284	668.6	(1)			0.245	(0.005)	646	
3-decanol	158.284	666.1	(1)			0.246	(0.005)	643	
4-decanol	158.284	663.7	(1)			0.246	(0.005)	643	
5-decanol	158.284	663.2	(1)			0.245	(0.005)	646	
1-undecanol	172.311	703.6	(1.5)	2.147	(0.05)	0.240	(0.005)	718	
1-dodecanol	186.338	719.4	(1.5)	1.994	(0.05)				

<sup>a</sup> Temperatures are expressed on ITS-90. <sup>b</sup>  $Z_c = p_c V_c / RT_c$  where  $R = 8.31451 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

represent averaged values of the first disappearance and reappearance of the meniscus. In a recent paper, Quadri and Kudchadker [94-qua/kud] repeated their measurements of the critical properties of some alkanols. They were able to obtain data with slightly different error margins. In addition, the critical properties of 1-pentanol were determined.

### Selection of Best Values

Critical property values reported in the literature (until June 1994) were collected, and the values obtained by different researchers for a particular critical property of a substance were statistically examined for outliers. Any outliers were eliminated from the set. The remaining data were then examined for their precision and accuracy as stated by the author. The method of calibration of the measurement devices was also considered. Particular importance was placed on the identification of the source and purification of the substances studied. High purity of the sample is extremely important because of the strong sensitivity of the critical properties to even small amounts of impurities.

Experimental values that agreed within the stated uncertainties were then used to calculate an average value. In cases where the discrepancies among the data were larger than the uncertainties stated, trends of internal consistency within a homologous series (e.g., 1-alkanols, 2-alkanols) were used to select the values that appeared more likely to be correct. Tests of internal consistency were done by examining various plots such as the critical temperature  $T_c$  against  $n$ ,  $T_c - T_b$  against  $n$ ,  $T_c(1\text{-alkanol}) - T_c(n\text{-alkane})$  against  $n$ ,  $T_c/T_b$  against  $n$ ,  $(M/P_c)^{0.5}$  against  $n$ , etc., where  $M$  is the molar mass,  $n$  represents the carbon number, and  $T_b$  is the normal boiling temperature. Examples of these plots for the 1-alkanols are shown in Figures 1–3. The selected values were then used to calculate an average value for recommendation. Table 1 shows the recommended values of the critical properties of all aliphatic alkanols. Table 2 lists all experimental values that were collected and gives the uncertainties stated by the author. The classification scheme proposed by Ambrose and Young [95-amb/you] was adopted in this work to indicate the method used by the author to determine the critical properties. The key to methods of

**Table 2. Critical Properties from the Literature**

year	values reported in nonstandard units	$T_{90}/\text{K}$	$p/\text{MPa}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	method	authors
METHANOL: molar mass 32.042 g; CASRN 67-56-1						
$T_{90} - T_{48} = 0.018 \text{ K}; T_{90} - T_{68} = -0.040 \text{ K}$ at 512.5 K						
1882-han	232.76 °C, 72.85 atm	505.9 ± 0.2	7.382 ± 0.12		1	Hannay
1882-nad	233 °C, 69.73 atm	506.2	70.65		1	Nadejdine
1887-ram/you	240 °C, 59700 mmHg 3.683 cm <sup>3</sup> ·g <sup>-1</sup>	513.2	7.959	0.2715	1, 7	Ramsay and Young
1888-deh	263.0 °C	536.2			1	de Heen
1891-sch	240.2 °C	513.4			1	Schmidt
1891-sch-1	242.0 °C	515.2			1	Schmidt
04-cen	240.2 °C	513.4 ± 0.2		0.275*	1, 7	Centnerzwer
04-cri	240.5 °C	513.7			1	Crismer
10-you	240 °C, 59660 mmHg	513.2	7.954	0.2722*	1, 7	Young
30-sal	240 °C, 72765 mmHg	513.2	9.701	0.3587	1, 7	Salzwedel
43-fis/rei	240.6 °C	513.8			1	Fischer and Reichel
55-gol/rav	232 °C	505.2			1	Golik <i>et al.</i>
55-kay/don	239.43 °C, 1174.4 psi	512.60 ± 0.05*	8.097 ± 0.003*	0.272 ± 0.006*	1, 7	Kay and Donham
56-noz	240 °C	513.2			4	Nozdrev
57-kri/kha	240 °C, 118 cm <sup>3</sup> mol <sup>-1</sup>	513.2		0.271	1, 7	Krichevskii <i>et al.</i>
60-mcc/sto	464 °F, 1154 psi	513.2	7.957		3	McCracken <i>et al.</i>
60-moc	240.7 °C	513.9			1	Mocharnyuk
67-mak/noz	239 °C	512.2			4	Makhanko and Nozdrev
64-ska/kay	239.51 °C, 1173.9 psi	512.68 ± 0.22*	8.094 ± 0.007*		1	Skaates and Kay
66-efr		513 ± 1		0.272*	1, 7	Efremov
69-zub/bag	239.5 °C, 81.04 bar 3.64 cm <sup>3</sup> ·g <sup>-1</sup>	512.7 ± 0.3*	8.104 ± 0.04*	0.275 ± 0.008*	3	Zubarev and Bagdonas
74-mar/jon	241.5 °C	514.7			1	Marshall and Jones
75-kay/khe		512.32 ± 0.1*	8.000 ± 0.002		1	Kay and Khera
81-fra/len	239.4 °C	512.6*	8.10*	0.2720*	2, 3	Francesconi <i>et al.</i>
88-bru		512.43 ± 0.1*	8.072 ± 0.005*		2	Brunner
88-del/poo		512.5 ± 0.2*	8.06*	0.02	1	de Loos <i>et al.</i>
90-lyd/tso		512.5*	8.06*		3	Lydersen and Tsochev
	recommended values	512.5 ± 0.2	8.084 ± 0.02	0.273 ± 0.002		
ETHANOL: molar mass 46.069 g; CASRN 64-17-5						
$T_{90} - T_{48} = 0.018 \text{ K}; T_{90} - T_{68} = -0.040 \text{ K}$ at 514.0 K						
1822-del	258.7 °C, 119 atm	531.9	12.06		1	de la Tour
1879-saj	234.3 °C, 62.1 atm	507.5	6.292		1	Sajotschewsky
1880-han	234.3 °C, 64.5 atm	507.5 ± 0.6	6.536 ± 0.8		1	Hannay
1880-han/hog	234.6 °C, 65 atm	507.8 ± 2	6.586 ± 0.1		1	Hannay and Hogarth
1881-sch	233.7 °C	506.9			?	Schuck
1882-han	235.47 °C, 67.07 atm	508.6 ± 0.2	6.796 ± 0.01		1	Hannay
1882-str	240.6 °C	513.8			1	Strauss
1886-ram/you	243.6 °C, 47700 mmHg 3.5 cm <sup>3</sup> ·g <sup>-1</sup>	516.8 ± 0.5	6.360	0.286	1, 7	Ramsay and Young
1891-sch	234.3 °C	507.5			1	Schmidt
1893-bat	241 °C, 62.30 atm	514.2	6.313	0.2283	?	Battelli
04-cri	245.4 °C	518.6			1	Crismer
10-you	243.1 °C, 47850 mmHg	516.3	6.380	0.2755*	1, 7	Young
10-pri	250 °C (249–251 °C)	523			1	Prideaux
43-fis/rei	241.7 °C	514.9			1	Fischer and Reichel
43-gri/han	243.0 °C, 925 psi	516.2	6.378		1, 2a	Griswold <i>et al.</i>
55-gol/rav	243 °C	516.2			1	Golik <i>et al.</i>
56-noz	243.5 °C	516.7			4	Nozdrev
60-mcc/sto	470 °F, 927 psi	516.5	6.391		3	McCracken <i>et al.</i>
60-moc	241 °C	514.2*			1	Mocharnyuk
64-ska/kay	240.83 °C, 889.2 psi	514.00 ± 0.22*	6.131 ± 0.007*	0.277 ± 0.003*	1, 7	Skaates and Kay
66-efr		516 ± 1		0.275*	1, 7	Efremov
72-rae/str		518.9			1	Rätzsch and Strauch
72-tas	243 °C	516.2			4	Tasmukhamedov
74-amb/bro		513.88 ± 0.005*	6.148 ± 0.006*		1	Ambrose <i>et al.</i>
74-mar/jon	243.0 °C	516.2			1	Marshall and Jones
77-hen	243 °C	516.2			4	Hentze
84-wil/lin		513.91 ± 0.1*	6.129 ± (0.0007)*		1	Wilson <i>et al.</i>
87-mou		516.11 ± 0.2	6.325 ± 0.001	0.273*	1, 7	Mousa
89-ros/tej		514.1 ± 0.6*	6.140 ± 0.02*		2c	Rosenthal and Teja
90-lyd/tso		515.0	6.17		3	Lydersen and Tsochev
	recommended values	514.0 ± 0.2	6.137 ± 0.02	0.275 ± 0.002		
Rosenthal and Teja [89-ros/tej] used the low residence time flow method.						

Table 2 (Continued)

year	values reported in nonstandard units	$T_{90}/\text{K}$	$p/\text{MPa}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	method	authors
1-PROPANOL: molar mass 60.096 g; CASRN 71-23-8						
$T_{90} - T_{48} = 0.025 \text{ K}; T_{90} - T_{68} = -0.040 \text{ K at } 536.8 \text{ K}$						
1882-nad-1	258.0 °C, 53.26 atm	531.2	5.397		1	Nadejdine
1883-nad	254.2 °C	527.4			1	Nadejdine
1888-deh	261.0 °C	534.2			1	de Heen
1889-ram/you	263.7 °C, 38120 mmHg 3.6 cm <sup>3</sup> ·g <sup>-1</sup>	536.9	5.082	0.2778	1, 7	Ramsay and Young
1891-sch	265.8 °C	539.0			1	Schmidt
1891-sch-1	270.5 °C	543.7			1	Schmidt
02-kue/rob	264.0 °C, 51.5 atm	537.2	5.218		1	Kuonen and Robson
04-cri	265 °C	538.2			1	Crismer
10-you	263.80 °C, 38120 mmHg	536.9*	5.082	0.2734*	1, 7	Young
43-fis/rei	264.1 °C	537.3			1	Fischer and Reichel
55-gol/rav	263 °C	536.2			1	Golik <i>et al.</i>
60-moc	263.0 °C	536.2			1	Mocharnyuk
63-amb/tow	263.56 °C, 51.02 atm	536.74 ± 0.1*	5.170 ± 0.005*	0.2754*	1, 7	Ambrose and Townsend
64-ska/kay	263.80 °C, 747.6 psi	536.98 ± 0.22*	5.155 ± 0.007*	0.278 ± 0.003*	1, 7	Skaates and Kay
66-efr		537 ± 1*		0.273*	1, 7	Efremov
74-bon/you		536.5 ± 0.2*			1	Bone and Young
82-zaw/vej		537.28	5.182*	0.2787*	1, 7	Zawisza and Vejrosta
89-ros/tej		536.7 ± 0.6*	5.168 ± 0.02*		2c	Rosenthal and Teja
90-lyd/tso		537.5	5.17*		3	Lydersen and Tsochev
	recommended values	536.8 ± 0.3	5.169 ± 0.02	0.276 ± 0.003		
2-PROPANOL: molar mass 60.096 g; CASRN 67-63-0						
$T_{90} - T_{48} = 0.016 \text{ K}; T_{90} - T_{68} = -0.040 \text{ K at } 508.3 \text{ K}$						
1882-nad-1	234.6 °C, 53.10 atm	507.8	5.38		1	Nadejdine
1888-deh	238.0 °C	511.2			1	de Heen
06-bro	243.47 °C	516.6			1	Brown
43-fis/rei	235.6 °C	508.8			1	Fischer and Reichel
54-kre	235.25 °C	508.4 ± 0.05*			1	Kreglewski
55-kre	235.0 °C, 53 atm	508.2*	5.37		1	Kreglewski
58-rav/sol	238.3 °C	511.5			1	Ravikovich and Solomko
63-amb/tow	235.05 °C, 47.02 atm	508.26 ± 0.1*	4.764 ± 0.005*	0.2727*	1, 7	Ambrose and Townsend
74-spr/you		508.3 ± 0.2*			1	Sprague and Young
78-amb/cou		508.3*	4.762*	0.269 ± 0.003*	1, 7	Ambrose <i>et al.</i>
89-ros/tej		508.0 ± 0.6*	4.761 ± 0.02*		2c	Rosenthal and Teja
90-lyd/tso		508.6*	4.77*		3	Lydersen and Tsochev
	recommended values	508.3 ± 0.3	4.764 ± 0.02	0.271 ± 0.004		
2-PROPEN-1-OL: molar mass 58.080 g; CASRN 107-18-6						
1882-nad-1	271.9 °C	545.1*			1	Nadejdine
	recommended values	545.1				
Ambrose and Townsend [63-amb/tow] omitted the values for 2-propanol, personal communication, 1992. Rosenthal and Teja [89-ros/tej] used the low residence time flow method.						
year	values reported in nonstandard units	$T_{90}/\text{K}$	$p/\text{MPa}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	method	authors
1-BUTANOL: molar mass 74.123 g; CASRN 71-36-3						
$T_{90} - T_{48} = 0.032 \text{ K}; T_{90} - T_{68} = -0.039 \text{ K at } 563.0 \text{ K}$						
1883-paw	287.1 °C	560.3			1	Pawlewski
1888-deh	270.5 °C	543.7			1	de Heen
23-her/neu	48.4 atm		49.04		1	Herz and Neukirch
43-fis/rei	288.0 °C	561.2			1	Fischer and Reichel
55-gol/rav	287 °C	560.2			1	Golik <i>et al.</i>
55-kay/don	289.74 °C, 640.4 psi	562.90 ± 0.05*	4.415 ± 0.0035*	0.267 ± 0.006*	1, 7	Kay and Donham
55-sin/she	286.95 °C, 48.60 atm	560.1 ± 0.05	4.924 ± 0.05	0.2700 ± 0.0002*	1, 7	Singh and Shemilt
58-rav/sol	291.0 °C	564.2			1	Ravikovich and Solomko
60-moc	287.0 °C	560.2			1	Mocharnyuk
63-amb/tow	289.83 °C, 43.55 atm	563.01 ± 0.1*	4.413 ± 0.004*	0.2699*	1, 7	Ambrose and Townsend
64-ska/kay	289.87 °C, 640.1 psi	563.05 ± 0.22*	4.413 ± 0.007*	0.275 ± 0.003*	1, 7	Skaates and Kay
66-efr		561 ± 1		0.271*	1, 7	Efremov
74-spr/you-1		562.2 ± 0.3			1	Sprague and Young
89-ros/tej		562.4 ± 0.6*	4.418 ± 0.02*		2c	Rosenthal and Teja
90-lyd/tso		563.6*	4.41*		3	Lydersen and Tsochev
	recommended values	563.0 ± 0.3	4.414 ± 0.02	0.271 ± 0.003		
2-BUTANOL: molar mass 74.123 g; CASRN 78-92-2						
$T_{90} - T_{48} = 0.025 \text{ K}; T_{90} - T_{68} = -0.040 \text{ K at } 536.2 \text{ K}$						
06-bro	265.1	538.3			1	Brown
63-amb/tow		535.98 ± 0.1*	4.194 ± 0.004*	0.2755*	1, 7	Ambrose and Townsend
89-ros/tej		536.1 ± 0.6*	4.203 ± 0.02*		2c	Rosenthal and Teja
90-lyd/tso		536.6*	4.21*		3	Lydersen and Tsochev
	recommended values	536.2 ± 0.3	4.202 ± 0.02	0.276 ± 0.004		

Table 2 (Continued)

year	values reported in nonstandard units	$T_{90}/\text{K}$	$p/\text{MPa}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	method	authors
2-METHYL-1-PROPANOL: molar mass 74.123 g; CASRN 78-83-1						
$T_{90} - T_{48} = 0.029 \text{ K}; T_{90} - T_{68} = -0.039 \text{ K at } 547.8 \text{ K}$						
1882-nad-1	265.0 °C, 48.27 atm	538.2	4.891		1	Nadejdine
06-bro	277.6 °C	550.8			1	Brown
54-kre	276.70 °C	549.9 ± 0.05			1	Kreglewski
55-kay/don	274.59 °C, 622.8 psi	547.77 ± 0.05*	4.294 ± 0.004*	0.269 ± 0.006*	1, 7	Kay and Donham
55-kre	277.6 °C, 48.0 atm	550.8	4.86		1	Kreglewski
56-noz	283.5 °C	556.7			4	Nozdrev
63-amb/tow	274.59 °C, 42.39 atm	547.74 ± 0.1*	4.295 ± 0.004*	0.2722*	1, 7	Ambrose and Townsend
90-lyd/tso		548.6	4.32		3	Lydersen and Tsochev
	recommended values	547.8 ± 0.3	4.295 ± 0.02	0.271 ± 0.005		
2-METHYL-2-PROPANOL: molar mass 74.123 g; CASRN 75-65-0						
1883-paw	234.9 °C	508.1			1	Pawlewski
56-kro/joh	456.3 °F, 613.8 psi	508.9 ± 0.06	4.232 ± 0.006	0.258 ± 0.005	1, 7	Krone and Johnson
63-amb/tow	233.0 °C, 39.20 atm	506.2 ± 0.2*	3.972 ± 0.004*	0.2700*	1, 7	Ambrose and Townsend
	recommended values	506.2 ± 0.3	3.972 ± 0.02	0.270 ± 0.005		
Rosenthal and Teja [89-ros/tej] used the low residence time flow method.						
Ambrose and Townsend [63-amb/tow] omitted the values for 2-methyl-1-propanol, personal communication, 1992.						
year	values reported in nonstandard units	$T_{90}/\text{K}$	$p/\text{MPa}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	method	authors
1-PENTANOL: molar mass 88.150 g; CASRN 71-41-0						
$T_{90} - T_{48} = 0.036 \text{ K}; T_{90} - T_{68} = -0.039 \text{ K at } 588.1 \text{ K}$						
66-efr		586 ± 1		0.270*	1, 7	Efremov
74-amb/bro		588.11 ± 0.1*	3.909 ± 0.01*		1	Ambrose <i>et al.</i>
86-smi/ans		587.7 ± 0.1*		0.273 ± 0.014	1c	Smith <i>et al.</i>
89-ros/tej		588.5 ± 0.6*	3.868 ± 0.02*		2c	Rosenthal and Teja
91-chr/sad		588.2*			1	Christou <i>et al.</i>
94-qua/kud		588.0 ± 0.3*	3.915 ± 0.01*		1	Quadri and Kudchadker
	recommended values	588.1 ± 0.5	3.897 ± 0.02	0.270 ± 0.003		
2-PENTANOL: molar mass 88.150 g; CASRN 6032-29-7						
86-smi/ans		560.4 ± 0.2*		0.268 ± 0.013*	1c	Smith <i>et al.</i>
89-ros/tej		560.4 ± 0.6*	3.710 ± 0.02*		2c	Rosenthal and Teja
91-qua/kud		560.0 ± 0.5*	3.64 ± 0.02*		1	Quadri <i>et al.</i>
	recommended values	560.3 ± 0.5	3.675 ± 0.02	0.268 ± 0.015		
3-PENTANOL: molar mass 88.150 g; CASRN 584-02-1						
86-smi/ans		559.6 ± 0.2*		0.271 ± 0.014*	1c	Smith <i>et al.</i>
	recommended values	559.6 ± 0.5		0.271 ± 0.015		
2-METHYL-1-BUTANOL: molar mass 88.150 g; CASRN 137-32-6						
91-qua/kud		575.4 ± 0.5*	3.94 ± 0.02*		1	Quadri <i>et al.</i>
	recommended values	575.4 ± 0.5	3.94 ± 0.02			
3-METHYL-1-BUTANOL: molar mass 88.150 g; CASRN 123-51-3						
1883-paw	306.6 °C	579.8			1	Pawlewski
1891-sch	306.0 °C	579.2			1	Schmidt
06-bro	309.77 °C	582.9			1	Brown
43-fis/rei	307.2 °C	580.4			1	Fischer and Reichel
54-kre	306.05 °C	579.2 ± 0.05			1	Kreglewski
55-kre	307 °C, 45 atm	580.2	4.56		1	Kreglewski
91-qua/khi		577.2 ± 0.5%	3.93 ± 0.02*		1	Quadri <i>et al.</i>
	recommended values	577.2 ± 0.5	3.93 ± 0.02			
2-METHYL-2-BUTANOL: molar mass 88.150 g; CASRN 75-85-4						
06-bro	271.77 °C	544.9			1	Brown
91-qua/khi		543.7 ± 0.5*	3.71 ± 0.02*		1	Quadri <i>et al.</i>
	recommended values	543.7 ± 0.5	3.71 ± 0.02			
3-METHYL-2-BUTANOL: molar mass 88.150 g; CASRN 598-75-4						
91-qua/khi		556.1 ± 0.5*	3.87 ± 0.02*		1	Quadri <i>et al.</i>
	recommended values	556.1 ± 0.5	3.87 ± 0.02			
CYCLOPENTANOL: molar mass 86.134 g; CASRN 96-41-3						
87-amb/ghi		619.5 ± 1.0*	4.9 ± 0.1*		1	Ambrose and Ghiassae
	recommended values	619.5 ± 1.0	4.9 ± 0.1			

Table 2 (Continued)

Smith *et al.* [86-smi/ans] used a loading density such that the meniscus disappearance and reappearance occurred approximately in the center of the ampule.  
Rosenthal and Teja [89-ros/tej] used the low residence time flow method.

year	values reported in nonstandard units	$T_{90}/K$	$p/MPa$	$\rho/g\text{cm}^{-3}$	method	authors
1-HEXANOL: molar mass 102.177 g; CASRN 111-27-3						
66-efr		610 ± 1*		0.268*	1, 7	Efremov
88-ans/tej		611.4 ± 0.3		0.260 ± 0.005*	1c	Anselme and Teja
89-ros/tej		610.4 ± 0.6*	3.413 ± 0.02*		2c	Rosenthal and Teja
91-qua/khi		610.4 ± 0.6*	3.42 ± 0.02*		1	Quadri <i>et al.</i>
	recommended values	610.3 ± 0.5	3.417 ± 0.02	0.264 ± 0.005		
2-HEXANOL: molar mass 102.177 g; CASRN 626-93-7						
78-law/lee		586.2 ± 0.3*			1	Lawrenson and Lee
88-ans/tej		586.0 ± 0.3*		0.266 ± 0.005*	1c	Anselme and Teja
89-ros/tej		585.4 ± 0.6*	3.310 ± 0.02*		2c	Rosenthal and Teja
	recommended values	585.9 ± 0.5	3.31 ± 0.02	0.266 ± 0.005		
3-HEXANOL: molar mass 102.177 g; CASRN 623-37-0						
88-ans/tej		582.5 ± 0.3*		0.267 ± 0.005*	1c	Anselme and Teja
91-qua/khi		582.2 ± 0.6*	3.36 ± 0.02*		1	Quadri <i>et al.</i>
	recommended values	582.4 ± 0.5	3.36 ± 0.02	0.267 ± 0.005		
2-METHYL-1-PENTANOL: molar mass 102.177 g; CASRN 105-30-6						
91-qua/khi		604.4 ± 0.5*	3.45 ± 0.02*		1	Quadri <i>et al.</i>
	recommended values	604.4 ± 0.5	3.45 ± 0.02			
4-METHYL-1-PENTANOL: molar mass 102.177 g; CASRN 626-89-1						
78-law/lee		603.5 ± 0.7*			1	Lawrenson and Lee
	recommended values	603.5 ± 0.7				
2-METHYL-2-PENTANOL: molar mass 102.177 g; CASRN 590-36-3						
78-law/lee		559.5 ± 0.7*			1	Lawrenson and Lee
	recommended values	559.5 ± 0.7				
4-METHYL-2-PENTANOL: molar mass 102.177 g; CASRN 108-11-2						
78-law/lee		574.4 ± 0.5*			1	Lawrenson and Lee
	recommended values	574.4 ± 0.5				
2-METHYL-3-PENTANOL: molar mass 102.177 g; CASRN 565-67-3						
91-qua/khi		576.0 ± 0.5*	3.46 ± 0.02*		1	Quadri <i>et al.</i>
	recommended values	576.0 ± 0.5	3.46 ± 0.02			
3-METHYL-3-PENTANOL: molar mass 102.177 g; CASRN 77-74-7						
91-qua/khi		575.6 ± 0.6*	3.52 ± 0.02*		1	Quadri <i>et al.</i>
	recommended values	575.6 ± 0.6	3.52 ± 0.02			
CYCLOHEXANOL: molar mass 100.161 g; CASRN 108-93-0						
26-nag/rot	377 °C	650.2*			1	Nagornov and Rotinyantz
57-gla/rue	352 °C, 37 atm	625.2	3.75		4	Glaser and Rüländ
87-amb/ghi		650.0 ± 2.0*	4.26 ± 0.05*		1	Ambrose and Ghiassae
	recommended values	650.1 ± 2.0	4.26 ± 0.05			

Anselme and Teja [88-ans/tej] used the rapid heating method.

Rosenthal and Teja [89-ros/tej] used the low residence time flow method.

year	values reported in nonstandard units	$T_{90}/K$	$p/MPa$	$\rho/g\text{cm}^{-3}$	method	authors
1-HEPTANOL: molar mass 116.203 g; CASRN 111-70-6						
06-bro	365.3 °C	638.5			1	Brown
66-efr		633 ± 1*		0.267*	1, 7	Efremov
86-smi/ans		632.3 ± 0.1*		0.266*	1c	Smith <i>et al.</i>
89-ros/tej		632.9 ± 0.6*	3.058 ± 0.02*		2c	Rosenthal and Teja
91-qua/khi		632.0 ± 0.6*	3.16 ± 0.02		1	Quadri <i>et al.</i>
	recommended values	632.6 ± 0.5	3.058 ± 0.02	0.267 ± 0.005		

Table 2 (Continued)

year	values reported in nonstandard units	$T_{90}/\text{K}$	$p/\text{MPa}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	method	authors
2-HEPTANOL: molar mass 116.203 g; CASRN 543-49-7						
86-smi/ans		$611.4 \pm 0.2$		$0.263 \pm 0.013^*$	1c	Smith <i>et al.</i>
89-ros/tej		$608.3 \pm 0.6^*$	$3.021 \pm 0.02^*$		2c	Rosenthal and Teja
	recommended values	$608.3 \pm 0.6$	$3.021 \pm 0.02$	$0.263 \pm 0.015$		
3-HEPTANOL: molar mass 116.203 g; CASRN 589-82-2						
86-smi/ans		$605.4 \pm 0.2^*$		$0.268 \pm 0.013^*$	1c	Smith <i>et al.</i>
	recommended values	$605.4 \pm 0.5$		$0.268 \pm 0.015$		
4-HEPTANOL: molar mass 116.203 g; CASRN 589-55-9						
86-smi/ans		$602.6 \pm 0.2^*$		$0.269 \pm 0.013^*$	1c	Smith <i>et al.</i>
	recommended values	$602.6 \pm 0.5$		$0.269 \pm 0.015$		
Rosenthal and Teja [89-ros/tej] used the flow residence time flow method.						
Smith <i>et al.</i> [86-smi/ans] used a loading density such that the meniscus disappearance and reappearance occurred approximately in the center of the ampule.						
year	values reported in nonstandard units	$T_{90}/\text{K}$	$p/\text{MPa}$	$\rho/\text{g}\cdot\text{cm}^{-3}$	method	authors
1-OCTANOL: molar mass 130.230 g; CASRN 111-87-5						
06-bro	385.46 °C	658.6			1	Brown
43-fis/rei	384.6 °C	657.8			1c	Fischer and Reichel
66-efr		$658 \pm 1$		$0.266^*$	1, 7	Efremov
74-amb/bro		$652.5 \pm 1.5^*$	$2.86 \pm 0.1$		1	Ambrose <i>et al.</i>
88-ans/tej		$650.6 \pm 0.3$		$0.257 \pm 0.005^*$	1c	Anselme and Teja
89-ros/tej		$652.9 \pm 0.4^*$			1c	Rosenthal and Teja
89-ros/tej		$652.4 \pm 0.6^*$	$2.777 \pm 0.02^*$		2c	Rosenthal and Teja
91-qua/khi		$652.2 \pm 0.6^*$	$2.85 \pm 0.02$		1	Quadri <i>et al.</i>
	recommended values	$652.5 \pm 0.5$	$2.777 \pm 0.03$	$0.262 \pm 0.005$		
2-OCTANOL: molar mass 130.230 g; CASRN 123-96-6						
06-bro	364.12 °C	637.3			1	Brown
88-ans/tej		$629.7 \pm 0.3^*$		$0.251 \pm 0.005^*$	1c	Anselme and Teja
89-ros/tej		$629.0 \pm 0.6^*$	$2.727 \pm 0.02^*$		2c	Rosenthal and Teja
90-amb/ghi		$638 \pm 2$	2.9		1, 6	Ambrose and Ghiassee
91-qua/khi		$630.2 \pm 0.6^*$	$2.78 \pm 0.02^*$		1	Quadri <i>et al.</i>
	recommended values	$629.6 \pm 0.5$	$2.754 \pm 0.05$	$0.251 \pm 0.005$		
3-OCTANOL: molar mass 130.230 g; CASRN 589-98-0						
88-ans/tej		$628.5 \pm 0.3^*$		$0.253 \pm 0.005^*$	1c	Anselme and Teja
	recommended values	$628.5 \pm 0.5$		$0.253 \pm 0.005$		
4-OCTANOL: molar mass 130.230 g; CASRN 589-62-8						
88-ans/tej		$625.1 \pm 0.3^*$		$0.253 \pm 0.005^*$	1c	Anselme and Teja
	recommended values	$625.1 \pm 0.5$		$0.253 \pm 0.005$		
2-ETHYL-1-HEXANOL: molar mass 130.230 g; CASRN 104-76-7						
78-law/lee		$640.2 \pm 0.3^*$			1	Lawrenson and Lee
90-amb/ghi		$641 \pm 1^*$	2.8		1, 6	Ambrose and Ghiassee
	recommended values	$640.6 \pm 1$	$2.8 \pm 0.1$			
4-METHYL-3-HEPTANOL: molar mass 130.230 g; CASRN 14979-39-6						
78-law/lee		$623.5 \pm 0.5^*$			1	Lawrenson and Lee
	recommended values	$623.5 \pm 0.5$				
5-METHYL-3-HEPTANOL: molar mass 130.230 g; CASRN 18720-65-5						
78-law/lee		$621.2 \pm 0.3^*$			1	Lawrenson and Lee
	recommended values	$621.2 \pm 0.5$				
Anselme and Teja [88-ans/tej] used the rapid heating method.						
For 1-octanol Rosenthal and Teja [89-ros/tej] later determined the sample had been contaminated.						
Rosenthal and Teja [89-ros/tej] used the low residence time flow method.						
Ambrose and Ghiassee [90-amb/ghi] calculated the critical pressure for 2-octanol and 2-ethyl-1-hexanol from vapor pressures up to 480 K using the Wagner equation.						



Table 2 (Continued)

year	values reported in nonstandard units	$T_{90}/K$	$p/MPa$	$\rho/g\text{cm}^{-3}$	method	authors
1-NONANOL: molar mass 144.257 g; CASRN 143-08-8						
66-efr		$683 \pm 1$		0.265	1, 7	Efremov
88-ans/tej		$670.5 \pm 0.7^*$		$0.252 \pm 0.005^*$	1c	Anselme and Teja
89-ros/tej		$670.4 \pm 0.6^*$	$2.546 \pm 0.02^*$		2c	Rosenthal and Teja
91-qua/khi		$671.3 \pm 0.8^*$	$2.51 \pm 0.03^*$		1	Quadri <i>et al.</i>
	recommended values	$670.7 \pm 1$	$2.528 \pm 0.05$	$0.252 \pm 0.005$		
2-NONANOL: molar mass 144.257 g; CASRN 628-99-9						
88-ans/tej		$649.1 \pm 0.3^*$		$0.251 \pm 0.005^*$	1c	Anselme and Teja
89-ros/tej		$650.1 \pm 0.6^*$	$2.530 \pm 0.02^*$		2c	Rosenthal and Teja
	recommended values	$649.6 \pm 1$	$2.53 \pm 0.05$	$0.251 \pm 0.005$		
3-NONANOL: molar mass 144.257 g; CASRN 624-51-1						
88-ans/tej		$648.0 \pm 0.3^*$		$0.250 \pm 0.005^*$	1c	Anselme and Teja
	recommended values	$648.0 \pm 1$		$0.250 \pm 0.005$		
4-NONANOL: molar mass 144.257 g; CASRN 5932-79-6						
88-ans/tej		$645.1 \pm 0.3^*$		$0.251 \pm 0.005^*$	1c	Anselme and Teja
	recommended values	$645.1 \pm 1$		$0.251 \pm 0.005$		
Anselme and Teja [88-ans/tej] used the rapid heating method. Rosenthal and Teja [89-ros/tej] used the low residence time flow method.						
year	values reported in nonstandard units	$T_{90}/K$	$p/MPa$	$\rho/g\text{cm}^{-3}$	method	authors
1-DECANOL: molar mass 158.284 g; CASRN 112-30-1						
66-efr		$708 \pm 1$		0.264	1, 7	Efremov
88-ans/tej		$687.3 \pm 1.3^*$		$0.244 \pm 0.005^*$	1c	Anselme and Teja
89-ros/tej		$687.0 \pm 0.6^*$	$2.32 \pm 0.02^*$		2c	Rosenthal and Teja
91-qua/khi		$687.7 \pm 0.8^*$	$2.31 \pm 0.03^*$		1	Quadri <i>et al.</i>
	recommended values	$687.3 \pm 1$	$2.315 \pm 0.05$	$0.244 \pm 0.005$		
2-DECANOL: molar mass 158.284 g; CASRN 1120-06-5						
88-ans/tej		$668.6 \pm 0.3^*$		$0.245 \pm 0.005^*$	1c	Anselme and Teja
	recommended values	$668.6 \pm 1$		$0.245 \pm 0.005$		
3-DECANOL: molar mass 158.284 g; CASRN 1565-81-7						
88-ans/tej		$666.1 \pm 0.3^*$		$0.246 \pm 0.005^*$	1c	Anselme and Teja
	recommended values	$666.1 \pm 1$		$0.246 \pm 0.005$		
4-DECANOL: molar mass 158.284 g; CASRN 2051-31-2						
88-ans/tej		$663.7 \pm 0.3^*$		$0.246 \pm 0.005^*$	1c	Anselme and Teja
	recommended values	$663.7 \pm 1$		$0.246 \pm 0.005$		
5-DECANOL: molar mass 158.284 g; CASRN 5205-34-5						
88-ans/tej		$633.2 \pm 0.3^*$		$0.245 \pm 0.005^*$	1c	Anselme and Teja
	recommended values	$663.2 \pm 1$		$0.245 \pm 0.005$		
Anselme and Teja [88-ans/tej] used the rapid heating method. Rosenthal and Teja [89-ros/tej] used the low residence time flow method.						
year	values reported in nonstandard units	$T_{90}/K$	$p/MPa$	$\rho/g\text{cm}^{-3}$	method	authors
1-UNDECANOL: molar mass 172.311 g; CASRN 112-42-5						
89-ros/tej		$703.0 \pm 0.8^*$	$2.147 \pm 0.03^*$		2c	Rosenthal and Teja
90-ans/tej		$704.2 \pm 2.2^*$		$0.240 \pm 0.005^*$	1c	Anselme and Teja
	recommended values	$703.6 \pm 1.5$	$2.147 \pm 0.05$	$0.240 \pm 0.005$		
1-DODECANOL: molar mass 186.338 g; CASRN 112-53-8						
89-ros/tej		$719.4 \pm 0.8^*$	$1.994 \pm 0.05^*$		2c	Rosenthal and Teja
	recommended values	$719.4 \pm 1.5$	$1.994 \pm 0.05$			
Rosenthal and Teja [89-ros/tej] used the low residence time flow method. Anselme and Teja [88-ans/tej] used the rapid heating method.						

**Table 3. Key to Methods of Critical Point Determination (Reprinted with Permission from 95-amb/you. Copyright 1995 American Chemical Society)**

1. visual—in glass tube
  2. visual—in cell with windows
  3. nonvisual—*pVT* measurement
  4. other nonvisual measurement
  5. critical pressure measurement combined with vapor pressure measurement up to the critical point
  6. critical pressure by extrapolation of vapor pressure curve
  7. orthobaric density measurements
  8. equation of state, thermodynamic study
  9. calculation from another physical property
  10. literature survey
- (a) with stirring  
 (b) instrumental detection of critical point  
 (c) special feature of apparatus

critical point determinations is given in Table 3. Values denoted by an asterisk were used to compute the average value recommended in Table 1. The recommended value is the arithmetic average of all accepted values without weighting. In a few cases, only a single value was available, and this value is the one recommended. All temperatures are reported according to ITS-90, and the conversions between the three temperature scales (IPTS-1948, IPTS-1968, and ITS-90) are given where adjustments were made. Some special cases where the general selection method outlined above had to be modified are addressed below.

**Ethanol.** Disregarding an obvious outlier [72-rae/str], the critical temperatures of ethanol reported in the literature seem to be divided into two distinct groups. The values reported by Young [10-you], Griswold *et al.* [43-gri/han], Golik *et al.* [55-gol/rav], Nozdrev [56-noz], McCracken *et al.* [60-mcc/sto], Efremov [66-efr], Marshall and Jones [74-mar/jon], Hentze [77-hen], and Mousa [87-mou] all fall in the range from 516.0 to 516.7 K with uncertainties of 1 K or less, whereas the values reported by Mocharnyuk [60-moc], Skaates and Kay [64-ska/kay], Ambrose *et al.* [74-amb/bro], Wilson *et al.* [84-wil/in], and Rosenthal and Teja [89-ros/tej] all lie between 513.88 and 514.2 K with uncertainties of less than 0.6 K. Two research groups, Fischer and Reichel [43-fis/rei] and Lydersen and Tsochev, [90-lyd/tso] report critical temperatures that fall in the middle of these two ranges. Similar behavior was observed in the case of the critical pressure, with values in the first group lying in the range of 6.325–6.391 MPa (reported uncertainties less than 0.001 MPa) and values in the second lying in the range of 6.129–6.148 MPa (uncertainties less than 0.02 MPa).

Ethanol, like all alkanols, is very hygroscopic; in addition, it forms an azeotrope with water. Critical property data for the ethanol + water system [75-hic/you] show that the influence of water is to increase the critical temperature and pressure of the mixture to a value above that for pure ethanol. Since the results of the second group of researchers show lower critical temperatures and pressures, it is possible that the samples of the first group were slightly contaminated with water. The data of the second group were therefore selected and averaged to obtain recommended values of the critical temperature and pressure.

**2-Heptanol.** After examination of various plots and fits of data for the 2-alkanol series, such as  $T_c(2\text{-alkanol}) - T_c(n\text{-alkane})$  against  $n$  or the difference in critical temperature between a particular 2-alkanol and the one having one additional carbon atom, the value of the critical temperature for 2-heptanol reported by Rosenthal and Teja [89-ros/tej] was chosen over that of Smith *et al.* [86-smi/ans], which appears to be too high.

**1-Octanol.** Three research groups have reported values for the critical pressure of 1-octanol. The values obtained

by Ambrose *et al.* [74-amb/bro] and Quadri *et al.* [91-qua/khi] agree within the experimental uncertainty stated, but the value reported by Rosenthal and Teja [89-ros/tej] is considerably lower (by about 0.09 MPa). The value given by Rosenthal and Teja agrees with that of Ambrose mainly because of the large uncertainty assigned by Ambrose to the critical pressure of 1-octanol as a result of rapid decomposition. In the technique used by Rosenthal, the sample is rapidly heated to the critical point in an apparatus which minimizes the amount of decomposition products formed. Decomposition is known to increase the critical pressure, and therefore a lower critical pressure would indicate less decomposition and a purer sample during the measurements. Examination of various plots and fits of data for the 1-alkanol series, such as  $p_c(1\text{-alkanol}) - p_c(n\text{-alkane})$  against  $n$ ,  $(M/p_c)^{0.5}$  against  $n$ , etc., indicated also that the value obtained by Rosenthal and Teja is consistent with the trend in the homologous series. Therefore, their value was chosen as the recommended critical pressure of 1-octanol.

**2-Octanol.** Critical temperatures for 2-octanol have been reported by five research groups. Although the values of Brown [6-bro] and Ambrose and Ghiassee [90-amb/ghi] agree well within experimental error, they are approximately 8 K higher than those obtained by the other research groups. In their paper, Ambrose and Ghiassee report their value to be “surprising” and indicate that, from correlations of vapor pressures, they would have expected a lower value than the one reported. Examination of the trend of the critical temperatures within the homologous series of 2-alkanols showed that the values obtained by Anselme and Teja [88-ans/tej], Rosenthal and Teja [89-ros/tej], and Quadri *et al.* [91-qua/khi] appear more likely to be correct and were therefore chosen to compute the recommended value.

**Isomeric Compounds.** As a hydroxy or a methyl group moves from the end of the carbon chain toward the center of the molecule (e.g., 1-hexanol to 3-hexanol or 2-methyl-2-pentanol to 4-methyl-2-pentanol), one would expect the critical properties to change in some regular fashion. The critical temperature exhibits this regularity as the location of the hydroxy group is altered along the carbon chain (e.g., 1-hexanol to 3-hexanol or 1-decanol to 5-decanol). However, moving the methyl group leads to irregular changes in this property. For instance, while the critical temperature of 4-methyl-1-pentanol is 0.9 K lower than that of 2-methyl-1-pentanol, it is 14.9 K higher for 4-methyl-2-pentanol than for 2-methyl-2-pentanol. The critical pressures and densities exhibit similar irregularities. It should be added here that a lack of experimental results and large uncertainties in the reported critical densities do not allow any clear trends to be observed for this property.

### Critical Densities

Only three studies have been published on the critical densities of 1-pentanol through 1-decanol [66-efr, 86-smi/ans, 88-ans/tej], and there exists only one published value for the critical density of 1-undecanol [90-ans/tej]. In addition, values for the critical densities of isomeric alkanols from pentanol through decanol have only been reported by Smith *et al.* [86-smi/ans] and Anselme and Teja [88-ans/tej]. Efremov obtained his critical densities from coexisting vapor and liquid densities along the saturation curve using the law of rectilinear diameters. Smith *et al.* [86-smi/ans] and later Anselme and Teja [88-ans/tej] obtained their critical densities from experiments where the meniscus disappearances and reappearances were exactly at the half volume position in an ampule.

Due to the nature of the critical density measurements, there is some scatter in the reported values. Furthermore,

the values obtained by Smith *et al.* and Anselme and Teja seem to follow a trend already noted for the normal alkanes [90-ans/gud] where, after attaining a maximum, the critical density decreases with increasing carbon number. It is believed that the critical densities of the straight chain alkanols, like any other critical property, will converge to those of the *n*-alkanes because the influence of the functional group diminishes with increasing size of the molecule. Therefore, the data reported by Smith *et al.* were chosen over those published by Efremov for the higher members of the 1-alkanol series.

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**Registry Numbers Supplied by the Author.** Methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 2-propen-1-ol, 107-18-6; 1-butanol, 71-36-3; 2-butanol, 78-92-2; 2-methyl-1-propanol, 78-83-1; 2-methyl-2-propanol, 75-65-0; 1-pentanol, 71-41-0; 2-pentanol, 6032-29-7; 3-pentanol, 584-02-1; 2-methyl-1-butanol, 137-32-6; 3-methyl-1-butanol, 123-51-3; 2-methyl-2-butanol, 75-85-4; 3-methyl-2-butanol, 598-75-4; cyclopentanol, 96-41-3; 1-hexanol, 111-27-3; 2-hexanol, 626-93-7; 3-hexanol, 623-37-0; 2-methyl-1-pentanol, 105-30-6; 4-methyl-1-pentanol, 626-89-1; 2-methyl-2-pentanol, 590-36-3; 4-methyl-2-pentanol, 108-11-2; 2-methyl-3-pentanol, 565-67-3; 3-methyl-3-pentanol, 77-74-7; cyclohexanol, 108-93-0; 1-heptanol, 111-70-6; 2-heptanol, 543-49-7; 3-heptanol, 589-82-2; 4-heptanol, 589-55-9; 1-octanol, 118-87-5; 2-octanol, 123-96-6; 3-octanol, 589-98-0; 4-octanol, 589-62-8; 2-ethyl-1-hexanol, 104-76-7; 4-methyl-3-heptanol, 14979-39-6; 5-methyl-3-heptanol, 18720-65-5; 1-nonanol, 143-08-8; 2-nonanol, 628-99-9; 3-nonanol, 624-51-1; 4-nonanol, 5932-79-6; 1-decanol, 112-30-1; 2-decanol, 1120-06-5; 3-decanol, 1565-81-7; 4-decanol, 2051-31-2; 5-decanol, 5205-34-5; 1-undecanol, 112-42-5; 1-dodecanol, 112-53-8.

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