SURVEY

CRITICAL PARAMETERS OF PURE SUBSTANCES.

I. HYDROCARBONS

E. S. Barkan

The solution of a number of theoretical and applied problems in thermophysics and thermodynamics requires reliable values for the critical parameters of individual substances, since the accuracy of these values in many cases significantly affects the results obtained. Unfortunately, in many handbooks and monographs [1-3], the magnitudes of the critical parameters are presented based either on old data or on simple averaging without taking into account the method by which they were obtained, the quality of the apparatus used, the calibration of the apparatus, etc. Naturally, these values have low accuracy.

Work on the determination of the critical properties of many organic substances published prior to 1968 was reviewed by Kudchadker, Alani, and Zvolinskii [4]. Subsequently, the values of the critical parameters recommended in this work were included in the handbook [5], the data in which is used most often. However, first of all, the experimental data presented were not analyzed in [4] and the tabulated values cannot always be assumed to be the best and, second, over the last 13 years, a large number of new works have appeared in which, based on very careful and precise measurements, the values of the critical parameters of various substances were determined again, permitting refinement of the old results. At the same time, in some cases, the new data for the same substance agree, while in other cases they do not agree. Since all of these data are widely spread out in the literature and in many cases are not well known, we felt that it would be useful to collect them in one place and to present a detailed analysis establishing the most accurate presently available values of the critical parameters. In the present work, we will examine the results for sixteen basic, technically important hydrocarbons.

Experimental Data. In accordance with the problem stated, only works published after 1968 are included in the analysis (Tables 1-7). In all cases, for comparison, data obtained by Kudchadker and others [4] are presented. In choosing the values of the critical density, preference was given to quantities found with the help of the rectilinear diameter law. This method has been repeatedly critized and some investigators even assumed that precise values cannot be obtained with this method [6-8]. However, new experiments, conducted in recent years with great care [44, 55, 59], did not confirm these objections and, recently, based on the mechanostatistical theory, we gave a rigorous proof of this rule [9]. The main and extremely important advantage of this method is the fact that it is not necessary to make measurements directly at the critical point and in a small region around it, where the complex problem of taking into account the effect of gravitational forces, small concentrations of impurities, and so on arises, which greatly affects the accuracy of the final results.

Methane. The data in all works, with the exception of [10], obtained by different methods, almost completely agree with each other and have high accuracy. The value of T_c obtained by Jansoone et al. [11] is 0.03°K lower than subsequent measurements. However, it was obtained using IPTS-48, while the others were obtained using IPTS-68. When we transform to this scale, we obtain 190.53°K, i.e., we have complete agreement (Table 1).

Ethane. All values of T_c within the limits of the total error agree with one another and have the required accuracy (Table 2).

The values of P_c, found by Khazanova and Siminskaya [16] and Berestov and Kiselev [22], are identical, but are 0.16 and 0.25% higher than the values obtained by Miniovich and Sorina [17] and by Douslin and Harrison [20], respectively. Several years ago, two groups of American researchers [23, 24] independently carried out precision measurements of the saturation vapor pressure of ethane up to the critical point. In both cases, an insignificant extrapolation to T_c gave the value $P_c = 48.71$ bar, agreeing within the limits of error with the quantity in

TABLE 1. Parameters of the Critical Point of Methane

Reference	T_c, K	P_c, bar	ρ_c, g/cm^3	Reference	T_c, K	P_c, bar	ρ_c, g/cm^3
[4]	190,5	46,03	0,1620	[13]	190,53	45,95	0,1629
[10]	190,77	46,25	0,1625	[14]	190,55	45,95	0,1627
[11]	190,50	45,94	0,1628	[15]	190,52	—	—
[12]	—	—	0,1630				

[20]. Keeping in mind that the error in determining P_c in [16] is quite high (0.3%), while the accuracy of [17, 20, 23, and 24] is very high, the base value was taken as the average of the latter quantities.

The critical density of ethane in most works [16, 17, 19, 20] was obtained using the rectilinear diameter method and, in addition, the results of the first three works coincide with one another, while the results of [20] are 1.3% higher, which exceeds the total error in determining ρ_c. Besides these works, the liquid—gas existence curve in the vicinity of the critical point was carefully investigated by Slivinskii [25] and the value of ρ_c that we computed from his data equals the quantity obtained in [16, 19]. For this reason, although the analysis of the original works did not permit establishing the reasons for the observed disagreement, we believe that the measurements of Douslin and Harrison are less precise. The method of neutron analysis was first used by Bulavin et al. [18]. All measurements were carried out with great care and the computational equations appear to be completely reliable. Nevertheless, since the measurement carried out with the given method is, as far as we know, singular, it is difficult to judge the true accuracy of the results obtained. Finally, the average of the data in [16, 17, 19] and [22] is taken as the recommended value, since in the latter case, ρ_c was determined from an analysis of the results on heat capacity with the help of the scale theory and has high accuracy. The result obtained by Strumf et al. [21], using the moving meniscus method, agrees with the value chosen within the limits of error.

Ethylene. The results of the measurements of all three works [26-28] coincide with one another within the limits of experimental error and their accuracy does not raise any doubts (Table 3). We only note that the quantity T_c obtained from P—V—T measurements [28] exceeded by 0.1°K the values found using the moving meniscus method [26] and from an analysis of data on the coexistence curve according to the equations of scale theory [27]. Starting from an analysis of these works and general considerations on the determination of the critical temperature [29], preference was given to the data in [26, 27].

Propane. Although the values of T_c in [30-32] agree with one another within the limits of the total error of the measurements, their absolute accuracy (0.2°K) is too low. In this connection, we calculated the value of the critical temperature T_c = 369.78 ± 0.02°K from data according to the coexistence curve near the critical point [25] using the least-square method from the linearity of the relation [33]

$$\ln |\rho_g - \rho_l| = \ln 2B_1 + \beta_1 \ln |(T - T_c)/T_c|. \tag{1}$$

Using this value of T_c, we calculated ρ_c from the data in [25] using the rectilinear diameter method and P_c from the saturated vapor pressure [32]. The new value of ρ_c is the average of the quantities in [30, 32] and differs from them by 2.7%. Keeping in mind that in the works indicated, the critical density was not found by the rectilinear diameter method, while Slivinskii's data [25] agree very well with the results of subsequent measurements made by other workers [20, 34, 35] and, therefore, are reliable and have high accuracy, preference was given to the value obtained in the present work. The value of ρ_c obtained by Clegg and Rowlinson [36], also obtained by the rectilinear diameter method, is recommended in [4]. However, analysis and comparison of the work in [20, 25, 34-36] showed that the data in [36] are less accurate.

Cyclopropane. The work carried out by Lin, Silberberg, and McKetta [37] (Table 4) is the first investigation of cyclopropane in which all critical parameters were determined (previously ρ_c was unknown). The purity of the substance was 99.93%, the temperature was measured to within 0.01°K, the pressure to within 0.04%, and the density to within 0.06%. The critical temperature and pressure were found from the P—V diagram and the density was found using the rectilinear diameter method. Here, it should be noted that, as shown in

TABLE 2. Parameters of the Critical Point of Ethane

Reference	T_c, K	P_c, bar	ρ_c, g/cm^3	Reference	T_c, K	P_c, bar	ρ_c, g/cm^3
[4]	305,43	48,79	0,2032	[19]	305,36	—	0,2040
[16]	305,34	48,84	0,2039	[20]	305,33	48,72	0,2066
[17]	305,35	48,76	0,2043	[21]	305,37	—	0,2055
[18]	305,34	—	0,2062	[22]	305,36	48,84	0,2050

[4], even if all P—V—T measurements are carried out with high accuracy, it is difficult to find the most accurate value of T_c from the P—V diagram. For this reason, as an additional check, we calculated the critical temperature from Eq. (1). The value obtained turned out to be equal to 398.28 ± 0.02°K and, within the limits of error, coincides with the original quantity. Taking this fact into account and the carefulness with which all measurements were performed as well, the reliability and accuracy of the values of P_c and ρ_c obtained do not give rise to any doubts.

Propylene. For propylene, the critical parameters were determined last a long time ago and they have low accuracy [4]. However, at the end of the 1960s, Voinov, Pavlovich, and Timrot [38] carried out new, highly accurate measurements of the densities of the gas and liquid phases on the coexistence curve over a wide region in the vicinity of the critical point. Using these data, we determined once again the critical temperature from Eq. (1) and then the critical density using the rectilinear diameter rule, which were then adopted as base values. The critical pressure was calculated for the value of T_c adopted from the data on the saturation vapor pressure [39].

n-Butane. It was noted in [4] that for normal butane, the critical parameters were not determined since 1940. However, this is incorrect. Connolly [40] first measured the critical temperature and pressure, and then Jones and Kay [41] determined all parameters. The values of the critical temperature and pressure, obtained in both works, coincide with one another within the limits of the total experimental error and have adequate accuracy.

The value of the critical density, found by Jones and Kay, is ≈2% lower than the corresponding value found by Kay [42], recommended by Kudchadker et al. [4]. At the same time, in [42], ρ_c was determined using the rectilinear diameter method, while in [41] this method was not used. In order to choose the most accurate value of ρ_c, we additionally determined ρ_c from data on the coexistence curve obtained by Slivinskii [25] and, in addition, since they encompass a region of temperatures that is quite far removed from the critical point, the expanded form of the rectilinear diameter law, taking into account terms of higher order, was used. The value of the critical density obtained in this manner turned out to be equal to 0.2287 ± 0.006 g/cm^3 and within the limits of accuracy coincided with the quantity in [42]. We chose this value as the best value.

Isobutane. For isobutane, there are only two works concerned with determining the parameters of the critical point. One of these, Connolly [40], unfortunately, was not included in the review in [4]. The value of T_c presented in it is 0.4°K lower than the value determined by Beattie et al. [43], while the value of P_c is lower by 0.5%. Since in both cases substances with a high degree of purity were used and the measurements were carried out with special care, it is difficult to give preference to one set of data over the other. For this reason, the averages of the results in both works were chosen as the base quantities. Using the value of T_c adopted, we refined the magnitude of the critical density from data in [25] and, at the same time, as in the case of n-butane, we used the expanded form of the rectilinear diameter rule. The value obtained turned out to be 2.3% higher than that found by the classical method from the P—V—T measurements [40] and, as already noted, it is more accurate.

n-Pentane. The disagreement between the values of the critical temperature, obtained in both works, is 0.8°K and greatly exceeds the total error. In both cases, the substance used had approximately the same purity (≥99.9%) and such a high difference observed is difficult to explain. However, since the technique used by Artyukhovskaya et al. [44] is more refined, their value was considered to be the best value. In [44], the critical temperature and pressure were obtained by studying the vertical distribution of density and subsequent investigation of the shape of the isotherm for small Δρ. This permitted approaching the values of the

TABLE 3. Parameters of the Critical Point of Ethylene

Reference	T_c, K	P_c, bar	ρ_c, g/cm^3	Reference	T_c, K	P_c, bar	ρ_c, g/cm^3
[4]	282,36	50,30	0,2175	[27]	282,35	50,42	0,2142
[26]	282,34	50,39	0,2146	[28]	282,45	—	0,2142

critical parameters by orders of magnitudes closer than in carrying out the usual P—V—T measurements [45] (T_c was approached to within 0.005°K). In order to obtain the vertical distribution of density, a flotation method and two optical techniques (Topler and molecular scattering) were used simultaneously, which permitted avoiding systematic errors. In addition, the critical temperature was determined directly from direct visual observations, while the critical density was determined using the rectilinear diameter method, and the values obtained in both cases coincide within the limits of error in the measurements. We note that all preceding precision measurements of T_c and ρ_c are not as accurate as the work in [44] and there is no need to examine them.

The value of P_c was recalculated for the chosen critical temperature from the results in [45] and the magnitude found coincided with the critical pressure calculated from the data on the saturation vapor pressure [46].

Neopentane. The critical parameters for neopentane were determined only once in the time period being examined [47] (Table 5). The experimental technique and the determination of the corresponding critical quantities are the same as for cyclopropane in [37]. In this connection, a control determination of T_c using Eq. (1) was carried out, which confirmed the high accuracy of the original value, which in its turn indicates the correctness of the magnitudes of P_c and ρ_c obtained. As in the case of isobutane, the value of ρ_c, recommended by Kudchadker et al. [4] and obtained by the classical method from the P—V—T measurements [48], differs by 2.6% from the value found using the rectilinear diameter method and is less accurate.

n-Hexane. The values of T_c obtained by different workers [31, 32, 50, 51] agree with one another within the limits of the total experimental error and the average of these quantities was adopted as the recommended value. Nondegassed substances were used in [49] so that these results can be viewed as only approximate.

Using the chosen value of the critical temperature, we recalculated the value of P_c from data on the saturated vapor pressure [32], which emcompassed the range of temperatures including the critical temperature and are accurate to within 0.07%. For ρ_c, there are no new data and Kay's value [52] remains the only value as before. In this case, it should be noted that it was obtained using the rectilinear diameter method and is quite reliable (in our opinion, the possible error does not exceed 1.5%).

Cyclohexane. New, high-accuracy measurements of the saturation vapor pressure over a wide range of temperatures, including the critical temperature (Table 6), were carried out by Hugill and McClashan [53]. Based on a quite detailed comparison of our data with all previous data, it is concluded that the results of other workers are the best results at the present time. Their analysis does not raise any objections and we adopt the values of T_c and P_c of this work as base values. New determinations of the critical density were not carried out in recent years and we recommend using the value ρ_c obtained by Kudchadker et al. [4], which was obtained using the rectilinear diameter method.

n-Heptane. The values of T_c obtained in both works differ by 1°K, which greatly exceeds the total error in their determination. As already mentioned in the case of n-pentane, the latest methods were used in [44, 55, 59] and the results obtained have the highest accuracy. At the same time, Kobe and Matthews [54] determined T_c by an old, very inadequate method, which gives a large error (0.3-0.6°K). Starting from this, the quantity in [55] was chosen as the best value. We note that the new value of the critical temperature agrees to within 0.14°K, i.e., within the limits of the total error, with previous, most accurate determination of T_c [56], which serves as an additional confirmation of the reliability of the value chosen.

The critical pressure was calculated at the chosen value of T_c from data of two works on the saturation vapor pressure [54, 56] and the average of these two values was chosen. Both values differed by 0.07 bar.

TABLE 4. Parameters of the Critical Point of
Propane and Cyclopropane

Substance	Reference	T_c, K	P_c, bar	ρ_c, g/cm^3
n-C$_3$H$_8$	[4]	369,82	42,48	0,217
	[30]	370,02	42,60	0,226
	[31, 32]	369,74	42,54	0,214
cyclo-C$_3$H$_6$	[4]	397,80	54,95	—
	[37]	398,30	55,79	0,258

TABLE 5. Parameters of the Critical Point for
n-Butane, Isobutane, Pentane, and Neopentane

Substance	Reference	T_c, K	P_c, bar	ρ_c, g/cm^3
n-C$_4$H$_{10}$	[4]	425,16	37,97	0,228
	[40]	425,12	37,87	—
	[41]	425,05	37,93	0,225
iso-C$_4$H$_{10}$	[4]	408,13	36,48	0,221
	[40]	407,77	36,32	—
n-C$_5$H$_{12}$	[4]	469,60	33,68	0,237
	[44]	469,62	—	0,232
	[45]	470,40	33,78	0,233
neo-C$_5$H$_{12}$	[4]	433,75	31,98	0,238
	[47]	433,75	31,95	0,232

The magnitudes of the critical density, found in [54, 55] using the rectilinear diameter method, coincide and their accuracy does not raise any doubts.

n-Octane. No new determinations of the parameters of the critical point have been carried out for normal octane in the last 15 years. For this reason, the data obtained by Kudchadker et al. [4], which were chosen based on the complete agreement of the results for the two latest works [56, 57], are presented as recommended values of T_c, P_c, and ρ_c. Analysis of these works (the apparatus and method used for making the measurements, their accuracy, and the purity of the substances used), as well as a comparison of the critical parameters of several other substances obtained in these works with similar more reliable independent measurements, lead to the conclusion that the recommended values are indeed the most accurate.

Benzene. While examining n-pentane, we indicated that in the work carried out by Art-yukhovskaya et al. [44, 55, 59] the most precise methods were used and the results obtained are reliable and have high accuracy. For this reason, these values are recommended as the standard values. The values of the critical density obtained by Campbell and Chatterjee [58] and Akhundov and Abdullaev [60], obtained by the rectilinear diameter method and a method based on the phenomenological Planck—Gibbs rule, respectively, coincide within the limits of the total error with the value in [59]. As far as the results of Kobe and Matthews [54] are concerned, here, undoubtedly, there is some kind of misunderstanding.

The recommended value of P_c was taken as the average of the results of four calculations from data on the saturation vapor pressure [54, 57, 61, 62] for the chosen value of T_c. The maximum disagreement between the separate calculations did not exceed 0.2 bar.

Toluene. No new determinations of T_c were carried out for toluene and, for this reason, we recommend the same value as Kudchadker et al. [4] (Table 7). For this temperature, the value of P_c was recalculated according to the latest data [64] and the value obtained coincides with the quantity in [62], used in [4], to within 0.25%. The value of ρ_c, found by Akhundov and Abdullaev [63] from the phenomenological Planck and Gibbs rule, within the limits of error, coincides with the magnitude calculated using the rectilinear diameter method [4] and verifies its reliability.

Discussion of Results. Table 8 presents the recommended values of the critical parameters of all substances examined and their allowable error. In most cases, the magnitudes

TABLE 6. Parameters of the Critical Point of Hexane, Cyclohexane and Heptane

Substance	Reference	T_c, K	P_c, bar	ρ_c, g/cm^3
n-C_6H_{14}	[4]	507,35	30,12	0,233
	[49]	507,25	30,46	—
	[31, 32]	507,68	30,35	—
	[50]	507,38	30,36	—
	[51]	507,55	30,48	—
cyclo-C_6H_{12}	[4]	553,45	40,73	0,273
	[53]	553,64	40,75	—
n-C_7H_{16}	[4]	540,2	27,35	0,232
	[54]	540,8	27,56	0,234
	[55]	539,86	—	0,234

TABLE 7. Parameters of the Critical Point for Benzene and Toluene

Substance	Reference	T_c, K	P_c, bar	ρ_c, g/cm^3
C_6H_6	[4]	562,09	48,97	0,302
	[58]	562,10	48,85	0,306
	[54]	562,20	49,03	0,316
	[59]	561,80	—	0,301
	[60]	562,60*	49,43	0,301
$C_6H_5CH_3$	[4]	591,72	41,08	0,292
	[63]	593,95*	42,36	0,290

*The value of T_c is chosen on the basis of data in the literature.

TABLE 8. Recommended Parameters of the Critical Point of Individual Hydrocarbons

Substance	T_c, K	ΔT_c, K	P_c, MPa	ΔP_c, %	ρ_c, g/cm^3	V_c, cm^3/mole	$\Delta \rho_c (\Delta V_c)$, %
CH_4	195,53	0,02	4,595	0,04	0,1628	98,54	0,2
C_2H_4	282,35	0,02	5,041	0,05	0,2142	130,97	0,3
C_2H_6	305,36	0,02	4,873	0,06	0,2045	147,05	0,3
C_3H_6	364,21	0,05	4,544	0,1	0,2308	182,33	0,4
cyclo-C_3H_6	398,28	0,02	5,579	0,05	0,2580	163,10	0,3
C_3H_8	369,78	0,02	4,246	0,1	0,2201	200,35	0,3
n-C_4H_{10}	425,09	0,05	3,790	0,1	0,2287	254,15	0,4
iso-C_4H_{10}	407,95	0,2	3,640	0,2	0,2264	256,73	0,4
n-C_5H_{12}	469,62	0,02	3,363	0,1	0,232	311,00	0,4
neo-C_5H_{12}	433,75	0,02	3,195	0,05	0,232	311,00	0,3
n-C_6H_{14}	507,54	0,2	3,028	0,1	0,233	369,82	1,5
cyclo-C_6H_{12}	553,64	0,03	4,075	0,05	0,272	309,42	1,0
n-C_7H_{16}	539,86	0,02	2,721	0,1	0,234	428,27	0,4
n-C_8H_{18}	568,76	0,2	2,486	0,1	0,232	492,37	1,0
C_6H_6	561,80	0,02	4,880	0,2	0,301	295,51	0,4
$C_6H_5CH_3$	591,72	0,2	4,115	0,2	0,292	315,55	1,0

of the errors indicated are based on the accuracy of the original works and disagreements in the data of different workers, chosen as the base data. For n-hexane, octane, and toluene, the errors in T_c and ρ_c are chosen on the basis of a comparison of the results of similar measurements for other substances, carried out in the works indicated [52, 56, 63], with the data in [44, 55, 59].

Thus, as is evident from Table 8, at the present time, we have reliable values for the critical parameters of the basic hydrocarbons determined with an accuracy sufficient for solving various theoretical and applied problems.

LITERATURE CITED

1. N. B. Vargaftik, Tables on the Thermophysical Properties of Liquids and Gases, Halsted Press (1975).
2. Handbook on Chemistry [in Russian], Khimiya, Leningrad (1971).
3. V. P. Glushko (ed.), Thermodynamic Properties of Individual Substances [in Russian], Vol. 2, Nauka, Moscow (1979).
4. A. P. Kudchadker, G. H. Alani, and B. J. Zwolinski, "The critical constants of organic substances," Chem. Rev., 68, 659-735 (1968).
5. Technical Data Book, Petroleum Refining, 2nd ed., API, Washington (1971), Chap. 1.
6. A. A. Vasserman and V. A. Rabinovich, Thermophysical Properties of Air and Its Components [in Russian], Standartov, Moscow (1968).
7. S. L. Rivkin and T. S. Akhundov, "Determination of the critical parameters of normal and heavy water," Teplofiz. Vys. Temp., 1, 329-337 (1963).
8. Ya. Z. Kazavchinskii and V. I. Kudashev, "Problem of determining the critical density of a real gas from data on the saturation state," Inzh.-Fiz. Zh., 5, No. 4, 31-34 (1962).
9. E. S. Barkan, "On the validity of the rectilinear diameter rule," Zh. Fiz. Khim., 54, 235-236 (1980).
10. A. J. Vennix, T. W. Leland, Jr., and R. Kobayashi, "Low-temperature volumetric properties of methane," J. Chem. Eng. Data, 15, 238-243 (1970).
11. V. Jansoone, H. Gielen, and J. De Boelpaep, "The pressure—temperature volume relationship of methane near the critical point," Physica, 46, 213-221 (1970).
12. J. D. Olson, "The refractive index and Lorenz—Lorentz function of fluid methane," J. Chem. Phys., 63, 474-484 (1975).
13. B. E. Gammon and D. R. Douslin, "The velocity of sound and heat capacity in methane from near-critical to subcritical conditions and equation-of-state implications," J. Chem. Phys., 64, 203-218 (1976).
14. J. V. Sengers and J. M. H. Levelt Sengers, in: Progress in Liquid Physics, C. A. Croxton (ed.), New York (1977), pp. 103-174.
15. B. J. Acherson and H. J. M. Hanley, "The thermal diffusivity of methane in the critical region," Chem. Phys. Lett., 53, 596-598 (1978).
16. N. E. Khazanova and E. É. Sominskaya, "Volume behavior of ethane near its critical point," Zh. Fiz. Khim., 45, 160-161 (1971).
17. V. M. Miniovich and G. A. Sorina, "P—V—T—N relations in dilute solutions of propane in ethane near the critical point of ethane," Zh. Fiz. Khim., 45, 552-555 (1971).
18. L. A. Bulavin, Yu. M. Ostanevich, A. P. Simkina, and A. V. Strelkov, "Density of ethane near the vapor—liquid critical point," Ukr. Fiz. Zh., 16, 90-98 (1971).
19. A. I. Voronel', V. G. Gorbunova, V. A. Smirnov, et al., "Thermodynamic quantities of pure liquids and applicability of asymptotic laws near the critical point," Zh. Eksp. Teor. Fiz., 63, 964-980 (1972).
20. D. R. Douslin and R. H. Harrison, "Pressure, volume, temperature relations of ethane," J. Chem. Thermodyn., 5, 491-512 (1973).
21. H. J. Strumf, A. F. Gollings, and G. J. Pings, "Viscosity of xenon and ethane in the critical region," J. Chem. Phys., 60, 3109-3123 (1974).
22. T. A. Berestov and S. B. Kiselev, "Possibility of joining the scale equation of state and the virial expansion," Teplofiz. Vys. Temp., 17, 1202-1209 (1979).
23. A. K. Pal, G. A. Pope, Y. Arai, N. F. Canakam, and R. Kobayashi, "Experimental P—V—T relations for saturated and compressed fluid ethane," J. Chem. Eng. Data, 21, 394-397 (1976).
25. G. S. Straty and R. Tsumura, "PVT and vapor pressure measurements on ethane," J. Res. NBS, 80A, 35-39 (1976).
25. P. Sliwinski, "Die Lorenz—Lorentz funktion von damfformigen und flussigen ätan, propan, und butan," Z. Phys. Chem. (Frankfurt am Main), 63, 262-279 (1969).
26. M. R. Moldover, "Visual observation of the critical temperature and density of CO_2 and C_2H_4," J. Chem. Phys., 61, 1766-1777 (1974).
27. D. R. Douslin and R. H. Harrison, "P, V, T relation of ethylene," J. Chem. Thermodyn., 8, 301-330 (1976).
28. N. J. Trappeniers, T. Wassenaar, and G. J. Wolkers, "Isotherms and thermodynamic properties of ethylene at temperatures between 0 and 150°C and at densities up to 500 amagat," Physica, 82A, 305-311 (1976).
29. V. V. Altunin, Thermophysical Properties of Carbon Dioxide [in Russian], Standartov, Moscow (1975).

30. J. R. Barber, Ph. D. Thesis, Ohio State University, Columbus, Ohio (1968).
31. A. H. N. Mousa, W. B. Kay, and A. Kreglewski, "The critical constants of binary mixtures of certain perfluoro-compounds with alkanes," J. Chem. Thermodyn., 4, 301-311 (1972).
32. A. H. N. Mousa, "The physical properties of highly purified samples of propane and n-hexane," J. Chem. Thermodyn., 9, 1063-1065 (1977).
33. M. A. Anisimov, "Investigation of critical phenomena in liquids," Usp. Fiz. Nauk, 114, 249-294 (1974).
34. J. F. Ely and R. Kobayashi, "Isochoric pressure-volume-temperature measurements for compressed liquid propane," J. Chem. Eng. Data, 23, 221-223 (1978).
35. W. M. Haynes and M. J. Hiza, "Measurements of the ortobaric liquid densities of methane, ethane, propane, isobutane, and normal butane," J. Chem. Thermodyn., 9, 179-187 (1977).
36. H. P. Clegg and J. S. Rowlinson, "The physical properties of some fluorine compounds and their solutions," Trans. Faraday Soc., 51, 1333-1340 (1955).
37. D. C.-K. Lin, I. H. Silberberg, and J. J. McKetta, "Volumetric behavior, vapor pressure, and critical properties of cyclopropane," J. Chem. Eng. Data, 15, 483-491 (1970).
38. Yu. F. Voinov, N. V. Pavlovich, and D. L. Timrot, "Tensometric method for measuring densities of equilibrium phases on the saturation line," Khim. Promyshl. Ukr., No. 3, 51-55 (1967).
39. A. Michels, T. Wassenaar, P. Louwerse, R. J. Lunbeck, and G. J. Wolkers, "Isotherms and thermodynamical functions of propane at temperatures between 25 and 150°C and at densities up to 340 amagat," Physica, 19, 287-297 (1953).
40. J. F. Connolly, "Ideality of n-butane: isobutane solutions," J. Phys. Chem., 66, 1082-1086 (1962).
41. A. E. Jones and W. B. Kay, "The phase and volumetric relations in the helium-butane system," AIChE J., 13, 717-720 (1967).
42. W. B. Kay, "Pressure-volume-temperature relations for n-butane," Ind. Eng. Chem., 32, 358-360 (1940).
43. J. A. Beattie, D. G. Edwards, and S. Marple, "The vapor pressure orthobaric liquid density and critical constants of isobutane," J. Chem. Phys., 17, 576-577 (1949).
44. L. M. Artyukhovskaya, E. T. Shimanskaya, and Yu. I. Shimanskii, "Investigation of the thermodynamic properties of pentane near the vapor-liquid critical point," Zh. Eksp. Teor. Fiz., 59, 688-695 (1970).
45. J. Aftienjew and A. Zawisza, "High-pressure liquid-vapor equilibria, critical state, and p(V, T, x) up to 503.15°K and 4.560 MPA for n-pentane + n-perfluoropentane," J. Chem. Thermodyn., 9, 153-166 (1977).
46. J. A. Beattie, S. W. Levine, and D. R. Douslin, "The vapor pressure and critical constants of normal pentane," J. Am. Chem. Soc., 73, 4431-4432 (1932).
47. P. P. Dawson Jr., I. H. Silberberg, and J. J. McKetta, "Volumetric behavior, vapor pressure, and critical properties of neopentane," J. Chem. Eng. Data, 18, 7-15 (1973).
48. J. A. Beattie, D. R. Douslin, and S. W. Levine, "The vapor pressure and critical constants of neopentane," J. Chem. Phys., 19, 948-949 (1951).
49. S. C. Pak and W. B. Kay, "The critical properties of binary hydrocarbon system," Ind. Eng. Chem. Fund., 11, 255-258 (1972).
50. A. V. M. Mandlekar, Sc. Thesis, Ohio State Univ. (1968).
51. R. M. Khera, Sc. Thesis, Ohio State Univ. (1968).
52. W. B. Kay, "The vapor pressure and saturated liquid and vapor densities of the isomeric hexanes," J. Am. Chem. Soc., 68, 1336-1339 (1946).
53. J. A. Hugill and M. L. McClashan, "The vapor pressure from 451°K to the critical temperature and the critical temperature and critical pressure of cyclohexane," J. Chem. Thermodyn., 10, 95-100 (1978).
54. A. K. Kobe and J. F. Matthews, "The critical properties and vapor pressure of some organic nitrogen and oxygen compounds," J. Chem. Eng. Data, 15, 182-186 (1970).
55. L. M. Artyukhovskaya, E. T. Shimanskaya, and Yu. I. Shimanskii, "Coexistence curve of heptane near the critical point," Zh. Eksp. Teor. Fiz., 63, 2159-2164 (1972).
56. J. H. McMicking and W. B. Kay, "Vapor pressure and saturated liquid and vapor densities of the isomeric heptanes and isomeric octanes," Proc. Am. Petrol. Inst., Sec. III, 45, 75-90 (1965).
57. J. F. Connolly and G. A. Kandalic, "Saturation properties and liquid compressibilities for benzene and n-octane," J. Chem. Eng. Data, 7, 137-139 (1962).
58. A. N. Cambell and R. H. Chatterjee, "The critical constants and orthobaric densities of acetone, chloroform, benzene, and carbon tetrachloride," Can. J. Chem., 47, 3893-3898 (1969).

59. L. M. Artyukhovskaya, E. T. Shimanskaya, and Yu. I. Shimanskii, "Investigation of the coexistence curve and isothermal compressibility of benzene near the liquid—vapor critical point," Ukr. Fiz. Zh., 15, 1974-1981 (1970).

60. T. S. Akhundov and F. G. Abdullaev, "Experimental investigation of the specific volumes of benzene in the critical region and determination of the critical specific volume," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 2, 73-77 (1977).

61. T. S. Akhundov and F. G. Abdullaev, "Experimental investigation of the temperature dependence of the saturated vapor pressure of benzene," Zh. Fiz. Khim., 45, 1862 (1971).

62. D. Ambrose, B. E. Broderick, and R. Townsend, "The vapor pressure above the normal boiling point and the critical pressures of some aromatic hydrocarbons," J. Chem. Soc. (A), 633-641 (1967).

63. T. S. Akhundov and F. G. Abdullaev, "Investigation of the specific volumes of toluene in the critical region of the state parameters," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 1, 62-66 (1974).

64. T. S. Akhundov and F. G. Abdullaev, "Saturated vapor pressure of toluene," Izv. Vyssh. Uchebn. Zaved., Neft' Gaz, No. 9, 44 (1969).