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THERMODYNAMIC PROPERTIES OF 1-PENTANOL AT ATMOSPHERIC PRESSURE

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Data is generalized on the density, sonic velocity, and isobaric specific heat of liquid 1-pentanol and calculations are made of the isochoric specific heat, coefficients of adiabatic and isothermal compression, and enthalpy in the temperature range 194.95–411.13°K.

This study is a continuation of our work [1, 2] on analyzing, systematizing, and succintly representing experimental information on the thermodynamic properties of monohydric aliphatic alcohols.

The following equation was chosen as the approximating function to describe the temperature dependence of density, sonic velocity, and isobaric specific heat from the normal melting point up to the boiling point:

$$y = \sum_{i=0}^{n} a_i \tau^i,$$ (1)

where $\tau = T/1000$, while y respectively denotes ρ^{-1}, W, and C_p.

The coefficients a_i of Eq. (1) for ρ^{-1}, W, and C_p were determined by the least-squares method on the "Minsk-32" computer.

Density. Numerical data on the density of liquid 1-pentanol has been systematized in several handbooks [3–5]. The available empirical data on density at atmospheric pressure and on the saturation curve for the period before 1970 was generalized in the survey [4] in the form of a Francis equation. This equation describes initial values within the estimated error and is valid in the temperature range 253–393°K. Of the recommended values of ρ [4], the most accurate are those for 293.15 and 298.15°K, the averaging error for which was evaluated as ±0.0002 and ±0.0003 g/cm^3. Comparison of the results of the generalization in [4] with later (1976) measured densities on the saturation curve [5] obtained at 293–490°K with an error less than 0.02% shows that they do not agree well with each other. Whereas the deviation at T = 293.15°K is 0.04%, it increases with temperature and reaches 0.5% at T = 393.15°K. Here, the values of density are too high in every case.

In the low-temperature range there is a limited amount of experimental data. The study [6] measured density on the saturation curve in the temperature range from 213 to 453°K with an error on the order of 0.1%. Comparison of the data in [5] and [6] shows that at 293–393°K the values agree to within 0.10–0.15% except for one point at T = 393.15°K, for which the de-

TABLE 1. Coefficients of Eq. (1)

Coefficient a_i	Property		
	ρ^{-1}	w	c_p
a_0	0,919493696	3279,97421	31,8377532
a_1	0,955010991	—14093,9248	—689,310441
a_2	2,15274778	42126,3745	6465,89767
a_3	—11,8569303	—71340,7378	—31713,6573
a_4	19,2229056	43524,8023	85573,0936
a_5	—.	—	—119647,448
a_6	—	—	67590,6073
Temperature range, °K	194,95—411,13	200—404	198,15—411,13

viation is 0.51%. The study [7] reported densities on the saturation curve at temperatures from 232.95 to 423.1°K. These values were obtained by the authors by graphical-analytical extrapolation of their data on density, measured to within 0.1% for 99.90% by wt. alcohol at higher pressures, to the saturation curve. Finally, the investigation [8] measured density at the melting point ($\delta\rho \simeq 0.1\%$).

As concerns the data [9-12], preliminary comparison of these results with the most reliable values [5] at T > 293°K showed that the deviations for them were within the range 0.1-0.5%. The range was significantly higher for some empirical points [12], a fact which seriously increases the total error of the values being compared. For example, the results in [9] are too high by an average of 0.1%, while the data in [10] and [11] is overstated by 0.5 and 0.2%, respectively.

The set of initial data that was analyzed included the results from [3-8, 13, 14], with priority here having been given to the results in [5]. The density values on the saturation curve [4-7] were corrected for atmospheric pressure by the method proposed in [2]. The size of the correction did not exceed 0.01%.

The values found for the coefficients a_i for Eq. (1) are shown in Table 1. Figure 1a compares density values calculated from Eq. (1) with the initial empirical values. It can be seen from the figure that the deviations lie within the experimental error in these studies. Results of comparison with values obtained in [15] at T = 292-379°K to within 0.1% show their good agreement within the range ±0.01-0.03%. However, if we consider that the measurements in [15] were made for 99.5% (by wt.) alcohol, then the agreement is not as good if we recalculate for a 100% concentration. This is indirectly confirmed by the results obtained in [16], in which special measurements at T = 293.15°K for methanol and ethanol showed that a slight water impurity (0.026% by wt.) in them increases density by about 0.01%. Similar results were obtained in [17] for propanol-1.

The possible error of the recommended density values in Table 2, calculated from (1) in the temperature range from the melting point (T = 194.95°K [4]) to the boiling point (T = 411.13°K [5]) at atmospheric pressure (101325 Pa), can be evaluated as ±0.02% at T $\gtrsim$ 293°K, ±0.05% at 253 < T < 293°K, and 0.10-0.15% at T $\leqslant$ 253°K. The error of the density calculation at low temperatures was evaluated with allowance for the character of the deviations of the values in [6, 7] from the results of the generalization and at higher temperatures (Fig. 1a).

Sonic Velocity. Table 3 shows the experimental studies of sonic velocity in 1-pentanol. It can be seen that the most extensive measurements of sonic velocity at atmospheric pressure and on the saturation curve were obtained by Otpushchennikov and his co-authors [22, 24, 26-29]. There is one work [25] in which the speed of sound was measured in the low-temperature region at the frequency 23.6 MHz. However, it must be kept in mind that measurements at this frequency at low temperatures may be accompanied by dispersion of sound [2].

Preliminary analysis of the initial values showed that most of them agree with each other to within 0.1-0.2%. The exception is the data in [18, 19, 21, 23]. The results in [19] and [21] are low by 3 and 0.4-0.6%, respectively, in every instance compared to the other data, while the sonic velocities in [18] and [23] are overstated by 5 and 2-5%. We should point out the substantial deviations of the results in [21] from most of the data. This difference is more pronounced in view of the fact that nearly all of the other results
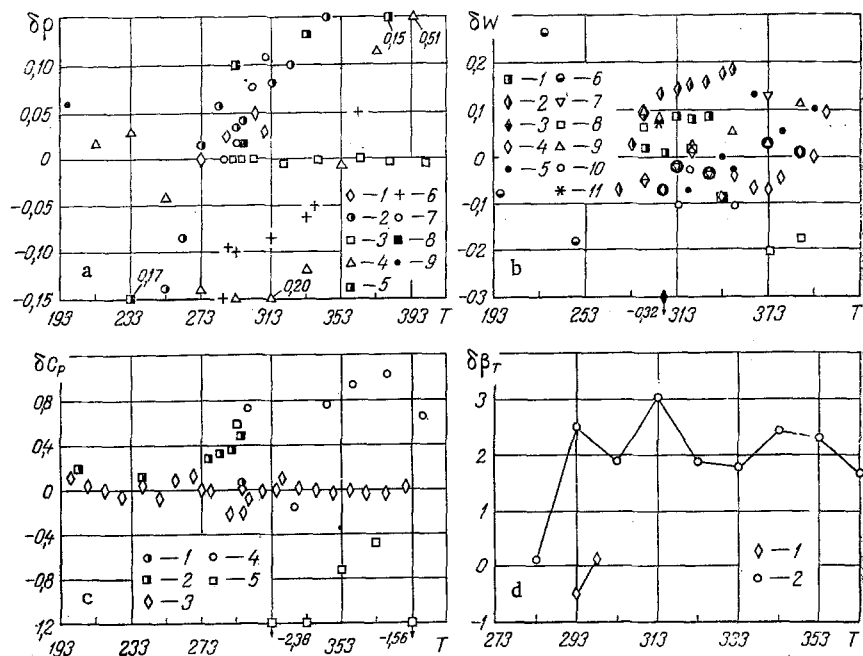
Fig. 1. Comparison of calculated values of density (a), sonic velocity
(b), isobaric specific heat (c), and the coefficient of isothermal com-
pression (d) with data of other authors:

a) $\delta\rho = (\rho\,[i] - \rho)\cdot 100/\rho$, % (1—[3]; 2—[4]; 3—[5]; 4—[6]; 5—[7]; 6—[9]; 7—[13]; 8—
[14]; 9—[8]); b) $\delta W = (W\,[i] - W)\cdot 100/W$, % (1—[11]; 2—[13]; 3—[20]; 4—[22]; 5—
[24]; 6—[25]; 7—[26]; 8—[27]; 9—[28]; 10—[29]; 11—[30]); c) $\delta C_p = (C_p\,[i] - C_p) \times$
$\times\,100/C_p$, % (1—[4]; 2—[31]; 3—[32]; 4—[33]; 5—[34]); d) $\delta\beta_T = (\beta_T\,[i] - \beta_T)\cdot 100/\beta_T$,
% (1—[38]; 2—[39]);

i is the number of the literature source. T, °K.

agree (to within 0.1-0.2%) for methanol and ethanol [1] and 1-propanol [2]. The deviations
not only exceed the estimated error (about 0.05%) but also exceed the total error of the data
being compared. The reasons for this discrepancy remain unclear.

In the final analysis made, we used the results from [11, 13, 22, 24-30].

The coefficients a_i for the speed of sound are shown in Table 1. Figure 1b shows devi-
ations of the initial data from the results of the generalization. It can be seen from the
figure that the deviations lie for the most part within the experimental error indicated in
these studies, except for two empirical points in [25] at temperatures of 213.15 and 294.15
°K. The deviation here is 1%. The possible error of the recommended values of sonic velocity
(see Table 2) can be evaluated as ±0.10% at T ⩾ 273°K. As concerns temperatures below 273°K
the calculated values of sonic velocity have the same error here as the values in [25].

Isobaric Specific Heat. Four studies have investigated the specific heat C_p of 1-penta-
nol in the liquid phase. The study [31] measured C_p in the range from 204 to 298°K with an
error of 0.5%. The most thorough investigation of specific heat on the saturation curve was
made in [32], in which 54 empirical points were obtained at 300-389°K. The error of the data
was evaluated as 0.1-0.2%. Also shown as a function of the temperature from the triple point
(195.56°K) up to 390°K are smoothed values of C_p. The smoothing was done by means of a Cheby-
shev polynomial, the coefficients of which are not presented in the work. The value of C_p at
the triple point was determined by the authors by graphical-analytical extrapolation of their
data. In [33] specific heat was determined in the liquid phase in the temperature range 301-
463°K and pressure range 0.098-0.81 MPa with an error of 0.9%. Specific heat was determined
in [34] in the ranges T = 293-393°K and P = 0.1-60 MPa with an error of 1.5%. The values of
C_p recommended in [4] for the melting and boiling points have errors of 2 and 5%.

We included all of the above-mentioned data in our analysis. The values of C_p on the
saturation curve [32] were corrected for atmospheric pressure. The size of the correction
did not exceed 0.01%.

TABLE 2. Calculated Values of the Density and Sonic Velocity of 1-Pentanol

T	ρ	W	T	ρ	W
194,95	0,8870	1667,7*	303,15	0,80719	1258,9
203,15	0,8805	1631,4	313,15	0,79974	1225,3
213,15	0,8728	1588,8	323,15	0,79213	1191,8
223,15	0,8653	1547,8	333,15	0,78434	1158,4
233,15	0,8578	1508,4	343,15	0,77632	1125,0
243,15	0,8505	1470,2	353,15	0,76804	1091,4
253,15	0,8433	1433,1	363,15	0,75949	1057,7
263,15	0,8361	1397,0	373,15	0,75061	1023,7
273,15	0,8290	1361,7	383,15	0,74140	989,5
283,15	0,8218	1327,0	393,15	0,73183	954,9
293,15	0,81452	1292,7	403,15	0,72188	920,0
298,15	0,81086	1275,8	411,13	0,71365	892,0

*Extrapolation.

TABLE 3. Experimental Studies of Sonic Velocity in 1-Pentanol

Literature source	Number of points	Temperature range, °K	Error, %
[18]	1	297,15	—
[19]	2	275,95; 301,65	—
[20]	1	303,15	0,2
[11]	6	293—343	0,1—0,2
[21]	Equation	273—373	0,52 m/sec*
[13]	Equation	273—353	0,1—0,2
[22]	30	293—583	+2 m/sec
[23]	7	293—413	1
[24]	11	303—403	0,2
[25]	5	198—294	0,5
[26]	4	293—373	0,1
[27]	4	293—393	0,1
[28]	7	293—423	0,1
[29]	3	313—353	0,1—0,2
[30]	1	303,15	0,15

*Error of approximation.

The coefficients a_i for C_p are shown in Table 1. Equation (1) describes the initial values with an error no greater than the error of the experiments (Fig. 1c). The most reliable results [32] are described with deviations not exceeding ±0.10%, except for seven points for which the deviations lie within the range 0.1-0.2%. Since the recommended values of C_p [4] at the melting and boiling points have a large error, we employed graphical-analytical extrapolation of the data in [32, 33] to refine the values of specific heat C_p at the nodal points (Table 4).

The possible error of the recommended values of C_p can be evaluated as ±0.1% in the temperature range 200-390°K and as ±0.2 and ±0.5% on the boundaries of this interval, including the nodal points.

It must be noted that the function $C_p = f(T)$ for liquid 1-pentanol is of a peculiar nature. Results of calculations show that in the temperature range from the melting point to about 338°K an increase in temperature is accompanied by an increase in the derivative dC_p/dT. The derivative then reaches a maximum in the neighborhood of 338°K and decreases appreciably with a further increase in temperature. For example, the values of the derivative at T = 338.15°K and at the boiling point differ by a factor greater than two. This behavior of the temperature dependence of the specific heat of the alcohol is evidently due to intermolecular association [35], since it is known that the latter affects nearly all properties of liquids. This effect is even more pronounced for the higher alcohols [33, 36, 37].

Calculation of the Thermodynamic Properties. In calculating values of enthalpy, for the reference point we took the state of the liquid at the normal melting point ($h_{mp} = 0$). In accordance with this, the formula for the enthalpy of 1-pentanol at the temperature T, with allowance for Eq. (1), has the form

TABLE 4. Calculated Values of the Thermodynamic Properties
of 1-Pentanol

T	C_P	C_V	h	$\beta_S \cdot 10^5$	$\beta_T \cdot 10^5$
194,95	1,8467*	1,493	0	40,54	50,13
203,15	1,8655	1,520	15,22	42,67	52,38
213,15	1,8926	1,555	34,00	45,39	55,25
223,15	1,9238	1,593	53,08	48,24	58,26
233,15	1,9592	1,634	72,49	51,24	61,44
243,15	1,9998	1,678	92,28	54,39	64,82
253,15	2,0467	1,727	112,51	57,73	68,43
263,15	2,1012	1,781	133,24	61,28	72,30
273,15	2,1643	1,842	154,6	65,06	76,47
283,15	2,2365	1,909	176,6	69,11	80,97
293,15	2,3180	1,983	199,3	73,46	85,87
298,15	2,3621	2,023	211,0	75,77	88,49
303,15	2,4083	2,064.	223,0	78,17	91,22
313,15	2,5062	2,149	247,5	83,29	97,11
323,15	2,6100	2,238	273,1	88,87	103,63
333,15	2,7173	2,328	299,7	95,01	110,88
343,15	2,8254	2,417	327,4	101,78	119,00
353,15	2,9313	2,501	356,2	109,31	128,12
363,15	3,0319	2,578	386,0	117,70	138,44
373,15	3,1242	2,645	416,8	127,13	150,19
383,15	3,2059	2,709	448,5	137,77	163,61
393,15	3,2753	2,742	480,9	149,85	179,02
403,15	3,3322	2,771	514,0	163,66	196,79
411,13	3,3695*	2,787	540,7	176,11	212,91

*Extrapolation.

$$h = h_{mp} + \int_{T_{mp}}^{T} C_p dT = 1000 \sum_{i=0}^{6} a_i (\tau^{i+1} - 0.19495^{i+1})/(i+1), \qquad (2)$$

where a_i are coefficients of Eq. (1) for C_p.

Table 4 shows values of enthalpy of 1-pentanol calculated from Eq. (2). The same table gives results of calculation of C_V, β_S, and β_T obtained with interpolation formulas for ρ^{-1}, W, and C_p and known thermodynamic relations. Figure 1d shows deviations of the calculated values of β_T from the experimental data [38, 39]. It can be seen from the figure that the values in [39] are 2% higher on the average. This is within the total error of the compared theoretical and empirical values. A comparison with theoretical values of C_p and C_V [40] at 293-393°K showed that the latter are too low relative to our values by an average of 10-20%.

NOTATION

T, temperature according to MPShT-68°K; T_{mp}, melting point, °K; ρ, density, g/cm^3; W, sonic velocity, m/sec; C_V and C_p, isochoric and isobaric specific heat, respectively, kJ/(kg·K); β_S and β_T, coefficients of adiabatic and isothermal compression, 1/MPa; h_{mp} and h, enthalpy at the melting point and at the temperature T, kJ/kg.

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