CALORIMETRIC C_V–V–T MEASUREMENTS AND THE EQUATION OF STATE FOR n-PROPYL ALCOHOL

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Calorimeteric C_V–V–T measurements have given a new equation of state for n-propyl alcohol, which incorporates qualitative features of the critical point and the stability limit for the homogeneous phase (spinodal).

The pseudospinodal hypothesis [8, 9] provides methods of calculating thermodynamic parameters [1-5] and transport ones [1, 6, 7], and it enables one to give a correct description of the behavior of a substance in the critical and metastable regions.

The pseudospinodal hypothesis indicates that the singular term in the equation for the isochoric specific heat takes the form

$$\frac{\rho C_V^{\text{sin}}}{T} = \frac{P_k}{T_k^2} A_{s0} (t_s^{-\alpha} - A_{s1} X_{\text{Oc}}^{2\beta} (\Delta\rho)^2 t_s^{\gamma-2}), \tag{1}$$

where $t_s = (T - T_s(\rho))/T_k$; $X_{\text{oc}} = B_c^{-1/\beta}$; $T_s(\rho)$ is the pseudospinodal curve.

We select an expression for $T_s(\rho)$:

$$T_s(\rho) = T_k \left[1 - \sum_{i=0}^{9} X_{is}^{\pm} |\Delta\rho|^{\varepsilon_i} \right]. \tag{2}$$

It is readily seen that (1) completely reproduces the power laws of scale theory [10] with this form for (2) on the asymptotic approach $T \to T_k$ and $\rho \to \rho_k$ on different lines on the thermodynamic surface (critical isochor, critical isotherm, saturation line). It has been shown that the form of (1) for C_V gives a qualitatively correct description [2] also of the structural features of P, ρ, T surface near the critical point.

We take the regular part of the equation for C_V in the form

$$C_V^{\text{reg}} = \frac{P_k}{\rho_k T_k} \sum_{j=1}^{6} \sum_{i=3}^{K_j} b_{ji} \omega^j \tau^{-i}. \tag{3}$$

The coefficients in (1) and (3) are determined by minimizing

$$S(A_{s0}, X_{is}^{\pm}, b_{ji}) = \sum_{i=1}^{M} W_i (C_{Vi}^{\text{en}} - C_{Vi}^{\text{sin}} - C_{Vi}^{\text{reg}})^2, \tag{4}$$

where $W_i = 1/\sigma_i^2$ is the weight of experimental point i as taken from the method of [11] and σ_i is the error variance $(C_{Vi}^{\text{en}} - C_{Vi}^{\text{cal}})$.

To minimize (4), we used 530 experimental values of C_V in the following ranges in specific volume and temperature: $1.457 \leqq V\ (\text{cm}^3/\text{g}) \leqq 10.026$ and $T_c(V) \leqq T(K) \leqq 658$. The coefficients in (1)-(3) derived from the reference set of C_V, V, and T data for n-propyl alcohol with minimization in (4) are given in Tables 1-3; the performance in the description of these data is illustrated by the histogram for the deviations (Fig. 1). The value δC_V^{en} indicated on the histogram has been calculated for the complete set of 530 points.

As reference curve we take the phase-equlibrium line $T_c(V)$ and use a standard thermodynamic relation to get the thermal equation of state from (1)-(3) as

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TABLE 1. Coefficients in the Singular Part of (1)

$A_{s0}=11,12345$	$\alpha=0,112$	$P_k=5,17$ MPa
$A_{s1}=0,52283$	$\beta=0,324$	$T_k=536,56$ °K
$X_{0c}=0,13136$	$\gamma=1,24$	$\rho_k=272,85$ kg/m³

TABLE 2. Coefficients in the Regular Part of (3) for the Isochoric Specific Heat of Propyl Alcohol

j	i	b_{ji}	j	i	b_{ji}
1	3	$0,12858098\cdot10^{4}$	3	4	$0,14247010\cdot10^{3}$
1	4	$-0,72091983\cdot10^{3}$	3	5	$-0,26179826\cdot10^{3}$
1	5	$-0,10924964\cdot10^{4}$			
1	6	$-0,35143243\cdot10^{3}$	4	3	$0,56840981\cdot10^{3}$
1	7	$0,99245674\cdot10^{3}$	4	4	$0,52490270\cdot10^{3}$
			4	5	$-0,65491396\cdot10^{3}$
2	3	$-0,43720945\cdot10^{3}$			
2	4	$0,11182753\cdot10^{3}$	5	3	$-0,43055578\cdot10^{3}$
2	5	$0,53121053\cdot10^{3}$	5	4	$0,24071513\cdot10^{2}$
2	6	$0,49694651\cdot10^{3}$	5	5	$0,27130452\cdot10^{3}$
2	7	$-0,43739373\cdot10^{3}$			
			6	3	$0,10260060\cdot10^{3}$
3	3	$-0,49041702\cdot10^{3}$	6	4	$-0,743357847\cdot10^{2}$
			6	5	$-0,12976357\cdot10^{2}$

TABLE 3. Coefficients in (2) for the Pseudospinodal Curve and Coexistence Curve

i	$\rho>\rho_k$		$\rho<\rho_k$	
	X_{is}^{+}	X_{ic}^{+}	X_{is}^{+}	X_{ic}^{-}
0	$0,459760\cdot10^{0}$	$0,131360\cdot10^{0}$	$0,45976\cdot10^{0}$	$0,131360\cdot10^{0}$
1	$0,134944\cdot10^{0}$	$0,385555\cdot10^{-1}$	$-0,227479\cdot10^{1}$	$-0,649940\cdot10^{0}$
2	$-0,117173\cdot10^{1}$	$-0,334781\cdot10^{0}$	$0,217978\cdot10^{1}$	$0,622795\cdot10^{0}$
3	$0,649257\cdot10^{0}$	$0,185502\cdot10^{0}$	$0,330098\cdot10^{1}$	$0,943136\cdot10^{0}$
4	$0,109001\cdot10^{1}$	$0,311430\cdot10^{0}$	$-0,285166\cdot10^{1}$	$-0,814761\cdot10^{0}$
5	$-0,034548\cdot10^{0}$	$-0,987080\cdot10^{-2}$	$-0,306561\cdot10^{1}$	$-0,875887\cdot10^{0}$
6	$-0,204209\cdot10^{0}$	$-0,583456\cdot10^{-1}$	$0,560837\cdot10^{1}$	$0,160239\cdot10^{1}$
7	$-0,102408\cdot10^{1}$	$-0,292594\cdot10^{0}$	$-0,223951\cdot10^{1}$	$-0,639861\cdot10^{0}$
8	$-0,681132\cdot10^{0}$	$-0,194609\cdot10^{0}$	$-0,113805\cdot10^{1}$	$-0,325156\cdot10^{0}$
9	$0,104434\cdot10^{1}$	$0,298382\cdot10^{0}$	$0,156932\cdot10^{1}$	$0,448378\cdot10^{0}$

$$\pi = \pi_c(\tau_c(\rho)) + \left(\frac{\partial\pi}{\partial\tau}\right)_c \Delta\tau_c + \pi_{reg} + \Delta\pi_{irr}, \tag{5}$$

where

$$\pi_{reg} = \sum_{j=1}^{6}\sum_{i=3}^{K_j}\left(\frac{j}{i}\right) b_{ji}\omega^{1+j}\left[\frac{\tau^{1-i}-\tau_c^{1-i}}{(1-i)} - \tau_c^{-i}\Delta\tau_c\right];$$

$$\Delta\pi_{irr} = A_{s0}\left[\frac{\Delta\tau_s^{2-\alpha}-\Delta\tau_{sc}^{2-\alpha}}{(1-\alpha)(2-\alpha)} - \frac{\Delta\tau_{sc}\Delta\tau_c}{(1-\alpha)} - A_{s1}X_{0c}^{2\beta}(\Delta\rho)^2F_1\right] +$$

$$+ A_{s0}\omega^{-1}\left[\frac{\Delta\tau_s^{1-\alpha}-\Delta\tau_{sc}^{1-\alpha}}{(1-\alpha)}\,t_s' - \Delta\tau_{sc}^{-\alpha}\Delta\tau_c t_s' + 2A_{s1}X_{0c}^{2\beta}\omega^2\,\Delta\rho F_1 - A_{s1}X_{0c}^{2\beta}(\Delta\rho)^2 t_s' F_2\right];$$

$$F_1 = \frac{\Delta\tau_s^{\gamma}-\Delta\tau_{sc}^{\gamma}}{\gamma(\gamma-1)} - \frac{\Delta\tau_{cs}^{\gamma-1}\Delta\tau_c}{(\gamma-1)};$$

$$F_2 = \frac{\Delta\tau_s^{\gamma-1}-\Delta\tau_{sc}^{\gamma-1}}{(\gamma-1)} - \Delta\tau_{sc}^{\gamma-2}\Delta\tau_c;$$

where $\Delta\pi_{irr}$ is the curvilinear part of the equation of state corresponding to the irregular term in (1), with π_c, $\tau_c(\rho)$ the equations for the vapor-pressure curve and the coexistence curve, and $(\partial\pi/\partial\tau)_c$ the partial derivative of the reduced pressure with respect to the reduced temperature on the coexistence curve from the side of the single-phase region.

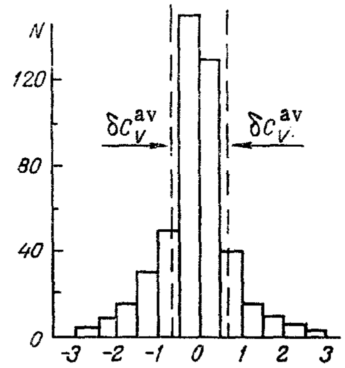

Fig. 1. Histogram for the deviations of the observed isochoric specific heat of n-propyl alcohol from the calculated values.

TABLE 4. Coefficients in (6) ($\Delta = 0.5$)

i	X_i	i	X_i
1	$0{,}259790 \cdot 10^{2}$	6	$0{,}227186 \cdot 10^{0}$
2	$-0{,}527378 \cdot 10^{1}$	7	$-0{,}300494 \cdot 10^{2}$
3	$0{,}995247 \cdot 10^{0}$	8	$0{,}155645 \cdot 10^{2}$
4	$-0{,}827189 \cdot 10^{1}$	9	$0{,}358681 \cdot 10^{2}$
5	$-0{,}774546 \cdot 10^{1}$	10	$0{,}269137 \cdot 10^{2}$

TABLE 5. Coefficients in (8)

i	Y_i^{+} $(\rho>\rho_k)$	Y_i^{-} $(\rho<\rho_k)$	i	Y_i^{+} $(\rho>\rho_k)$	Y_i^{-} $(\rho<\rho_k)$
1	$0{,}12285705 \cdot 10^{4}$	$-0{,}45006606 \cdot 10^{3}$	7	$-0{,}84806141 \cdot 10^{3}$	$-0{,}48855787 \cdot 10^{1}$
2	$0{,}58832476 \cdot 10^{3}$	$0{,}86248916 \cdot 10^{2}$	8	$-0{,}34844294 \cdot 10^{3}$	$-0{,}32752811 \cdot 10^{0}$
3	$0{,}84795402 \cdot 10^{1}$	$0{,}73332492 \cdot 10^{1}$	9	$-0{,}12075210 \cdot 10^{3}$	$-0{,}19725931 \cdot 10^{-1}$
4	$-0{,}15599185 \cdot 10^{4}$	$0{,}51205206 \cdot 10^{3}$	10	$-0{,}38607973 \cdot 10^{2}$	$-0{,}11202897 \cdot 10^{-2}$
5	$0{,}57992722 \cdot 10^{3}$	$-0{,}32636607 \cdot 10^{3}$	11	$-0{,}11817937 \cdot 10^{2}$	$-0{,}61402886 \cdot 10^{-4}$
6	$-0{,}12819169 \cdot 10^{4}$	$-0{,}57798635 \cdot 10^{2}$	12	$-0{,}35262614 \cdot 10^{1}$	$-0{,}32889476 \cdot 10^{-5}$

For $\pi_c(\tau_c)$ we used an expression implied by the extended law from scale theory [12]:

$$\pi_c = X_1 t_c^{2-\alpha} + X_2 t_c^{2-\alpha+\Delta} + \sum_{i=3}^{10} X_i t_c^{i-3}. \tag{6}$$

The values of $(\partial\pi/\partial\tau)_c$ on the coexistence curve were calculated from the thermodynamic relation

$$\left(\frac{\partial\pi}{\partial\tau}\right)_c = \left(\frac{d\pi_c}{d\tau}\right)\left(1 + \frac{\Delta C_V}{\sigma}\right), \tag{7}$$

where ΔC_V is the step in the specific heat on traversing the phase-equilbrium boundary, $\sigma = -(\tau/\rho)(d\pi_c/d\tau)(d\rho/d\tau)_c$; $d\pi_c/d\tau$ is the total derivative of the reduced pressure for the saturated vapor with respect to the reduced temperature, and $(d\rho/d\tau)_c$ is the derivative of the density on the coexistence curve with respect to the reduced temperature. It is evident from (7) that $(\partial\pi/\partial\tau)_c$ on the coexistence curve has two values corresponding to different values of $(\partial\rho/d\tau)_c$ on the vapor and liquid sides.

The values of $(\partial\pi/\partial\tau)_c$ derives from (7) are described by

$$\left(\frac{\partial\pi}{\partial\tau}\right)_c = Y_1^{\pm} t_c^{1-\alpha} + Y_2^{\pm} t_c^{1-\alpha+\Delta} + \sum_{i=3}^{12} Y_i^{\pm} t_c^{i-3}, \tag{8}$$

where the superscript + in $Y_i^{\pm}$ corresponds to $\rho > \rho_k$ and the superscript − to $\rho < \rho_k$.

Tables 4 and 5 give the coefficients in (6) and (8); when we determined the coefficients in (6), we used the experimental data of [13, 14] for the range 400-536°K as the reference set.

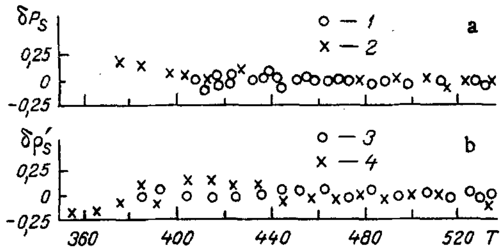

Fig. 2. Deviations of the observed values for the saturation vapor pressure [13, 14] (a) and density of the boiling liquid [13, 15] (b) from the calculatted values for n-propyl alcohol: 1) [13]; 2) [14]; 3) [13]; 4) [15]. δP_s; $\delta \rho_s'$, %; T, °K.

TABLE 6. Thermodynamic Parameters of Propyl Alcohol: V in m³/kg, P in MPa, S in kJ/kg, and H in kJ/kg

$V\cdot10^{-3}$	P	S	H
T = 450 °K			
1,55	4,20	1,5018	551,07
1,50	13,41	1,4709	551,27
1,45	27,39	1,4389	556,89
T = 475 °K			
1,65	5,18	1,7041	646,15
1,60	10,70	1,6860	645,68
1,55	18,34	1,6630	647,49
1,50	29,13	1,6325	649,56
1,45	47,55	1,5982	659,79
T = 500 °K			
1,90	2,34	1,9507	761,21
1,85	3,69	1,9376	757,40
1,80	5,59	1,9251	754,65
1,75	8,24	1,9042	748,43
1,70	11,88	1,8833	744,40
1,65	16,80	1,8543	738,51
1,60	23,39	2,8365	739,30
1,55	32,26	1,8136	742,49
1,50	45,46	1,7820	746,92
T = 525 °K			
11,0	3,84	2,6514	1129,40
10,0	4,00	2,6271	1117,93
9,0	4,16	2,6010	1105,50
8,0	4,29	2,5661	1087,81
2,2	4,67	2,1636	875,40
2,1	5,80	2,1397	865,10
2,0	7,17	2,1173	856,46
1,95	8,36	2,1038	851,66
1,90	9,91	2,0928	848,37
1,85	11,92	2,0789	845,02
1,80	14,55	2,0659	842,93
1,75	18,00	2,0447	837,53
1,70	22,52	2,0237	834,44
1,65	28,43	1,9944	829,51
1,60	36,20	1,9759	831,23
1,55	46,85	1,9512	835,59
T = 550 °K			
11,0	4,33	2,7873	1207,70
10,0	4,57	2,7667	1198,55
9,0	4,83	2,7455	1189,15
8,0	5,10	2,7160	1175,30
7,0	5,39	2,6772	1155,53
6,0	5,69	2,6368	1134,76
5,0	5,94	2,5867	1100,50
4,0	6,10	2,5197	1066,67
3,8	6,13	2,5038	1060,06
3,6	6,27	2,4873	1061,14
T=550 °K			
3,4	6,33	2,4693	1046,39
3,2	6,43	2,4525	1031,84
3,0	6,57	2,4302	1018,20
2,8	6,80	2,4052	1006,44
2,6	7,94	2,4014	1011,80
2,4	8,04	2,3311	973,27
2,2	9,84	2,2975	958,71
2,0	13,88	2,2502	941,28
1,9	17,63	2,2258	934,50
1,8	23,62	2,1986	930,57
1,7	33,50	2,1548	923,57
1,6	50,19	2,1022	921,48
T = 600 °K			
11,0	5,16	3,0212	1351,23
10,0	5,50	3,0034	1343,73
9,0	5,89	2,9865	1337,08
8,0	6,36	2,9639	1327,19
7,0	6,97	2,9315	1312,65
6,0	6,78	2,8991	1297,90
5,0	8,78	2,8550	1268,70
4,0	9,99	2,7858	1234,91
3,8	10,29	2,7677	1227,33
3,6	11,11	2,7485	1228,48
3,4	11,57	2,7272	1212,23
3,2	12,15	2,7067	1196,12
3,0	12,84	2,6807	1180,87
2,8	13,65	2,6525	1167,63
2,6	14,75	2,6204	1156,00
2,4	16,56	2,5764	1134,68
2,2	20,01	2,5450	1123,33
2,0	21,13	2,4995	1111,05
1,90	33,56	2,4734	1107,07
1,80	43,68	2,4405	1105,63
1,75	50,84	2,4136	1101,96
T = 650 °K			
9,0	6,79	3,2028	1480,28
8,0	7,40	3,1824	1472,03
7,0	8,29	3,1532	1460,38
6,0	9,62	3,1243	1449,63
5,0	11,53	3,0826	1424,62
4,0	14,16	3,0126	1393,25
3,8	14,79	2,9940	1385,79
3,6	16,34	2,9743	1388,34
3,4	17,19	2,9526	1372,18
3,2	18,21	2,9321	1356,35
3,0	19,32	2,9066	1341,46
2,8	20,47	2,8771	1328,70
2,6	21,91	2,8499	1317,98
2,4	24,41	2,8086	1298,56
2,2	29,74	2,7785	1290,60
2,0	41,85	2,7277	1283,01
1,95	46,87	2,7103	12,81
1,90	53,14	2,6932	1281,49

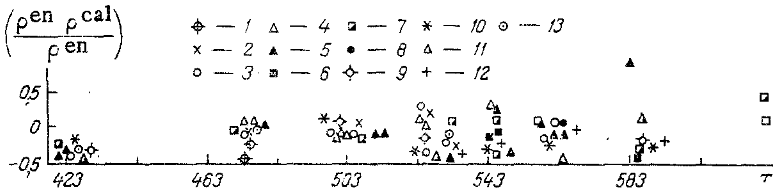

Fig. 3. Deviations of the observed densities [16, 17] of n-propyl alcohol from the calculated ones (P in bar): 1) 25; 2) 35; 3) 50; 4) 75; 5) 99; 6) 69; 7) 146.3; 8) 194.6; 9) 243; 10) 291; 11) 388; 12) 485; 13) 170.4.

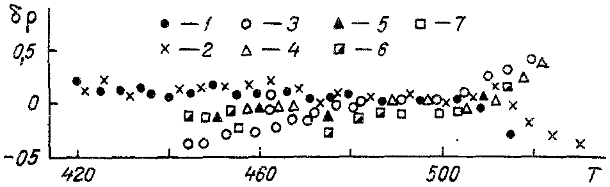

Fig. 4. Deviations of observed densities [18] of n-propyl alcohol from the calculated values (P in bar): 1) 66.7; 2) 60; 3) 53; 4) 73.4; 5) 46.7; 6) 40; 7) 33.3. $\delta\rho$, %.

The equation for the coexistence curve $\tau_c(\rho)$ appearing in (5) was taken in a form analogous to the pseudospinodal equation of (2); the coefficients were determined from the T_c, ρ_c, and ρ_s data of [14, 15] in the range 390-536°K and are given in Table 3.

Figures 2-4 show the deviations of the experimental data [13-18] from the calculated densities; Table 6 gives the calculated values for some thermodynamic parameters of n-propyl alcohol.

NOTATION

B_c, amplitude of coexistence curve; $_0$, β, γ, Δ, critical indices; $\Delta\rho = (\rho - \rho_k)/\rho_k$; $\varepsilon_0 = 1/\beta$, $\varepsilon_1 = (1 + \Delta)/\beta$, $\varepsilon_2 = \delta$, $\varepsilon_3 = 2/\beta - 1$, $\varepsilon_4 = (1 + 2\Delta)/\beta$, $\varepsilon_5 = (\beta + \delta\Delta)/\beta$, $\varepsilon_6 = 2(\delta - 1)$, $\varepsilon_7 = (2 + \Delta)/\beta - 1$; $\varepsilon_8 = (3 - \alpha)/\beta - 2$, $\varepsilon_9 = 3/\beta - 2$; $\tau = T/T_k$; $\omega = \rho/\rho_k$; $\pi = P/P_k$; $\tau_c(\rho) = T_c(\rho)/T_k$, coexistence curve; $\Delta\tau_s = \tau - \tau_s(\rho)$; $\Delta\tau_c = \tau - \tau_c(\rho)$; $\Delta\tau_{sc} = \tau_c(\rho) - \tau_s(\rho)$; $t_c = |\tau_c(\rho) - 1|$; $t_s' = -(d\tau_s/d\rho)$. Subscripts: c, value of corresponding quantity on coexistence curve; s, value on pseudospinodal curve.

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DEBYE TEMPERATURE IN THE HIGH-TEMPERATURE LIMIT AND ANHARMONIC COMPONENT OF THE HEAT CAPACITY OF VANADIUM

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Values are presented for the Debye temperature in the high-temperature limit and the anharmonic component of the specific heat of vanadium at constant volume, based on heat-capacity measurements over the range 77-300°K.

In the high-temperature limit the Debye temperature characterizes the mean frequency $\langle\omega\rangle$ of the phonon spectrum [1] and is defined by the expression

$$\Theta_\infty^2 = \frac{5\hbar^2}{3k^2}\langle\omega^2\rangle. \qquad (1)$$

To determine Θ_∞ by the absolute adiabatic method, the heat capacity of single-crystal vanadium was measured over the temperature range 77-300°K. Measurements were performed by a method similar to that used for study of the heat capacity of scandium, yttrium, and lanthanum [2], to an accuracy of 2% over the indicated temperature range. The specimen studied had a ratio of resistances at T = 300°K and T = 6°K (ρ_{300}/ρ_6) equal to 30.

The curve of the temperature dependence of heat capacity of vanadium showed anomalies in the form of a peak at a temperature of 210°K with ΔC_p = 2.5 J/°K·mole and an increase in C_p by 3-4% at 240°K.

The specific heat of vanadium at constant volume C_V was calculated from the mean values of specific heat at constant pressure C_p. In calculating C_V the temperature dependence of the volume expansion coefficient β of vanadium given in [3] was used with the electronic component of the specific heat C_{el} with consideration of electron—phonon interaction from [4]. Using the values of the lattice component of specific heat thus obtained ($C_{lat} = C_V - C_{el}$) the temperature dependence of the Debye temperature of vanadium Θ(T) (Fig. 1, curve 1) was calculated from the relationship

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