THE CALCULATION OF THE THERMODYNAMIC PROPERTIES OF LIQUID ARGON

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Analysis and correlation of experimental p, v, and T data for liquid argon, limited to a pressure of 300 bar, and their extrapolation to pressures of 500 bar, yields a reference network of isotherms and isobars correlated to the saturation and freezing curves. An equation of state is derived to describe with sufficient accuracy the experimental and reference data in the temperature interval 83.78–170° K at pressures up to 500 bar. Results are presented for the comparison of the calculated quantitites with the experimental and tabular data on the thermodynamic properties of liquid argon.

An insignificant number of papers have been devoted to experimental and calculational-theoretical investigations of the thermodynamic properties of fluids. This pertains in full measure to liquid argon for which until 1958 there were no experimental thermal data.

The experimental p, v, and T data for liquid argon were first derived by Michels, Levelt, and De Graaff [1] on the −122.5, −125, −130, −135 and −140° C isotherms; in addition, 11 experimental points for 10 different temperatures in the interval from −124 to −155° C have been obtained. The maximum pressure on the isotherms diminished as the temperature dropped (from 301 atm at −122.5° C to 157 atm for −140° C). The isotherms of the liquid were described by equations of the form

$$pv = A + B\rho + C\rho^3 + D\rho^5, \tag{1}$$

whose maximum error is 0.1% with respect to pv. The coefficients of the equations do not exhibit a smooth dependence on temperature.

Rogovaya and Kaganer [2] soon thereafter investigated the compressibility of argon in the temperature interval from −183 to 0° C at pressures to 200 atm; the experimental data are shown on 11 isotherms of which three (−135.08, −150.08 and −183.02° C) pertain to the region of the liquid. The authors estimate the possible error in their experimental data at ±0.05% with respect to density. At the same time, they note that individual experimental points deviate by 0.5% from the Holborn and Otto data [3], and from those of Michels and his co-authors [1]. The existence of divergence relative to reliable data [1, 3] raises doubt as to the validity of the evaluation of accuracy in the data presented in [2].

Van Itterbeek and Verbeke [4] initially determined the density of liquid argon in a narrow range of temperatures for four isotherms (86.637, 87.915, 89.13, and 90.55° K) for pressures below 150 kgf/cm². Van Itterbeek, Verbeke, and Staes [5] published data on the density of liquid argon for 11 isotherms in the temperature interval 90.13–148.25° K, increasing the maximum pressure in the experiments to 300 kgf/cm². These measurement results served as the basis for the author's [5] comparison of equations of state having the form

$$v = A(T) + B(T)p + C(T)p^2 + D(T)p^3 + E(T)p^4 + F(T)p^5, \tag{2}$$

where the temperature functions are given as polynomials of T in degrees from zero to five, inclusively.

From this brief review we see that among the experimental p, v, and T data of the various authors, the most detailed are the data of Van Itterbeek and his co-workers [4, 5], these data in their entirety encompassing virtually the entire range of temperatures from the triple point to the critical. The results of [4] and [5] at a temperature of 90° K agree with each other with an accuracy of 0.05–0.10%; however, on the 134.40 and 136.02° K isotherms the quantities from [5] at a number of points are underestimated by 0.3–0.4%, which can be seen in the construction of the isobars. When compared with the data of other authors for a wide temperature interval the results of [4, 5] show no systematic errors, unlike the analogous data of Van Itterbeek and Verbeke [4,6,7] for nitrogen and oxygen.

The density values derived by Michels, Levelt, and De Graaff [1] for the 133.15 and 148.15° K isotherms are higher than the data of [5] by 0.2%, while at temperatures of 138.15 and 143.15° K they fundamentally agree with these, accurate to ±0.1%; only two points [1] at 143.15° K and at pressures of up to 70 bar are reduced by 0.4–0.5%. The data of Rogovaya and Kaganer [2] on the 138.12° K isotherm virtually coincide with the quantities of [5], but in the region of lower temperatures are systematically lower than the latter (by 0.2% at 123.07° K and by 0.3–0.4% at 90.13° K). The results of [2] for the liquid are in completely satisfactory agreement with the data of [1], although in the vicinity of the critical region between the two groups of data there are the divergences noted in [2].

The selection of the reference density values for liquid argon was initially carried out to the maximum pressure of 300 bar attained in the experiments. The network of reference data was based on the Van Itterbeek data and those of his co-authors [4,5], while for the region of temperatures encompassed by the Michels, Levelt, and DeGraaff [1] experiment, the results of these investigators were also used. The supercritical isobars of the reference network were coordinated with the theoretical data [8] for a gas. In the low-temperature region the isobars for the liquid were extrapolated slightly to the freezing curve. In

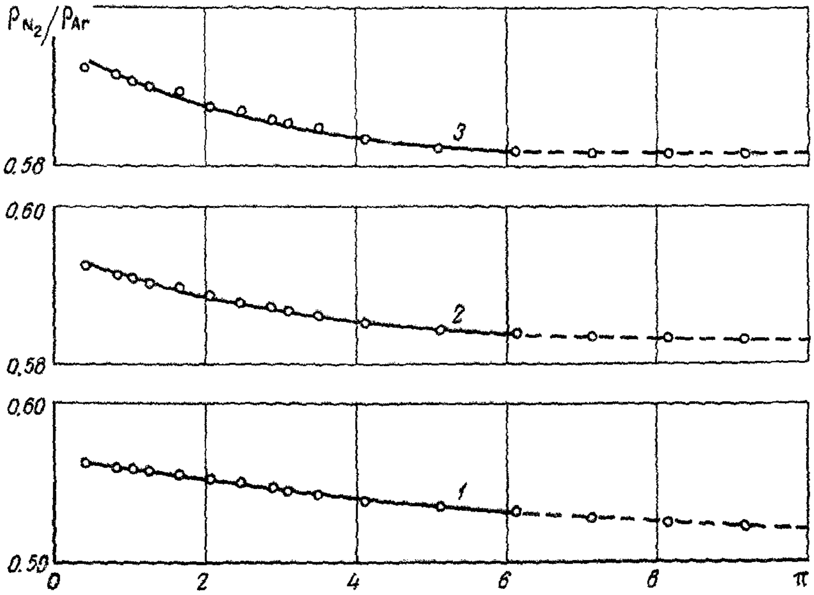

Fig. 1. Density ratios of liquid nitrogen and argon at equal reduced temperatures and pressures: 1) τ = 0.6586; 2) 0.7378; 3) 0.8170; extrapolated portions of the curves are indicated by dashed line.

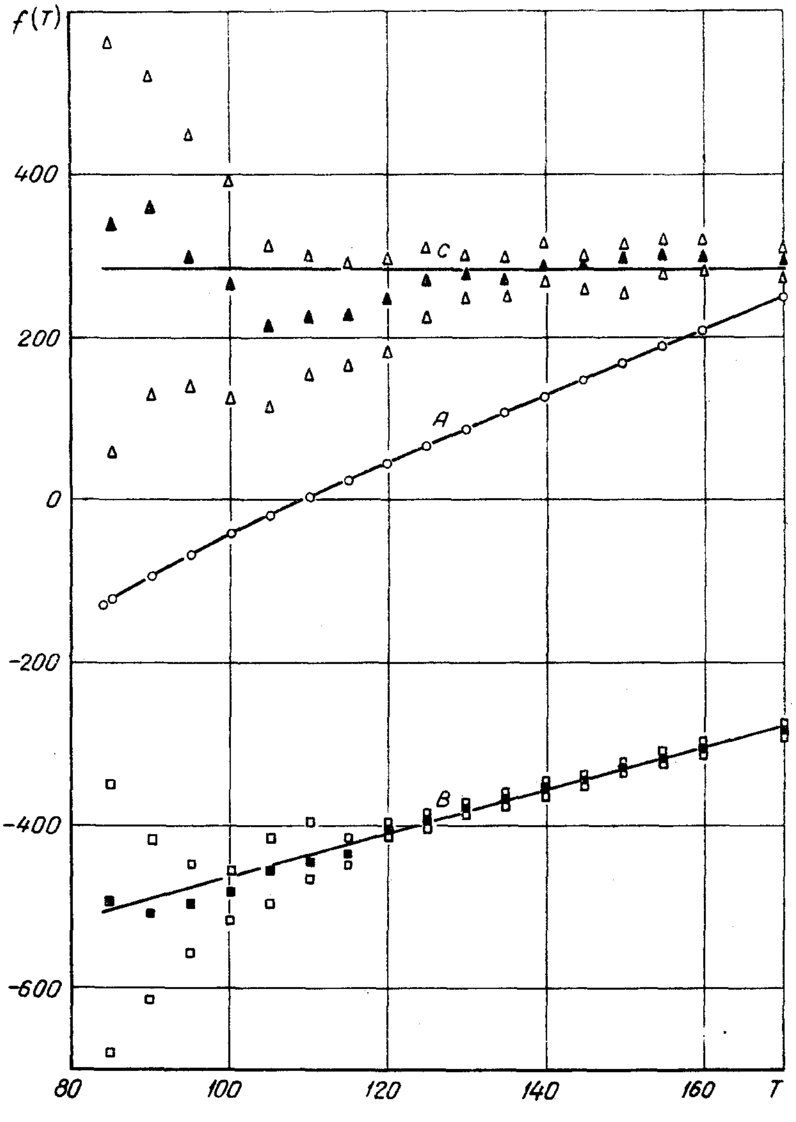

Fig. 2. Temperature functions of state equation for liquid argon. Dark points refer to optimal values of the functions providing the best satisfaction of the initial data; light points refer to limit values of the functions corresponding to maximum deviations from the reference data of 0.2 per cent; T° K; $f(T)$, temperature functions oi formula (3).

Table 1

Comparison of Theoretical Values for Argon Density ρ (kg/dm^3) (Line 2) with the Reference Data (Line 1)

P, bar	T, °K								
	90	100	110	120	130	140	150	160	170
20	1.382	1.317	1.247	1.167					
	1.382	1.317	1.247	1.166					
40	1.389	1.325	1.258	1.182	1.092	0.967			
	1.388	1.325	1.258	1.182	1.090	0.965			
60	1.395	1.333	1.267	1.196	1.113	1.009			
	1.394	1.333	1.268	1.196	1.112	1.007			
80	1.400	1.340	1.277	1.208	1.131	1.039			
	1.399	1.340	1.278	1.208	1.131	1.038			
100	1.406	1.348	1.285	1.219	1.147	1.064	0.963		
	1.405	1.347	1.286	1.221	1.147	1.063	0.963		
120	1.411	1.354	1.294	1.230	1.161	1.084	0.995		
	1.410	1.354	1.295	1.231	1.162	1.084	0.995		
140	1.416	1.361	1.302	1.241	1.174	1.102	1.021		
	1.415	1.360	1.303	1.241	1.175	1.102	1.021		
170	1.425	1.370	1.315	1.255	1.192	1.125	1.053	0.973	
	1.423	1.369	1.314	1.256	1.193	1.126	1.053	0.974	
200	1.432	1.379	1.326	1.269	1.209	1.146	1.079	1.009	
	1.430	1.378	1.324	1.269	1.210	1.146	1.080	1.009	
250	1.443	1.393	1.343	1.289	1.233	1.175	1.116	1.054	0.991
	1.441	1.391	1.341	1.288	1.234	1.176	1.116	1.054	0.992
300		1.406	1.358	1.307	1.255	1.202	1.146	1.090	1.034
		1.404	1.356	1.306	1.255	1.202	1.147	1.091	1.034
350		1.419	1.372	1.324	1.274	1.223	1.172	1.120	1.069
		1.416	1.369	1.322	1.274	1.224	1.173	1.121	1.069
400		1.430	1.384	1.338	1.291	1.243	1.195	1.146	1.098
		1.427	1.382	1.337	1.291	1.243	1.196	1.147	1.098
450		1.440	1.397	1.352	1.306	1.261	1.215	1.170	1.124
		1.437	1.394	1.351	1.306	1.261	1.216	1.170	1.124
500		1.450	1.408	1.365	1.321	1.277	1.234	1.190	1.147
		1.447	1.405	1.363	1.321	1.278	1.234	1.191	1.147
$\delta\rho_{av}$ %	0.09	0.13	0.13	0.09	0.07	0.10	0.06	0.08	0.04
$\delta\rho_{max}$, %	0.14	0.21	0.22	—0.16	0.18	0.21	—0.09	—0.10	—0.10

this connection it would be advantageous to examine the existing data for the cited curve.

The melting (freezing) point of argon as a function of pressure in the moderate-pressure region of interest to us has been investigated by Clusius and Weigand [9] (up to 200 atm). Michels and Prins [10] then derive experimental data for the argon melting-point curve at pressures from 0.68–1497 atm. The results of [9,10] agree within limits of 1 atm and have been accepted by us as reference data. Unfortunately, for the specific volume of the argon on the freezing curve we have presented only the four values given in the work by Bridgman [11] for pressures of 1, 2000, 4000, and 6000 kgf/cm^2, from which the value of 0.702 dm^3/kg for p – 1 kgf/cm^2 is in unsatisfactory agreement with the magnitude of the specific volume v' = 0.7067 dm/kg^3 of the liquid at the triple point, obtained in [8] on the basis of the Mathias, Crommelin, and Kamerlingh Onnes data in [12]. The argon density on the freezing curve for the given pressures was therefore determined by extrapolation of the isobars of the reference network to the freezing temperatures so that a smooth curve in density-temperature coordinates was obtained.

For extrapolation of data to the region of higher pressures (to 500 bar) we use the law of corresponding states and experimental p, v, and T data for liquid nitrogen [13], encompassing a wide range of the reduced parameters. We analyze the ratios of the liquid nitrogen and argon densities for identical reduced temperatures of $\tau = T/T_k$ and pressures $\pi = p/p_k$. On nine of the subject's isotherms in the interval $\tau = 0.5727–0.9755$ and $\pi = 0.408–6.125$ these ratios vary as a function of pressure by 1–2%, where the interval of their variations on the isotherms increases as temperature rises. This can be seen from Fig. 1 which shows the nitrogen and argon density ratios on three isotherms.

The density ratios ρ_{N_2}/ρ_{Ar} on the isotherms were extrapolated to pressures of 500 bar. The argon densities were then calculated and smoothed over the isobars. The isobars were coordinated with the data of [8] for the gaseous phase and extrapolated to the freezing curve. The processing of the isotherm and isobar data ensured smoothness for the extrapolated portion of the surface of the liquid-argon state. Since the ρ_{N_2}/ρ_{Ar} ratios on most of the isotherms vary within rather narrow limits, it may be assumed that the error in the extrapolated and smooth values of the liquid-argon densities lies within limits of 0.2–0.4%.

In accordance with the earlier derived recommendations [14] for the analytical presentation of the reference network of thermal data we employed the equation of state

$$p = A(T)\rho^2 + B(T)\rho^4 + C(T)\rho^6, \tag{3}$$

containing even powers of density.

The temperature functions of Eq. (3) were defined according to a method described in detail in [14]; these are given in Fig. 2. In the determination of the these functions on the postcritical isotherms (155–170° K) we used data for high values of the reduced density ($\rho/\rho_k > 1.8$) which can be described entirely by Eq. (3). After analytical presentation of the functions A(T) and B(T) the equation of state for argon assumed the form

$$p = (-465.6 + 4.157T + 4274 \cdot 10^2 T^{-2} - 360553 \cdot 10^4 T^{-4})\rho^2 - (733.5 - 2{,}67T)\rho^4 + 287\rho^6. \tag{4}$$

In (4) the pressure is expressed in units of bar and density is expressed in units of kg/dm^3.

The reliability of the derived equation of state for argon was tested by comparison of the theoretical density values with the reference and experimental data. The deviations in the theoretical data from the reference data for 138 of 181 points does not exceed 0.001 kg/dm^3 (0.07–0.10%) and reaches 0.20–0.22% at only 17 points. The mean square deviation of the theoretical quantities from the reference data amounts to 0.10%. This is illustrated in Table 1 in which the results of the comparison between the theoretical and reference quantities on a number of isotherms are presented.

Without presenting the tables showing the calculated density values for liquid argon in comparison with the experimental quantities cited earlier by the authors, we will point out that for 81 points out of 113, according to the Van Itterbeek, Verbeke, and Staes [5] data, the divergences do not exceed 0.2%. At 19 points the deviations amount to 0.3–0.4%, but ten of these are found on the 134.40 and 136.02° K isotherms, where the data of [5] show an error of the same order, which we noted earlier in the analysis of the original quantities. In the lower-temperature region (86.6–90.5° K), covered by the experiments [4], the divergence between the calculated density values and the experimental values amount to 0.04–0.17%.

The overwhelming majority of experimental data from Rogovaya and Kaganer [2] and Michels and co-

Table 2

Comparison with the Reference Data of [8] of the Theoretical Values of Liquid-Argon Density on the Saturation Curve

T, °K	P, bar	ρ, kg/dm^3		$\delta\rho$, %	T, °K	P, bar	ρ, kg/dm^3		$\delta\rho$, %
		[8]	calc.				[8]	calc.	
85	0.7898	1.407	1.407	0	120	12.11	1.160	1.160	0
90	1.337	1.374	1.376	—0.15	125	15.78	1.115	1.114	0.09
95	2.134	1.342	1.343	—0.07	130	20.20	1.066	1.064	0.19
100	3.242	1.309	1.310	—0.08	135	25.45	1.009	1.007	0.20
105	4.727	1.276	1.276	0	140	31.64	0.942	0.942	0
110	6.653	1.239	1.240	—0.08	145	38.90	0.853	0.869	—1.84
115	9.088	1.201	1.201	0					

Table 3

Comparison with the Reference Data of the Theoretical Argon Density Values on the Freezing Curve

P, bar	T, °K	ρ, kg/dm^3		$\delta\rho$, %	P, bar	T, °K	ρ, kg/dm^3		$\delta\rho$, %
		ref.	calc.				ref.	calc.	
10	84.04	1.416	1.416	0	170	87.95	1.435	1.434	0.07
20	84.28	1.417	1.417	0	200	88.69	1.438	1.437	0.07
40	84.78	1.419	1.420	−0.07	250	89.88	1.443	1.442	0.07
60	85.27	1.422	1.422	0	300	91.09	1.449	1.447	0.14
80	85.76	1.424	1.424	0	350	92.23	1.454	1.452	0.14
100	86.25	1.426	1.426	0	400	93.40	1.459	1.457	0.14
120	86.75	1.429	1.429	0	450	94.54	1.464	1.461	0.21
140	87.24	1.432	1.431	0.07	500	95.71	1.468	1.465	0.20

Table 4

Comparison of Enthalpy and Entropy Differences According to the Din Tables and According to Those Derived from Eqs. (5) and (6)

T, °K	Enthalpy kJ/kg		δi, kJ/kg	Entropy kJ/kg · deg		δs, kJ/kg · deg
	Δi 202.6			Δs 202.6		
	[15]	(6)		[15]	(5)	
90	9.8	9.0	0.8	−0.057	−0.062	0.005
100	9.2	8.3	0.9	−0.061	−0.065	0.004
110	7.3	6.9	0.4	−0.078	−0.075	−0.003
120	4.5	4.8	−0.3	−0.099	−0.090	−0.009
130	0.4	1.3	−0.9	−0.126	−0.113	−0.013
140	−6.4	−4.3	−2.1	−0.166	−0.145	−0.021
150	−23.5	−21.5	−2.0	−0.276	−0.250	−0.026
	Δi 304.0			Δs 304.0		
100	12.6	13.0	−0.4	−0.088	−0.091	0.003
110	9.9	11.4	−1.5	−0.112	−0.104	−0.008
120	6.3	8.8	−2.5	−0.141	−0.122	−0.019
130	1.3	4.6	−3.3	−0.174	−0.149	−0.025
140	−6.6	−1.8	−4.8	−0.223	−0.188	−0.035
150	−24.9	−20.0	−4.9	−0.341	−0.301	−0.040
	Δi 506.6			Δs 506.6		
100	21.1	22.7	−1.6	−0.142	−0.135	−0.007
110	15.1	20.7	−5.6	−0.173	−0.131	−0.022
120	10.8	17.7	−6.9	−0.208	−0.174	−0.034
130	4.9	13.0	−8.1	−0.249	−0.206	−0.043
140	−4.0	5.8	−9.8	−0.305	−0.250	−0.055
150	−23.5	−13.4	−10.1	−0.432	−0.368	−0.064

Table 5

Comparison of Theoretical Heat-Capacity Values for c_p [kJ/kg · deg] with the Din Data [15]

T, °K.	p, bar							
	101.3		202.6		304.0		506.6	
	[15]	(7)	[15]	(7)	[15]	(7)	[15]	(7)
100			1.107	1.010	1.026	0.988	0.951	0.962
110	1.244	1.097	1.109	1.041	1.029	1.006	0.951	0.964
120	1.264	1.161	1.117	1.072	1.034	1.022	0.951	0.965
130	1.317	1.244	1.142	1.107	1.044	1.039	0.954	0.967
140	1.407	1.357	1.177	1.144	1.059	1.056	0.954	0.969
150	1.592	1.534	1.227	1.180	1.082	1.070	0.956	0.971
$\delta c_{p_{av}}$, %	8.0		5.6		1.9		1.4	
$\delta c_{p_{max}}$, %	13.4		9.6		3.8		—1.5	

authors [1] are in agreement with the calculated quantities within limits of 0.1–0.2%, and larger deviations appear only at several points.

The equation of state describes the curve of argon saturation with a high degree of accuracy for a wide range of temperatures. We see from Table 2 that in the 85–140° K interval the deviation of the calculated density values from the reference values does not exceed 0.2%, and for most of the temperatures the deviation is less than 0.1%. We have taken the data derived in the monograph [8] by graphical correlation of the experimental results of Michels and co-authors [1] and the Leiden researchers [12] as the reference data. At temperatures of 140° K ($\rho < 1.75\ \rho_k$) the divergences between the theoretical values and the reference data on the saturation curve increase substantially.

The argon density values on the freezing curve, calculated according to the equation of state, are in good agreement with the reference data derived by extrapolation of the isobars to the freezing points. At pressures below 250 bar the divergence between the two groups of data does not exceed 0.07%, while for pressures below 500 bar the divergence does not exceed 0.21% (Table 3).

By means of the equation of state (4) and the known thermodynamic relationships we derived expressions for the determination of the entropy, enthalpy, and heat capacity:

$$s = s' - 0.1\,[(4.157 - 854.8\vartheta^{-3} + 144221.2\vartheta^{-5})(\rho - \rho_s) + 0.89(\rho^3 - \rho_s^3)], \tag{5}$$

$$i = i' - 0.1\,[(-931.2 + 41.57\vartheta + 170960\vartheta^{-2} - 2163318\vartheta^{-4})(\rho - \rho_s) - (978 - 26.7\vartheta)(\rho^3 - \rho_s^3) + 344.4(\rho^5 - \rho_s^5)], \tag{6}$$

$$c_p = c_v' + \vartheta\, \{ ([(4.157 - 854.8\vartheta^{-3} + 144221.2\vartheta^{-5}) \times \rho + 2{,}67\rho^3]^2)((-931.2 + 83.14\vartheta + 85480\vartheta^{-2} - 721106\vartheta^{-4})\rho - (2934 - 106.8\vartheta)\rho^3 + 1722\rho^5)^{-1} - (256.44\vartheta^{-4} - 72210.6\vartheta^{-6})(\rho - \rho_s)\}, \tag{7}$$

where $\vartheta = 0.1T$.

In these formulas ρ_s, i', s', and c_v' are the magnitudes in the saturation state. The values of i' and s' for argon are cited in [8], with the reckoning origin for heat capacity c_p selected after determination of the derivative $(\partial i/\partial T)_p$ for pressures of 300 bar.

The theoretical values for the caloric properties of argon were compared with the tabular data of Din [15]. In the temperature interval from 120 to 270° K and at pressures of 60–200 atm these tables were derived by processing the experimental data of Roebuck and Osterberg [16] on the adiabatic throttling effect. At higher pressures and temperatures below 270° K the tables in [15] were prepared by extrapolation of the isobars to the melting curve, followed by processing of the extrapolated p, v, and T data. For pressures below 200 atm and for temperatures below 120° K there are virtually no data on the liquid properties in the Din tables (with the exception of the point having the parameters 100 atm and 110° K).

In view of the difference at the reckoning origin we compared the values of $\Delta i = i - i'$ and $\Delta s = s - s'$ on the isotherms according to our data (Table 4) and those of Din. At a pressure of 202.6 bar (200 atm) both groups of data agree satisfactorily: the divergences do not exceed 2.1 kJ/kg and 0.026 kJ/kg · deg. On the 101.3 bar isobar, not shown in the table, the maximum deviations are smaller by a factor of two than for p = 202.6 bar. At pressures of 304.0 and 506.6 bar the quantities Δi and Δs according to the tables in [15] and on the basis of our data differ more substantially, and this is apparently explained by the reduced accuracy of the Din results in the region for which there are no experimental data.

Comparison of the Din data [15] for the heat capacity c_p and those obtained from Eq. (7) demonstrated that the divergences between these lie primarily within limits of −1.5 and +4.2%, with more substantial deviations noted at only certain points for temperatures below 130° K (Table 5).

This comparison permits us to draw the conclusion that our data are reliable and that the calculation of tables for the thermodynamic properties of liquid argon on the basis of the derived equation of state is an expedient procedure.

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