EXPERIMENTAL STUDY OF THE THERMAL CONDUCTIVITY OF ARGON AT LOW TEMPERATURES

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Results are shown of an experimental study concerning the thermal conductivity of argon at temperatures from –160 to –20°C under pressures from 100 to 1000 kg/cm². An equation is proposed for describing the thermal conductivity characteristic of argon.

The thermal conductivity of argon under pressure has been determined by several authors. The parallel plates method was used by A. Michels, A. Botzen, A. Friedman, and I. V. Sengers [1] at temperatures 0, 25, 50, and 75°C under pressures from 1 to 2431 kg/cm², by A. Michels, I. V. Sengers, and Van de Klundert [2] at the same temperature under pressures from 1 to 2504 kg/cm². The coaxial cylinders method was used by I. M. Lenoir and W. E. Comings [3] at 41.1°C under 1.03 to 200 kg/cm², by I. M. Lenoir, W. A. Iunk, and W. E. Comings [4] at 52.8°C under 1.03 to 224 kg/cm², by H. Ziebland and I. T. Burton [5] from –179 to –77°C under 1.03 to 124 kg/cm², by R. U. Ullir [6] from –182.7 to –79°C under 1 to 99.3 kg/cm², by F. G. Keyes and R. G. Baines [7] from –139.8 to +347.3°C under 6 to 140 kg/cm², by B. M. Rosenbaum, S. Oshen, and G. Thodos [8] at 6.2, 20.7, 25, and 48.8°C under 28.8 to 727 kg/cm², by B. I. Bailai and K. Kellner [9] from –183 to +27°C under 1 to 500 kg/cm². The hot filament method was used by N. V. Tsederberg, V. N. Popov, and N. A. Morozova [10] in the –70 to +390.5°C range along the 1, 100, 200, 300, 400, and 500 kg/cm² isobars. Only at pressures above 500 kg/cm² was the thermal conductivity of argon measured within a narrow temperature range (from 0 to 75°C) [1, 2 , 8]. For this reason, the authors undertook a study to determine the thermal conductivity of argon under high pressures at low temperatures.

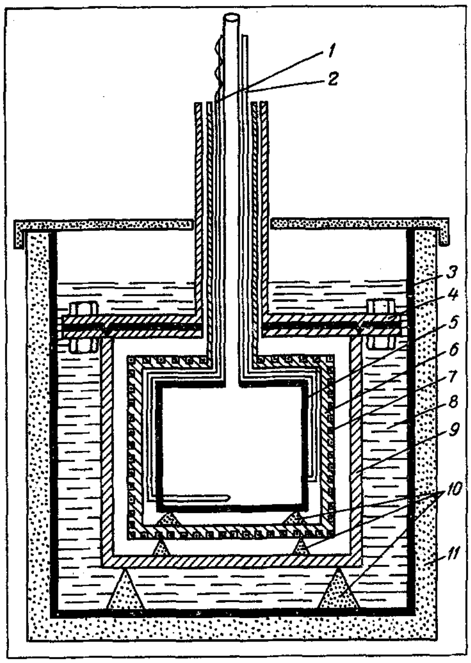

Fig. 1. Thermostat for maintaining low temperatures: 1) thermocouple, 2) argon inlet tube, 3) Dewar flask, 4) lid of the thin-walled autoclave, 5) high-pressure autoclave, 6) copper can, 7) heater, 8) liquid nitrogen, 9) housing of the thin-walled autoclave, 10) insulting supports, 11) phenoplastic insulation.

The thermal activity of argon was studied by the plane-horizontal layer method. The apparatus and its operating principles have been described in [11-13]. In low-temperature measurements the use of cuprous oxide as the thermoelement is limited on account of its increasing resistance. For this reason, the space between the inner and the outer copper slab of the instrument was filled with 88 : 12 bismuth–antimony alloy, which does not have this undesirable characteristic [14]. Such a thermoelement operates well within the –200 to –20°C temperature range. The device had the following dimensions: outside diameter 102 mm, diameter of the active area 76.25 mm, height 22 mm. The active gap between the operating surface of the instrument and of the cooler was set to 0.0273 cm by means of vertically adjustable cylindrical porcelain spacers.

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TABLE 1. Thermal Conductivities of Argon and Helium Established by the Control Tests (λ, W/m · deg)

Item No.	P, kg/cm^2	Temperature, °C				Substance
		0	100	200	300	
1	1	0,1431	0,1787	0,2121	0,2436	Helium
2	1	0,1418	0,1789	0,2102	0,2417	"
3	100	0,1469	0,1824	0,2154	0,2464	"
4	100	0,1476	0,1838	0,2150	0,2483	"
5	200	0,1508	0,1861	0,2187	0,2492	"
6	200	0,1511	0,1844	0,2174	0,2509	
7	1	0,01645	0,02118	0,02549	0,02943	Argon
8	1	0,01633	0,02140	0,02558	0,02966	"

Note. No. 1, 3, 5 according to the data in [16], No. 7 according to the data in [17], No. 2, 4, 6, 8 according to our data; P denotes the pressure.

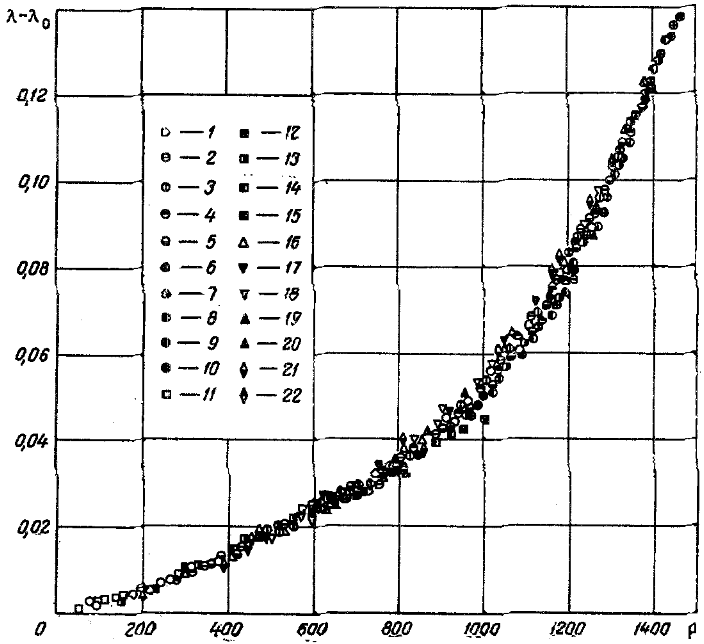

Fig. 2. Excess thermal conductivity of argon $\lambda - \lambda_0$ as a function of the density μ. Our data: 100 kg/cm^2 (1), 200 kg/cm^2 (2), 300 kg/cm^2 (3), 400 kg/cm^2 (4), 500 kg/cm^2 (5), 600 kg/cm^2 (6), 700 kg/cm^2 (7), 800 kg/cm^2 (8), 900 kg/cm^2 (9), 1000 kg/cm^2 (10). According to the data in [10]: 100 kgf/cm^2 (11), 200 kg/cm^2 (12), 300 kg/cm^2 (13), 400 kg/cm^2 (14), 500 kg/cm^2 (15). According to the data in [9]: 100 kg/cm^2 (16), 200 kg/cm^2 (17), 300 kg/cm^2 (18), 400 kg/cm^2 (19), 500 kg/cm^2 (20). According to the data in [5] (21). According to the data in [6] (22).

The instrument was placed inside a high-pressure autoclave made of grade 1Kh18N10T stainless steel. During measurements the autoclave was placed in a thermostat meant for low temperatures. This thermostat is shown schematically in Fig. 1. The high-pressure autoclave 5 was placed inside a copper can [6], separated from it by spacers 10. This copper can, in turn, was placed inside another thin-walled autoclave 9 protecting the autoclave 5 from coming in direct contact with the liquid nitrogen which had been poured into the Dewar flask 3. Different temperatures were obtained by means of two heaters 7 around this copper can. One of these heaters, with a high-power rating, brought the temperature up close to the required level. The other heater, with a lower power rating, served as an automatic temperature regulator in conjunction with a photo relay and a model R-308 potentiometer. The nitrogen level in the Dewar vessel was maintained constant by means of a condensation-type regulator with a siphon [15]. The temperature fluctuations inside the autoclave did not exceed 0.01°C.

TABLE 2. Test Values of Thermal Conductivity of Argon

t_m, C	P, kg /cm^2	Δt_λ, °C	$\lambda \cdot 10^{-1}$ W/m·°C	t_m, °C	P, kg /cm^2	Δt_λ, °C	$\lambda \cdot 10^{-1}$ W/m·°C
—20,16	100	0,868	0,213	—90,34	100	1,606	0,284
—20,19	200	1,728	0,314	—90,15	200	0,665	0,486
—20,15	300	1,682	0,393	—90,28	300	0,746	0,594
—20,21	400	0,813	0,458	—90,29	400	1,346	0,705
—20,09	500	0,780	0,514	—90,18	500	0,866	0,766
—20,35	600	1,444	0,582	—90,32	600	1,485	0,846
—20,07	700	1,57)	0,631	—90,39	700	1,455	0,894
—20,30	800	1,539	0,680	—90,11	800	1,415	0,954
—20,13	900	0,888	0,722	—90,20	900	0,891	1,013
—20,28	1000	1,399	0,766	—90,24	1000	0,855	1,054
—40,25	100	0,749	0,215	—100,33	100	0,877	0,346
—40,42	200	0,793	0,334	—100,41	200	0,578	0,545
—40,39	300	0,854	0,422	—100,17	300	0,776	0,667
—40,36	400	0,896	0,508	—100,38	400	1,344	0,741
—40,36	500	0,929	0,570	—100,28	500	1,542	0,832
—40,29	600	0,963	0,615	—100,26	600	0,889	0,887
—40,35	700	1,485	0,690	—100,55	700	0,832	0,959
—40,38	800	0,941	0,735	—100,44	800	0,996	1,008
—40,32	900	0,902	0,789	—100,41	900	1,437	1,064
—40,40	1000	1,466	0,839	—100,33	1000	0,922	1,117
—50,01	100	1,469	0,219	—109,71	100	0,732	0,444
—49,94	200	0,912	0,343	—109,88	200	0,768	0,612
—49,95	300	1,483	0,445	—109,70	300	0,790	0,710
—50,11	400	0,760	0,528	—109,96	400	1,320	0,798
—50,17	500	0,806	0,601	—109,72	500	0,851	0,884
—50,01	600	1,521	0,658	—109,84	600	0,912	0,949
—50,08	700	1,518	0,721	—109,60	700	1,123	0,994
—49,99	800	1,448	0,770	—109,75	800	1,056	1,059
—49,87	900	0,950	0,826	—109,82	900	1,404	1,110
—50,13	1000	1,456	0,861	—109,76	1000	1,364	1,145
—59,57	100	0,703	0,218	—120,51	100	0,593	0,552
—59,64	200	0,783	0,372	—120,57	200	0,658	0,699
—59,54	300	1,688	0,466	—120,39	300	1,117	0,790
—59,65	400	1,468	0,545	—120,45	400	0,810	0,883
—59,61	500	1,372	0,644	—120,40	500	1,317	0,935
—59,54	600	0,876	0,696	—120,61	600	0,901	1,003
—59,70	700	0,875	0,758	—120,67	700	1,355	1,080
—59,55	800	1,367	0,811	—120,53	800	1,437	1,119
—59,51	900	1,446	0,852	—120,42	900	0,957	1,171
—59,57	1000	0,866	0,906	—120,37	1000	0,911	1,228
—69,79	100	0,699	0,231	—129,97	100	1,178	0,660
—69,80	200	1,690	0,398	—129,76	200	0,626	0,781
—69,87	300	1,528	0,491	—129,88	300	1,310	0,858
—69,77	400	0,804	0,601	—129,74	400	1,437	0,942
—69,76	500	0,812	0,669	—129,91	500	1,521	1,021
—69,75	600	1,470	0,729	—129,82	600	1,433	1,086
—69,69	700	1,535	0,787	—129,99	700	0,740	1,146
—69,81	800	1,444	0,853	—129,87	800	0,921	1,192
—69,80	900	1,488	0,890	—129,81	900	1,488	1,234
—69,84	1000	0,879	0,957	—129,78	1000	1,446	1,271
—80,09	100	0,897	0,242	—139,66	100	0,972	0,759
—80,13	200	0,768	0,441	—139,58	200	0,867	0,872
—80,16	300	1,439	0,559	—139,85	300	1,436	0,956
—80,22	400	1,458	0,636	—139,57	400	1,421	1,028
—80,01	500	1,472	0,729	—139,68	500	1,338	1,099
—80,26	600	0,950	0,788	—139,72	600	0,859	1,156
—80,28	700	1,549	0,837	—139,77	700	0,958	1,197
—79,97	800	1,503	0,883	—139,85	800	0,944	1,238
—80,23	900	0,882	0,964	—139,71	900	1,585	1,295
—80,05	1000	1,442	1,009	—139,98	1000	1,533	1,343
—150,31	100	1,453	0,869	—159,88	100	1,659	0,974
—150,38	200	1,344	0,963	—159,96	200	0,883	1,055
—150,03	300	1,463	1,034	—160,01	300	1,478	1,139
—150,30	400	1,068	1,117	—159,92	400	0,911	1,186
—150,24	500	1,009	1,184	—160,14	500	1,665	1,231
—150,49	600	0,685	1,216	—160,21	600	0,997	1,291
—150,21	700	1,374	1,273	—159,98	700	1,641	1,343
—150,52	800	0,896	1,325	—159,77	800	1,038	1,381
—150,21	900	0,886	1,369	—159,94	900	1,594	1,425
—150,43	1000	0,861	1,414	—159,96	1000	1,028	1,449

Note: P, kgf/cm^2 denotes the pressure; t_m, °C denotes the mean test temperature; Δt_λ denotes the temperature drop across a layer of test substance; $\lambda \cdot 10^{-1}$ W/m·°C.

The absolute temperature of the cooler t_c and of the heater t_h as well as the temperature difference between them Δt_λ were measured with copper-constantan thermocouples which had been calibrated against a standard resistance thermometer. The thermal conductivity measurement of argon included a correction for variations in the form factor of the instrument l/S (l denoting the width of the measuring gap and S denoting the area of the active instrument surface). The gap with l did not vary significantly with the temperature, because the linear thermal expansivity of the porcelain cylinders used for setting the gap was low.

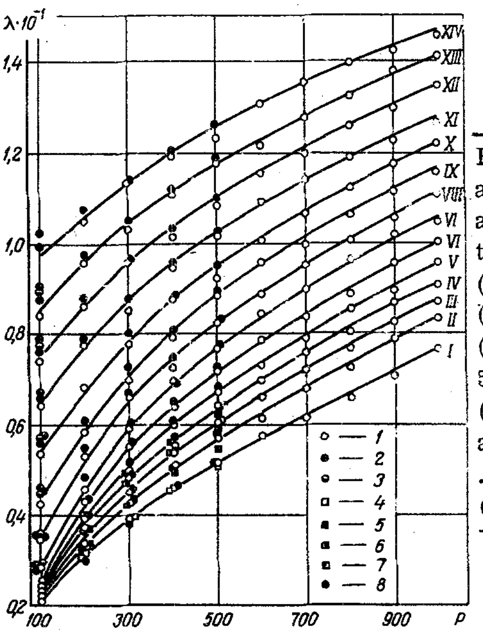

Fig. 3. Thermal conductivity of argon as a function of the pressure, along isotherms: according to our test data (1), according to the data in [5] (2), in [6, 10] (3), at −20°C (4), at −40°C (5), at −60°C (6), at −70°C (7), according to the data in [9] (8), at 20.19°C (I), at 40.35°C (II), at 50.03°C (III), at 59.58°C (IV), at 69.80°C (V), at 80.12°C (VI), at 90.25°C (VII), at 100.35°C (VIII), at 109.35°C (IX), at 120.51°C (X), at 129.86°C (XI), at 139.70°C (XII), at 150.31°C (XIII), at 159.96°C (XIV).

The correction was factored into the active surface S. The variation in the l/S ratio was calculated on the basis of the linear thermal expansivity of copper given in [16]. The maximum value of this correction, at −160°C, was 0.5% of nominal value at 20°C. The correction for radiant heat transmission was maximum 0.015% at −20°C and, therefore, not included in the measurements.

The pressure in the autoclave was varied and measured from 100 to 1000 kg/cm^2 with a model MP-2500 manometer of accuracy class 0.05, the latter connected to the high-pressure autoclave through a separating column.

Special precautions in these tests were taken to ensure a strictly horizontal position of the instrument, because in a thermal conductivity measurement by the plane layer method the position of the layer has an important effect on the results. The position of the instrument was checked with a leveler with 0.05 mm divisions per 1 m.

The total measurements error was 2.4% in gaseous argon and 3% in liquid argon.

Since data necessary for calculating the product GrPr of the Grashof number and the Prandtl number were not available, we checked for convection in the measuring gap by a direct test: at two different values of Δt_λ, one approximately double the other. Within the given spread of test points, the values of thermal conductivity corresponding to these different temperature differences Δt_λ were the same, which indicated that no convective heat transfer had occurred.

We used pure grade-A argon containing 0.01% nitrogen and 0.003% oxygen. Prior to injection into the autoclave, the argon was purged of water vapor by passing it through a filter with calcium chloride. The instrument was checked beforehand on materials for which reliable data had already been established. Such materials include argon and helium [17, 18]. The values of thermal conductivity obtained by these control measurements are given in Table 1. Our data agree closely with those in [18, 19]: the maximum discrepancy does not exceed 1%.

The thermal conductivity of argon was measured along isotherms every 10°C from −160 to −20°C under pressures from 100 to 1000 kg/cm^2 in 10 kg/cm^2 steps. The thermal conductivities of argon measured over these ranges of temperature and pressure are shown in Table 2.

The excess thermal conductivity $\lambda - \lambda_0$ has been plotted in Fig. 2 as a function of the density ρ, according to our data and those by other authors. The curve is smooth and can be represented by the following equation:

$$\lambda - \lambda_0 = a + b\rho + c\rho^2 + d\rho^3 + e\rho^4 + f\rho^5, \qquad (1)$$

with λ denoting the thermal conductivity at temperature t under pressure P, λ_0 denoting the thermal conductivity at the same temperature under atmospheric pressure, and ρ denoting the density of argon.

TABLE 3. Thermal Conductivity of Argon at Equal Temperature and Pressure Intervals ($\lambda \cdot 10^{-1}$ W/m · deg)

P, kg/cm²	Temperature, °C						
	—20	—40	—50	—60	—70	—80	—90
100	0,215	0,219	0,222	0,226	0,235	0,249	0,281
200	0,311	0,326	0,343	0,363	0,396	0,442	0,488
300	0,392	0,421	0,442	0,469	0,503	0,548	0,598
400	0,458	0,501	0,526	0,559	0,596	0,635	0,692
500	0,520	0,566	0,599	0,633	0,672	0,716	0,769
600	0,578	0,626	0,661	0,700	0,736	0,782	0,838
700	0,626	0,687	0,720	0,754	0,795	0,840	0,899
800	0,677	0,739	0,772	0,801	0,855	0,901	0,962
900	0,723	0,788	0,821	0,862	0,908	0,956	1,012
1000	0,770	0,836	0,850	0,909	0,957	1,003	1,054

P, kg/cm²	Temperature, °C						
	—100	—110	—120	—130	—140	—150	—160
100	0,344	0,442	0,553	0,665	0,759	0,863	0,978
200	0,548	0,615	0,698	0,789	0,870	0,959	1,057
300	0,659	0,720	0,791	0,870	0,955	1,041	1,136
400	0,745	0,803	0,877	0,953	1,035	1,108	1,196
500	0,830	0,882	0,948	1,020	1,101	1,176	1,253
600	0,894	0,951	1,016	1,088	1,157	1,221	1,300
700	0,956	1,010	1,070	1,138	1,210	1,274	1,348
800	1,011	1,061	1,125	1,186	1,252	1,317	1,390
900	1,062	1,113	1,177	1,232	1,298	1,368	1,429
1000	1,108	1,155	1,220	1,261	1,340	1,411	1,467

The values of λ and λ_0 are in W/m · deg, the density is in kg/m³. The λ_0 data were taken from [10] and the ρ data were taken from [19, 20]. The coefficients in Eq. (1) were determined by the method of least squares: $a = 6058 \cdot 10^{-7}$, $b = 26{,}924 \cdot 10^{-9}$, $c = 54{,}960 \cdot 10^{-11}$, $d = -11{,}482 \cdot 10^{-14}$, $e = 11{,}150 \cdot 10^{-16}$, $f = -25{,}398 \cdot 10^{-21}$.

Equation (1) was set up on the basis of thermal conductivity data according to I. M. Lenoir and W. E. Comings [3] at 41.1°C under pressures from 65.8 to 200 kg/cm², according to H. Ziebland, I. T. Burton [5], and R. U. Ullir [6] at –100 to –80°C under a pressure of 100 kg/cm², according to N. V. Tsederberg, V. N. Popov, and N. A. Morozova [10] at –70 to +600°C under pressures from 100 to 500 kg/cm². The data by A. Michels, A. Friedman, A. Botzen, and I. V. Sengers [1] as well as the data by F. G. Keyes and R. G. Baines [7] are on the high side, as has been pointed out in [10], due to a convective heat transfer and, for this reason, have not been used here.

A. Michels, I. V. Sengers, and Van de Klundert [2] measured the thermal conductivity of argon again over the same ranges of temperature and pressure as in [1], after having modified their earlier instrumentation and eliminated the second-order thermoelectric effect which had given rise to convection in [1] and had thus caused a sharp increase in thermal conductivity at high densities. The values in [2] are also higher than our values. The test data by B. M. Rosenbaum, S. Oshen, and G. Thodos [8] do not differ much from those in [2] and have not been used here. The isotherms plotted according to the data in [8] show a wide spread of test points, up to 4%, from the mean values and, therefore, the test accurracy there could not have been within 1%, as asserted by the authors. Furthermore, the 20.7 and 25°C data indicate an anomalous trend of the thermal conductivity characteristic: the 25°C isotherm lies above the 20.7°C isotherm, while the other isotherms are spaced in the regular order.

An additional check has revealed that the test values do not deviate from these calculated according to Eq. (1) by more than 3%.

The thermal conductivity of argon as a function of the pressure along isotherms is shown in Fig. 3, on the basis of graphically evaluated data by other researchers [5, 6, 9]. The values of thermal conductivity according to Eq. (1) are indicated here by solid lines. The data from [5, 6] and our data for the –100 to –80°C temperature range agree within 2%, while within the –160 to –100°C temperature range they differ by as much as 3.6%. The values from [9] are higher than ours by up to 3.3%.

The thermal conductivity of argon under pressures from 1 to 500 kg/cm² was calculated by the Vargaftik equation for compressed gases:

$$\lambda = \lambda_0 + B\rho^n, \quad (2)$$

at temperatures equally spaced within the −90 and +600°C range, with λ, λ_0, and ρ denoting the same quantities as in Eq. (1), with coefficient $B = 0.646 \cdot 10^{-5}$, and with exponent $n = 1.26$.

These calculations have shown that Eq. (2) fits our test values of thermal conductivity at a density up to 850 kg/m^3: the deviations do not exceed 2%. At higher densities the deviations increase up to 6.4% at −70°C and under 500 kg/cm^2.

According to [21], Eq. (2) describes correctly the thermal conductivity of gases at densities $\rho \leq 1.5\,\rho_{\text{crit}}$ (ρ_{crit} denoting the critical density) and this has been confirmed in our case too. In order to interpret the relation $\lambda - \lambda_0 = f(\rho)$ for argon, therefore, we used all values of thermal conductivity in [10] corresponding to densities up to 850 kg/m^3.

The thermal conductivities of argon at equal temperature and pressure intervals are given in Table 3, calculated according to Eq. (1) and recommended for practical use.

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