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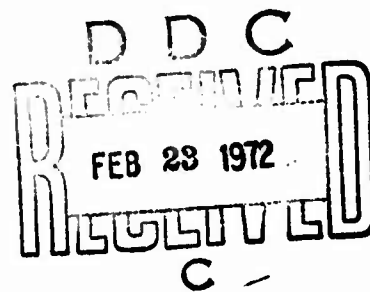
## FOREIGN TECHNOLOGY DIVISION



HEAT CONDUCTIVITY OF GASES AND LIQUIDS

by

N. B. Vargaftik, L. P. Filippov,  
A. A. Tarzimanov, and R. P. Yurchak

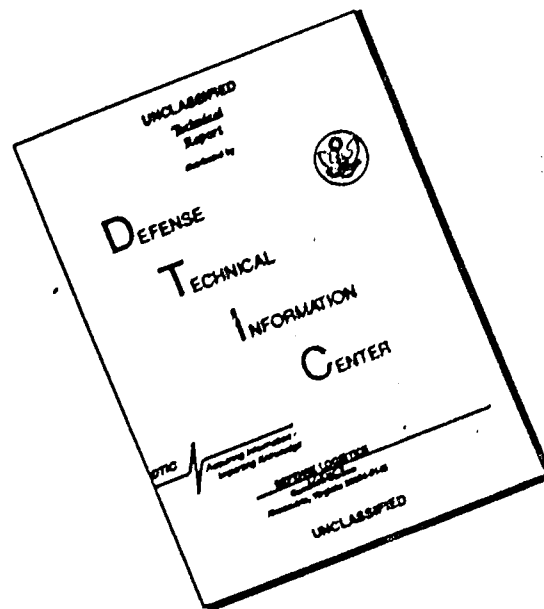


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# EDITED MACHINE TRANSLATION

THERMAL CONDUCTIVITY OF GASES AND LIQUIDS

By: N. B. Vargaftik, L. P. Filippov,  
A. A. Tarzimanov, and R. P. Yurchak

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Translator's note: On several occasions, symbols found in formulae and calculations appear to have been rendered incorrectly in the original document. They will be shown exactly as they appear in the original.



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# U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

\* ye initially, after vowels, and after ъ, ы; e elsewhere.  
 When written as ѣ in Russian, transliterate as yѣ or ѣ.  
 The use of diacritical marks is preferred, but such marks  
 may be omitted when expediency dictates.

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH  
DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	sin <sup>-1</sup>
arc cos	cos <sup>-1</sup>
arc tg	tan <sup>-1</sup>
arc ctg	cot <sup>-1</sup>
arc sec	sec <sup>-1</sup>
arc cosec	csc <sup>-1</sup>
arc sh	sinh <sup>-1</sup>
arc ch	cosh <sup>-1</sup>
arc th	tanh <sup>-1</sup>
arc cth	coth <sup>-1</sup>
arc sch	sech <sup>-1</sup>
arc csch	csch <sup>-1</sup>
<hr/>	
rot	curl
lg	log

This reference book represents a systematized and critical survey of the basic experimental data for the most widely studied substances in liquid and gaseous states (for helium, neon, argon, krypton, xenon, hydrogen, nitrogen, oxygen, air, carbon dioxide, ammonia, ten hydrocarbons, carbon tetrachloride, ethyl alcohol and water).

Tables of the most reliable values of the thermal conductivity of all the cited substances in a wide range of temperatures and pressures have been compiled.

There are 70 tables, 61 illustrations, and 256 bibliography entries.

The book is intended for a wide circle of engineers and scientific workers of various branches of technology, and also for students and graduate assistants.

## FOREWORD

In the most diverse branches of modern science and technology data on heat conductivity of many gases and liquids are employed. In connection with this there exists the need for the compilation of tables of the recommended reference values of the thermal conductivity based on a careful analysis of the existing experimental results.

This work should be viewed as a part of the program of the State Bureau of Standard and Reference Data (GSSSD) for the publication of fundamental manuals on the properties of substances, which are widely used in modern technology and are necessary for the successful development of new scientific-research works.

Recently in the USA on commission of the National Bureau of Standards the same work was partially carried out at the Thermophysical Properties Research Center Purdue University. As a result there was published in 1966-1968 a book in two parts [1], which gives the recommended values of the thermal conductivity of 20 solid substances and 12 substances in the liquid and gaseous states. In this publication of the NBS the temperature dependence of the thermal conductivity was established only for rare gases (with  $p = 1$  atm), and for liquids the values of the thermal conductivity was given only on the saturation line. The dependence of the thermal conductivity on the pressure was not established. It is natural that such data cannot satisfy the demands of modern science and technology. It should be noted that for many substances, presented in the tables

of the NBS, there exists in the literature experimental data on the thermal conductivity at sufficiently high pressures.

It is also significant that in a number of cases the values of the thermal conductivity of gases and liquids recommended in [1] are based on averaged curves constructed according to the data of various authors without the necessary analysis of the methods of measurement employed for the degree of accuracy of the initial experimental results. The methods of obtaining referenced data by means of simple averaging of existing experimental values, without consideration of their qualities has led to the fact that in the tables of the National Bureau of Standards of the USA [1] the values of the thermal conductivity of water vapor at elevated temperatures significantly differ from those adopted in the international tables in 1964 [2, 3] and go beyond the limit of tolerances established in these tables.

We suggest that the referenced recommendations must be compiled by means of a careful selection of the most reliable initial data for a significant number of substances. For liquids and gases, in those cases where it is possible, it is essential to represent the dependence of the thermal conductivity on the temperature and pressure.

Such work in the compilation of tables of recommended values of the thermal conductivity is very laborious. It can be done sufficiently well only by persons having experience in experimental research in this area. As a result, a series of books must be published. The present book is the first of this series. It includes data on the thermal conductivity of 25 substances in the liquid and gas phases, most widely studied in an experimental respect in a wide range of temperatures and pressures.

The authors thought it necessary that the compilation of the tables be preceded by a serious analysis of certain principal problems of the methodical character and by a discussion of new methods, which are being developed and used at the present time for the measurement of the thermal conductivity of gases and liquids.

Therefore, special attention was given to the role of the processes of heat transfer by radiation of a medium (proton heat conductivity). The importance of this problem has recently been clarified in connection with the carrying out of a number of theoretical and experimental investigations, from which, in particular, it was concluded that these processes can noticeably influence the results of measurements of thermal conductivity of liquids and compressed gases even at low temperatures. Work on the compilation of reference tables and especially the selection of the sample substances make this problem an urgent one. The corresponding material expounded in Chapter I has been written by L. P. Filippov.

The authors also examine the problem of natural convection, since recently there have appeared new interesting results on the investigation of natural convection in narrow clearances.

Of great significance is the principal of selecting material for the compilation of tables of reference data on thermal conductivity. At the present time, unfortunately, there are as yet no generally accepted criteria and tenets which might serve as the basis for a corresponding analysis.

The basic material must be compiled from the results of systematic experimental investigations, conducted in a wide range of states by well worked out methods. The necessary conditions are a thorough consideration by the author of all the possible sources of error of the experiments and a proven estimate of the accuracy. Besides this material, it is advisable to use the data of authors, which refer to a narrow range of states, if the investigations of each of them encompass a large number of substances. The results of nonsystematic measurements, conducted in a narrow range of temperatures and pressures, can be examined only in the case where there is a detailed description of the experiment, the method of introduction of corrections is described, and no error estimates which suggest doubt have been given. One should not use the data of investigations carried out by those authors whose results differ



anomalously without visible reasons from the totality of the most reliable data even if only in one substance, especially if the experiment was described with insufficient detail. The formulated criteria have, of course, a general character; during their practical employment it goes without saying that the compilers will have experience in carrying out experimental research in the given field, and a thorough familiarity with the original works and with their criticism.

Even more complicated is the problem of evaluating the results used, and of the selection of weights, which should be prescribed for those data during the processing of the material for sample liquids. Here it is especially desirable to have more or less objective methods of such an evaluation. One of the possible methods is described in work [4], where the weights of data, belonging to individual authors, have been described by the computation of divergences from the totality of the most reliable values, established during the averaging of the data of all the authors. Such a method allowed us to characterize the results of each author by a concrete number. A similar device was used in combination [5], where the data of all the authors was broken down into three groups depending on the divergence from the results, selected as the most reliable. In several instances the estimates of the degree of reliability by the work method [4] were used in this reference book also, primarily when the authors' evaluations of the error were clearly contradictory with the variation of the corresponding data from the averaged values of the whole. However, the use of this method for all the data was not thought advisable, even if only because there arises the problem of the possible difference in the weighting factors for various temperatures. In connection with this, in the processing of the data for sample liquids - toluene, carbon tetrachloride, and also for benzoyl and ethyl alcohol - the most simple method of evaluation was employed: the selected data were broken down into two groups depending on whether the probable error of the experiment was within 2% or whether it exceeded this value. In evaluating the boundary limit of error for this first group we

used the criterion of Shovene [6], which gives a definite value to the limiting variation from the concrete totality of the data, which when exceeded does not take into consideration the corresponding values.

In an examination of the experimental material in Chapter II there were clarified those regions of the parameters of state, where the existing data were clearly inadequate, and in a number of cases - contradictory. The authors of this book have called the attention of researchers to the necessity of the experimental study of the thermal conductivity in these regions, not even speaking of those regions in which the corresponding substances have altogether not been studied. In the proposed book tables of the values of the thermal conductivity have been compiled only for those regions of temperatures and pressures, for which there are sufficiently reliable experimental data.

For the rare gases ( $p \leq 1$  bar) the following equation was selected

$$\lambda = f(T) \quad (1)$$

in the form of a polynomial.

The experimental data for compressed gases and liquids have been generalized with respect to the relationship for the excess thermal conductivity  $\Delta\lambda$  as a function of the density  $\rho$

$$\Delta\lambda = f(\rho), \quad (2)$$

where  $\Delta\lambda = \lambda - \lambda_1$ ;  $\lambda_1$  is the thermal conductivity when  $p = 1$  bar. This dependence, based on the investigations of A. S. Predvoditelev [7] and N. B. Vargaftik [8], have been widely used in numerous works (see for example [9, 10]). The value of this regularity consists in the fact that the dependence  $\lambda$  on the two variables - on  $p$  and  $T$  - can be reduced to the dependence on one variable - the density  $\rho$ .

For all substances examined in this book the dependence of the excess thermal conductivity is a unique function of the density in those regions of the parameters of state, in which generalization of the experimental data has been carried out. An exception is water vapor, for which in a certain interval of densities the stratification of  $\Delta\lambda$  with respect to isotherms is observed.

With respect to correlations (1) and (2) tables have been compiled for the smoothed data for those substances represented in the book at equal intervals of temperatures and pressures. Not given are the values of the thermal conductivity for regions close to critical, although recently there has been a large number of corresponding investigations. Here there was detected a very strong dependence of the thermal conductivity on the temperature and pressure, however there are still no sufficiently reliable data to be recommended. Therefore, in the book there are no tabulated values of  $\lambda$  for the region  $0.9 < \tau < 1.15$  when  $0.6 < \phi < 1.4$ , where

$$\tau = \frac{T}{T_{kp}}; \phi = \frac{p}{p_{kp}}.$$

The book contains tables of values of the thermal conductivity for 25 substances: all the monatomic and the group of diatomic substances (hydrogen, nitrogen, oxygen, air); certain tri- and polyatomic substances (water,  $H_2O$  and  $D_2O$ , carbon dioxide, ammonia, and carbon tetrachloride); the hydrocarbons (benzoyl and toluene), ethyl alcohol and substances of the methane series — from methane to octane. Also given are values of the thermal conductivity for certain liquids and gases which in a certain temperature region can be recommended as sample substances for calibration and for checking instruments, intended for the measurement of thermal conductivity. Included in the sample substances are: water, toluene, argon, nitrogen and air. Besides this, it is possible to recommend for use in calibrating the relatively well studied substances: carbon tetrachloride, krypton, xenon and helium.

The totality of recommended substances encompasses a wide range of values of thermal conductivity from 0.005 to 0.5 W/(m.deg). The book gives the range of temperatures, in which each of the cited substances can be employed as a sample substance. We also estimated the possible tolerances for the values of the thermal conductivity for these substances.

On the basis of an analysis of a large body of experimental data on thermal conductivity of mixtures and solutions of various types it is possible to conclude that the effect of mixtures on the thermal conductivity of gases and liquids is comparatively small. The content of mixtures in tenths of a fraction of a percent, as a rule, does not noticeably change the thermal conductivity. Requirements for the purity of substances, therefore, are not overly strict.

## CHAPTER I

### QUESTIONS OF THE MEASUREMENT PROCEDURE OF THERMAL CONDUCTIVITY

#### Natural Convection

The exclusion of the effect of convective heat transfer is one of the most essential questions in the practice of measurements of the thermal conductivity of liquids and gases.

For the description of natural convection in the form of connection in dimensionless criteria we usually use relationship

$$Nu = f(Gr, Pr) = f(Ra) \quad (3)$$

or

$$\epsilon = \frac{\lambda'}{\lambda} = f(Ra), \quad (4)$$

where

$$Gr = \frac{g \beta \Delta t}{\nu^2}; \quad Pr = \frac{\nu_f}{\lambda}$$

$Ra = Gr \cdot Pr$  - Rayleigh number;  $\lambda'$  - effective thermal conductivity, which includes molecular thermal conductivity  $\lambda$  and convective heat transmission;  $\epsilon$  - the coefficient of convection.

In 1934 Kraussold, [11] generalized the experimental data available at that time about natural convection in a limited space, using relationship (4). As the determining dimension  $d$  he selected the thickness of the liquid layer  $\delta$ ; then  $Ra = \frac{g\beta\Delta T \delta^3}{\nu\lambda}$ . For horizontal and vertical layers, regardless of their configuration Kraussold obtained a single curve (Fig. 1). In this case the beginning of convection ( $\epsilon > 1.00$ ) occurs when  $Ra > 1000$ . During measurement of  $\lambda$  all the authors were usually guided by this Kraussold curve for the selection of dimension  $\delta$  of the measuring cell and the difference of temperatures in the investigated layer of liquid. In certain cases corrections were inserted into measured values of  $\lambda$ , by using this curve. [Translator's note: unable to find exact spelling of foreign names in text. When English spelling is common, I will use it, otherwise I will transliterate the names.]

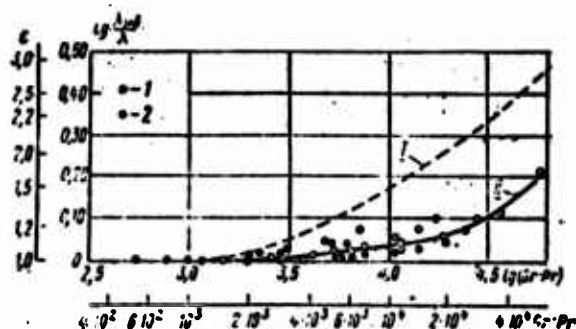


Fig. 1. The relationship of the coefficient of convection to  $Gr$  and  $Pr$  criteria according to data of: I - Kraussold [11]; II - Shingarev [14] for Saratov gas (1); for  $CO_2$  (2).

In the last 10 years a number of new experimental investigations of natural convection has been conducted, mainly in liquids, which are located in the space between coaxial cylinders. The results of these investigations were presented by the 3rd International Conference on Heat Exchange (1966) in three reports: Lees, Sherrif, Grigul' and Gauf [12]. Grigul' and Gauf studied local and average coefficients of heat emission during natural convection in a horizontal annular clearance. They applied optical methods of investigation of convection, determining the distribution of temperatures and heat flows with the aid of an interferometer. Generally

the greatest quantity of experimental data is obtained for horizontal annular clearances and considerably less - for vertical. In some works, for example [13], the Kraussold curve has been refined, some differences have been revealed in the value of  $\epsilon$  for horizontal and vertical clearances.

However, all these investigations, as the results of earlier experiments, generalized by Kraussold [11], have been obtained in comparatively wide clearances:  $\delta = 7-300$  mm. At the same time, when  $\lambda$  of liquids and gases is determined at high pressures,  $\delta = 0.2-0.5$  mm, and the length of measuring cylinders  $l = 100$  mm. Therefore, the investigation of natural convection at such comparatively small values of  $\delta$  and  $l$ , was of interest.

R. V. Shingarev [14] during investigation of the thermal conductivity of  $\text{CO}_2$  by the method of a heated filament ( $d = 0.1$  mm;  $\delta = 0.4$  mm;  $l = 100$  mm) conducted experiments at various  $\Delta t$  and extrapolated the measured values of  $\lambda'$  to  $\Delta t \rightarrow 0$  for the purpose of obtaining true values of  $\lambda$ . The installation was located in a vertical position. Measurements indicated that curve  $\epsilon = f(Ra)$ , constructed from experimental data, lies noticeably lower than the Kraussold curve, as is evident from Fig. 1. From experiments it also followed that the beginning of convection ( $\epsilon > 1.00$ ) takes place at  $Ra > 2500$ . The author offered two equations for determination of the coefficient of convection  $\epsilon$ :

when  $2500 < Ra < 2 \cdot 10^4$

$$\epsilon = 0.58 (Ra)^{0.47} \quad (5)$$

when  $2 \cdot 10^4 < Ra < 6 \cdot 10^4$

$$\epsilon = 0.059 (Ra)^{0.43} \quad (6)$$

A. A. Berkenheim studied natural convection in narrow annular clearances at various values of  $\delta$  from 1.5 to 6 mm and  $l = 100$  mm. As an internal cylinder there served a platinum filament ( $d = 0.1$  mm), external - a glass tube, the diameter of which varied. Experiments were conducted with water and ethyl alcohol with vertical and horizontal position of the measuring tube. Results of experiments (Fig. 2) showed that natural convection with vertical and horizontal position of the measuring tube is described by various curves. They both lie below the Kraussold curve. With vertical position of cylinders the author proposed equations:

for region  $2400 < Ra < 35000$

$$\epsilon = 0.46(Ra)^{0.1}, \quad (7)$$

for region  $35000 < Ra < 170000$

$$\epsilon = 0.23(Ra)^{0.14}. \quad (8)$$

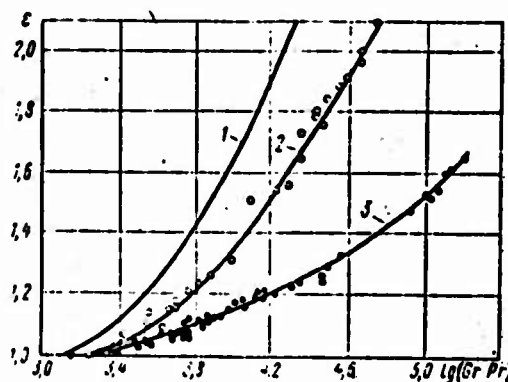


Fig. 2. Relationship of  $\epsilon$  to  $Gr$  and  $Pr$  [13]: 1 - according to Kraussold-Mikheyev equation; 2 and 3 - according to experimental data of Berkenheim with horizontal and vertical position of the tube respectively.



Yu. L. Rastorguyev and V. Z. Heller [15] on an installation, based on the heated filament method ( $\alpha = 0.1$  mm;  $\delta = 0.67$  mm;  $l = 100$  mm), arranged vertically, determined the values of  $\epsilon$  and on the basis of experiments with various liquids (Fig. 3), for this quantity in region  $2400 < Ra < 5000$  proposed equation

$$\epsilon = 0.402(Ra)^{0.08} \quad (9)$$

The examination of all the new works, in which natural convection was studied in narrow annular clearances on installations by the heated filament method, allows making the following conclusions:

1. Curves  $\epsilon = f(Ra)$  are located lower than the Kraussold curve.
2. The beginning of convection ( $\epsilon > 1.00$ ) is observed at number  $Ra > 2000$ , i.e., greater than Kraussold ( $\epsilon > 1.00$  when  $Ra > 1000$ ). The initial section of curves  $\epsilon = f(Ra)$  is considerably flatter than for the Kraussold curve.
3. With horizontal position of the clearance the value of  $\epsilon$  is higher than with vertical, but lower than according to Kraussold curve.

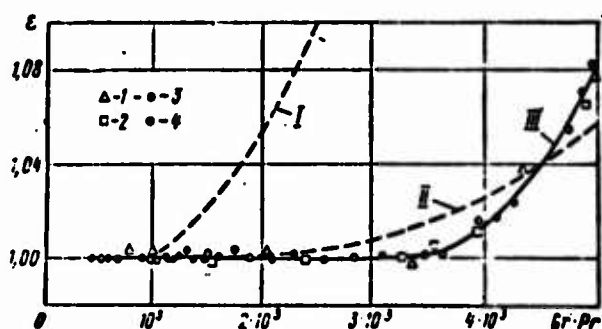


Fig. 3. Relationship of  $\epsilon$  to  $Gr$  and  $Pr$  [15]: I - according to Kraussold-Mikheyev equation; II - according to data of Berkenheim; III - according to data of Rastorguyev and Heller for carbon tetrachloride (1), hexane (2), toluene (3) and benzene (4).

It should be indicated that geometric dimensions ( $\delta$  and  $l$ ) in [13-15] are very close to the dimensions, usually utilized in the heated filament method during measurement of thermal conductivity. In this case the clearances are usually placed vertically. On the basis of results of [13-15] for vertical clearances it is possible to draw an averaged curve for  $\epsilon = f(Ra)$ . The curve constructed by us up to  $Ra = 30,000$  is given in Fig. 4. The beginning of convection is selected at  $Ra = 2000$ . Experimental values of  $\epsilon$ , obtained in [13-15], are deflected from this curve within 2%. The curve can be recommended for evaluation of natural convection during the measurement of thermal conductivity of liquids and gases by the method of a vertical heated filament.

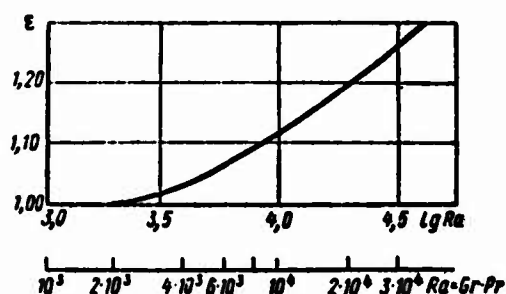


Fig. 4. Generalized relationship of the coefficient of convection to Rayleigh criterion (experiments with vertical heated filament).

Natural convection in a narrow annular clearance ( $\delta = 1$  mm) with cylinder diameter  $d = 10$  mm and  $l = 100$  mm was studied by Yu. L. Rastorguyev and A. A. Nemzer [16]. The cylinders were placed vertically. On the basis of experiments, conducted up to values  $Ra = 5000$ , the authors proposed equation

$$\epsilon = 0.402 (Ra)^{0.118} \quad (10)$$

for region  $1700 < Ra < 5000$ . The beginning of convection ( $\epsilon > 1.00$ ) is when  $Ra > 1700$ .

This equation can be used for vertical coaxial cylinders at  $Ra$  numbers up to 5000.

### Temperature Jump

The effect of temperature jump is substantial during measurement of the thermal conductivity of gases.

During experimental determination of the thermal conductivities of gases we usually measure the wall temperature of an instrument. But it is known that between a solid and gas, which are located at a distance of a mean free path, there exists temperature jump  $\delta t$ . This phenomenon was experimentally studied by many investigators: Smolukhovskiy, Knudsen, Timiryazev, Lazarev and others. The question is described in detail in literature, for example, in the books of Kennard [17], Devien [18] and Clark and McChesney [19].

As is established, the temperature jump  $\delta t$  for a moderately rarefied gas is proportional to the temperature gradient  $dt/dn$  along the normal to the wall surface ( $\delta t = \gamma dt/dn$ ), and the proportionality factor  $\gamma$  is inversely proportional to the gas pressure ( $\gamma = A/P$ ). Usually, by measuring the thermal conductivity of gases at low pressures (when  $P \approx 1$  atm), quantity  $\delta t$  is taken into account by conducting tests at various pressures;

$$\Delta t_{\text{meas}} = \Delta t_{\text{res}} + \frac{B}{P}.$$

The consideration of this correction is especially essential for gases with comparatively low molecular weight and at high temperatures. As applied to coaxial cylinders the method of account of the correction is substantiated in [20], and for heated filament - in [21]. The measured values of thermal conductivity not allowing for the correction are always lower than true values of  $\lambda$ .

The neglect of this effect at high temperatures can lead to substantial errors, especially for gases with comparatively low

molecular weight, as, for example, took place in the case of nitrogen. Figure 5, taken from [30], shows the results of measurements of the thermal conductivity of nitrogen, obtained by various authors. At elevated temperatures the discrepancies were very noticeable - they reached 12%. Neglect of the temperature jump especially appeared in the results of experiments of Schafer and Reuter [31], inasmuch as their data refer to the region of high temperatures - up to 1400°K.

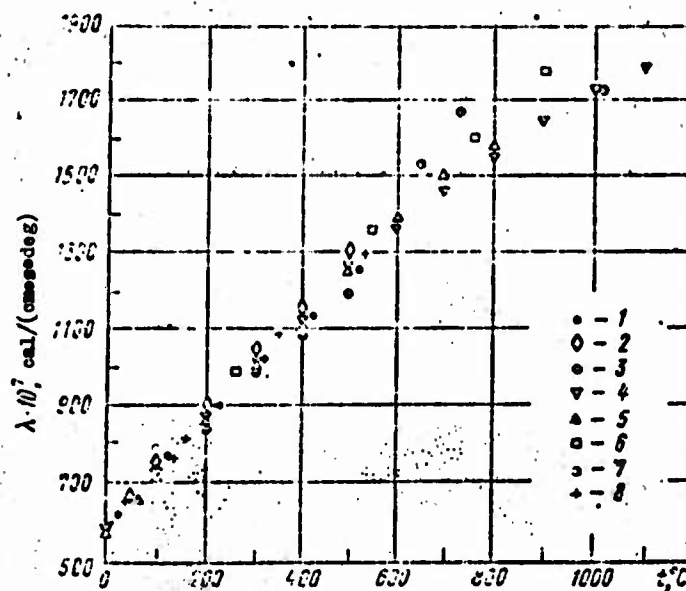


Fig. 5. Experimental data of various authors on the thermal conductivity of nitrogen: 1 - Frank [22]; 2 - Natell, Jennings [23]; 3 - Shotki [24]; 4 - Geier, Schafer [25]; 5 - Blays, Mann [26]; 6 - Weiss [27]; 7 - Stops [28]; 8 - Zibland, Barton [29].

After the introduction of correction for temperature jump the corrected experimental data lay well on one curve, as is evident from Fig. 6, taken from [30]. The deviations of experimental data, obtained by various methods, lie within 2%.

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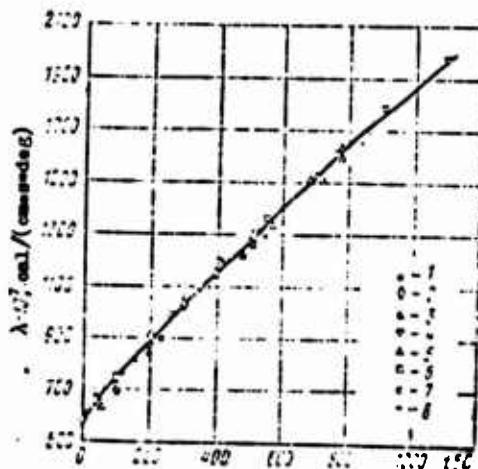


Fig. 6. The relationship of thermal conductivity of nitrogen to temperature according to various data, corrected taking into account the temperature jump. Designations are the same as in Fig. 5.

An analogous situation took place with experimental data on the thermal conductivity of argon [32], although in less clearly expressed form, inasmuch as the molecular weight of argon is higher than nitrogen.

#### The Role of the Process of Heat Transfer by Radiation

There is every reason to believe that heat transfer caused by the "photon" mechanism in a number of practically important cases plays a very significant role in the process of energy transfer, especially at relatively high temperatures. In particular, there are theoretical and experimental arguments to the effect that the process of the radiation transfer may noticeably distort the usual, molecular heat conductivity of liquids, beginning with temperatures of the order of 70°S. At the same time, the information which we have now available to us is very small, and the problem requires thorough study.

Taking this into account, the authors thought it possible to thoroughly analyze the process of radiant transfer. To a significant degree the material presented here is original.<sup>1</sup>

The existence of processes of radiation and absorption of radiant energy leads to the appearance of a supplementary mechanism for heat transfer. This radiation mechanism coexists with the molecular heat conductivity and in general complicates considerably the total process of heat transfer. The simplest is the process in media, which may be examined as almost transparent in the region of frequencies close to the maximum of a Planck function. It takes place, for example, in gases of relatively low density, where heat transfer by radiation leads to heat exchange between the boundary surfaces and the resulting heat flow is a simple total of molecular and radiant heat. What is more complex is the transfer of heat in partially transparent media.

The essential role of the process of radiation of a medium was first understood and discussed, apparently, by V. G. Guton, who was occupied with the study of the thermal conductivity of molten glass [34]. Then this problem was examined in approximation (for a flat layer, without consideration of the diffusion nature of the radiation) by L. P. Filippov [35] in connection with a debate between N. B. Vargaftik [36, 37], on the one hand, and Keys and Sandell [38] on the other, on the problem of thermal conductivity of water vapor, in the course of which the American authors advanced the proposition that the then existing difference in the results could be attributed to the role of heat transfer by radiation [38, 39]. The mathematical formulation of the problem in the general form was put together by Yu. A. Surinov [40]. Later, recognition was given to the works of Kelett [41] and Genzel [42]. In the first of these an approximate examination was made for the case of a flat layer on the assumption of independence of the coefficient of absorption from the frequency

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<sup>1</sup>For more detail, see the monograph of L. P. Filippov "The study of heat conductivity of liquids" [33].

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("gray medium") and without consideration of the diffusion nature of the radiation. In the second work the distribution of intensity with respect to angles was taken into account and a number of important particular cases were examined for transfer in a flat layer (transfer by radiation in the absence of molecular thermal conductivity, the general case of transfer in a medium with strong absorption, and the general case of transfer in a "gray" medium). In L. P. Filippov's work [43] the general problem for a flat layer was examined and an analysis was given for two limiting cases: strong and weak absorption. A generalization of these results was made in the work of E. A. Sidorov [44]. The case of transfer in a flat layer of a "gray" medium was examined of late in the works of Poltz [45-48] and Hohler [49]. The results of the development of work [43] are presented below.

The initial relationship for an analysis may be the equation of transfer of radiant energy, written on the assumption of the existence of local thermodynamic equilibrium,

$$\cos \theta \frac{\partial I}{\partial x} = \alpha n^2 - \alpha I. \quad (11)$$

This equation expresses the fact that the change in the intensity of radiation  $I$  in a direction which comprises angle  $\theta$  with the axis  $x$  is caused by the natural radiation of an element of the volume of the medium (the first term of the right side) and by the attenuation of intensity as a result of absorption (the second member of the right side). Equation (11) obeys Kirchhoff's law, expressing the coefficient of volumetric radiation of the medium through the intensity of the equilibrium radiation in a vacuum  $\epsilon$ , the coefficient of absorption  $\alpha$  and the index of refraction  $n$  (the process of dispersion in this case is not taken into account).

Integration of equation (11) for a flat layer of width  $L$  with the temperature gradient, perpendicular to the walls (axis  $s$ ), gives the formulas for the intensity of radiation in a positive ( $I^+$ ) and negative ( $I^-$ ) direction of the axis:

$$I^+ = I^+(0) e^{-\frac{1}{\cos \theta} \int_0^x \alpha z n^2 dz} + \frac{1}{\cos \theta} \int_0^x \alpha z n^2 e^{-\frac{1}{\cos \theta} \int_t^x \alpha z n^2 dz} dz;$$

$$I^- = I^-(L) e^{-\frac{1}{\cos \theta} \int_x^L \alpha z n^2 dz} + \frac{1}{\cos \theta} \int_x^L \alpha z n^2 e^{-\frac{1}{\cos \theta} \int_t^L \alpha z n^2 dz} dz.$$

To find the values of the intensity on the boundaries  $I^+(0)$  and  $I^-(L)$  we use the relationships for the mirror reflection:

$$I^+(0) = \epsilon_1 + R_1 I^-(0),$$

$$I^-(L) = \epsilon_2 + R_2 I^+(L),$$

where  $R_1$  and  $R_2$  are the coefficients of reflection. For the differences in intensities  $I^+$  and  $I^-$  we obtain the expression

$$\begin{aligned} I^+ - I^- = \beta & \left\{ \left[ 1 - R_2 e^{-\frac{1}{\cos \theta} \int_x^L \alpha z n^2 dz} \right] \cdot \left[ \epsilon_1 n^2 (1 - R_1) e^{-\frac{1}{\cos \theta} \int_0^x \alpha z n^2 dz} + \right. \right. \\ & + \frac{1}{\cos \theta} \int_0^x \alpha z n^2 e^{-\frac{1}{\cos \theta} \int_t^x \alpha z n^2 dz} dt + R_1 \frac{1}{\cos \theta} e^{-\frac{1}{\cos \theta} \int_0^x \alpha z n^2 dz} \int_x^L \alpha z n^2 e^{-\frac{1}{\cos \theta} \int_t^L \alpha z n^2 dz} dt \\ & \left. - e^{-\frac{1}{\cos \theta} \int_0^x \alpha z n^2 dz} \right] - \left[ 1 - R_1 e^{-\frac{1}{\cos \theta} \int_0^x \alpha z n^2 dz} \right] \left[ \epsilon_2 n^2 e^{-\frac{1}{\cos \theta} \int_x^L \alpha z n^2 dz} \times \right. \\ & \times (1 - R_2) + \frac{1}{\cos \theta} \int_x^L \alpha z n^2 e^{-\frac{1}{\cos \theta} \int_t^L \alpha z n^2 dz} dt + \\ & \left. \left. + R_2 \frac{1}{\cos \theta} e^{-\frac{1}{\cos \theta} \int_x^L \alpha z n^2 dz} \int_0^x \alpha z n^2 e^{-\frac{1}{\cos \theta} \int_t^0 \alpha z n^2 dz} dt \right] \right\}, \end{aligned}$$

where  $\beta$  is the factor of the recurrence of reflections;

$$\beta = \left( 1 - R_1 R_2 e^{-\frac{1}{\cos \theta} \int_0^L \alpha z n^2 dz} \right)^{-1}.$$



The total thermal flow is made up of the flow of energy of radiation and the flow of molecular thermal conductivity:

$$Q = \iint (I^+ - I^-) \cos \theta d\omega d\nu - \lambda \frac{dT}{dx}, \quad (12)$$

(here  $d\omega$  is the elementary solid angle;  $\nu$  is the frequency). In the stationary state

$$\frac{dQ}{dx} = 0.$$

i.e.,

$$\iint \frac{d(I^+ - I^-)}{dx} \cos \theta d\omega d\nu = \frac{d}{dx} \lambda \frac{dT}{dx}. \quad (13)$$

Expression (13) is a complex integral-differential equation, determining the function  $T(x)$  - the distribution of temperature in the layer. It is clear that in the general case the distribution of temperature at fixed temperatures of the surfaces depends simultaneously on the functions

$$T(x) \left\{ \begin{array}{l} \lambda(T) \\ \alpha(T, \nu) \\ n(T, \nu) \\ R_1(\theta) \\ R_2(\theta) \end{array} \right.$$

Through the agency of  $T(x)$  on these same values also depends the heat flow. It is significant that in general both terms in expression (12) for heat flow are interdependent; the integral radiation term through the agency of  $T(x)$  depends on  $\lambda$ , the second term for the same reasons depends upon the optical characteristics. The radiation and molecular (contributions) to the thermal flow prove to be nonadditive, despite the assumption about the additivity of transfer mechanisms.

To analytically investigate the general case, determined by formulas (11)-(13), without additional assumptions is too complex. Therefore, we will henceforth limit ourselves to the following special assumptions:

1. We will examine cases of small differences in temperature on boundaries, which will allow us to limit ourselves to the first two terms of the expansion of the function  $\epsilon$  into a series.

2. We will assume that it is possible to disregard the dependence of the coefficients of absorption and refraction on the temperature.

3. For the sake of simplicity we will assume that  $R_1 = R_2 = R$ .

The enumerated assumptions simplify the investigation, but they do not deprive it of sufficient generality and do not impose any significant limit on the applicability of its results to actual systems.

Equation (13) in this case can be transformed to the form

$$\frac{dy}{dx} = \int_0^L K(\xi, x) y(\xi) d\xi, \quad (14)$$

where

$$y = \frac{dT}{dx}; \quad (15)$$

$$K(\xi, x) = \begin{cases} K_1(\xi, x) & 0 \leq \xi \leq x; \\ K_2(\xi, x) & x \leq \xi \leq L; \end{cases} \quad (16)$$

$$K_1 = \frac{2\pi}{\lambda} \int_0^\infty dv_2 \frac{dv_2}{dT} n^2 \times \\ \times \int_0^{\frac{\pi}{2}} \frac{d\theta}{\sin^3 \theta} [1 + Re^{-2(L-x)\sin \theta}] [e^{-(x-\xi)\sin \theta} - Re^{-(x+\xi)\sin \theta}] ds; \quad (17)$$

$$K_2 = -\frac{2\pi}{\lambda} \int_0^\infty dv_2 \frac{dv_2}{dT} n^2 \times \\ \times \int_0^{\frac{\pi}{2}} \frac{d\theta}{\sin^3 \theta} [1 + Re^{-2\xi \sin \theta}] [e^{-(L-x)\sin \theta} - Re^{-(L+\xi)\sin \theta}] ds; \quad (18)$$

$$\beta = (1 - K_2 e^{-2L\sin \theta})^{-1}. \quad (19)$$

From formula (4)-(8) it is clear that  $K \rightarrow 0$  when  $\lambda^{-1} \rightarrow 0$  and the distribution of temperatures in the layer approaches a linear one. In correspondence with this the solution for the temperature can be found in the form:

$$T - T_1 = \frac{\Delta T}{L} x + \frac{1}{\lambda} \varphi(x) + \dots, \quad (20)$$

disregarding the higher terms of the expansion  $T$  to series with respect to  $\lambda^{-1}$  and examining thereby only the conditions, under which divergences of the temperature field from a linear one are sufficiently small in comparison with  $\Delta T$ . Physically, this means the examination of the processes under which the decisive factor is the molecular heat transfer, while radiation plays the role of a distortion factor.

In the approximation of (20) the solution of equation (15) has the form

$$T - T_1 = \frac{\Delta T}{L} \left[ x + \psi(x) - \left(1 - \frac{2x}{L}\right) \psi(0) \right], \quad (21)$$

where

$$\psi = \frac{2\pi}{\lambda} \int_0^{\infty} n^2 \frac{dn}{dn} dv \int_0^{\infty} \frac{(1+R)\beta}{s^2 s^3} \left[ e^{-(L-x)s} [1 + Re^{-2xs}] - e^{-xs} [1 + Re^{-2(L-x)s}] \right] ds. \quad (22)$$

An analysis of formulas (21), (22) allows us to establish that the temperature distribution curve has a bending point in the middle of the layer ( $L/2$ ) and is convex in the wall with the lesser temperature and is concave in the opposite wall. It is also possible to demonstrate a number of particular peculiarities of the temperature distribution in these or other concrete instances [33].

The distribution of temperature, described by formulas (21), (22), allows us to also obtain a general formula for the total heat flow in the examined approximation

$$Q = -\lambda \frac{\Delta T}{L} - \frac{4\pi}{3} \frac{\Delta T}{L} \int_0^\infty \frac{n^3}{s} \frac{\partial \epsilon}{\partial T} dv + \frac{4\pi \Delta T}{L^3} \int_0^\infty \frac{n^3}{s^3} \frac{\partial \epsilon}{\partial T} dv \times \\ \times \int_0^\infty \frac{(1+R)(L - e^{-Ls})}{(1 + eR^{-Ls}) s^3} ds. \quad (23)$$

For low-absorbing media the formula assumes the form

$$Q = -\frac{\lambda \Delta T}{L} - 2\pi \Delta T \int_0^\infty \frac{\partial \epsilon}{\partial T} dv \int_0^\infty \frac{1-R}{1+R} \frac{1}{s^3} ds + \\ + \frac{\Delta T L}{3} 2\pi \int_0^\infty dv \frac{\partial \epsilon}{\partial T} \int_0^\infty \frac{1-4R+R^3}{(1+R)^3} \frac{ds}{s^3}. \quad (24)$$

The first term of this formula expresses the heat flow due to molecular heat conductivity, the second describes the effect of radiation of the walls, and the third - the sought for change in the heat flow as a result of the processes of radiation and absorption of radiant energy by the medium. The maximum value of this term is equal to  $\frac{2\lambda T \pi L}{3} \int_0^\infty \frac{\partial \epsilon}{\partial T} dv$ .

For the value of the relative change in heat flow as the upper limit (for an absolutely black body) we obtain the expression

$$\frac{\Delta Q}{Q} \approx \frac{2\pi}{3} \frac{L^3}{\lambda} \frac{\partial}{\partial T} \int_0^\infty \epsilon dv. \quad (25)$$

In a practical estimate the value  $\frac{\Delta Q}{Q}$  for gases which are low-absorbing media the integral of formula (25) can be conveniently replaced by expression

$$\int_0^\infty \epsilon dv = \frac{B}{3} \frac{p}{L}, \quad (26)$$

where  $p$  is the gas pressure;  $B$  is the limit of the relationship of the degree of blackness of the flat layer of gas to the product  $pL$ , with the latter tending toward zero; and  $\sigma$  is the constant of the Stefan-Boltzmann law for hemispherical radiation.

In the evaluation of (26) the temperature dependence of B can be disregarded in comparison with  $T^4$ . As a result we obtain

$$\frac{\Delta Q}{Q} = \frac{8}{3} \frac{B \pi L^3 p}{\lambda}. \quad (27)$$

This formula can be used for evaluating the influence of boundaries of the investigated effect. Thus, for carbon dioxide gas at room temperature and a pressure of 1 bar  $\frac{\Delta Q}{Q} \approx 10^{-3} L^3 \text{ cm}^{-3}$ , i.e., the change in the heat flow as a result of radiation of the medium can in this case become noticeable at a distance of several centimeters. At a pressure of 1000 bar this effect is said to be (at distances far removed from a critical point) already at a distance of several millimeters. We will also obtain a similar order of values for water vapors. The role of radiation increases with extraordinary intensity with the increase in temperature.

In the other limiting case, for strongly-absorbing media formula (23) assumes the form

$$Q = -\frac{\lambda \Delta T}{L} - \frac{4\pi}{3} \int_0^\infty \frac{n^2}{\pi} \frac{\partial n}{\partial T} d\nu \frac{\Delta T}{L}. \quad (28)$$

The effective coefficient of heat conductivity is composed of two terms which are independent one from the other – the coefficient of molecular heat conductivity and the coefficient of radiant (radiational) heat conductivity, in which the latter also characterizes only the medium as such and does not depend on the conditions on the walls and the configuration of the system. The coefficient of radiation heat conductivity is expressed by the formula

$$\lambda_{\text{rad}} = \frac{4}{3} \pi \int_0^\infty \frac{n^2}{\pi} \frac{\partial n}{\partial T} d\nu \quad (29)$$

(the derivation of this formula is also given in work [50], which was especially reserved for the problem of conditions of applicability of the concept of the coefficient of radiation heat conductivity in connection with attempts at the distribution of formulas of such type, existing in the literature, for cases of media with poor absorption).

It should be noted that it is precisely the total effective heat conductivity, expressed by formula (28), which must be figured in the Prandtl and Nusselt criteria for these cases, when the thickness of the thermal limiting layer is considerably greater than the opposite value of the effective coefficient of absorption of the medium.

Let us turn to formula (23), which describes the heat flow in the general case. Effective radiation heat conductivity may be represented as

$$\lambda^* = \frac{4\pi}{3} \int_0^\infty n^2 \frac{d\alpha}{dT} \Phi(\alpha, L) d\alpha, \quad (30)$$

where,

$$\Phi(\alpha, L) = \frac{L}{\alpha L} \left[ 1 - \frac{3}{\alpha L} \int_0^\infty \frac{(1+R)(1-e^{-L\alpha s})}{(1+Re^{-L\alpha s})} \frac{ds}{s^3} \right]. \quad (31)$$

In the general case the effective radiation heat conductivity and its dependence on parameters L and R, being a functional of  $\alpha(\nu)$ , will be different for various media. Only for the hypothetical "gray" medium, for which  $\alpha = \text{const}$ , can we write

$$\lambda^* = \frac{16}{3} \pi n^2 T^3 \Phi(\alpha, L). \quad (32)$$

Formula (32) is the basic result of the work of Poltz [46]. The function  $\Phi$  was obtained by him in a somewhat different but similar form:

$$\Phi = \frac{L}{\alpha L} \left[ 1 - \frac{3}{4\alpha L} (1 - 4K_0) - \frac{3R}{\alpha L} \int_0^\infty \frac{(1 - e^{-L\alpha s})^2}{(1 + Re^{-L\alpha s})} \frac{ds}{s^3} \right], \quad (33)$$

where

$$K_0 = \int_0^\infty e^{-L\alpha s} \frac{ds}{s^3}. \quad (34)$$

The set of curves  $\frac{\Phi}{L}(\alpha L, R)$  is depicted in Fig. 7. From the form of this dependence it is possible to draw the following significant conclusions:

1. The radiation heat conductivity of the walls with a level of blackness of  $(1 - R) < 0.3$  may exceed the value of heat transfer by radiation through the corresponding layer of a transparent medium. i.e.,  $4(1-R)\sigma\Delta T T^2$ .

2. Practically speaking, the role of the degree of blackness of the walls stops being noticeable, beginning with  $\alpha L \approx 4-5$ .

3. The effective radiation heat conductivity cannot exceed the effective radiation heat conductivity of a layer of the transparent medium with absolutely black walls ( $\frac{\Phi}{L} = \frac{3}{4}$ ), in practice — it cannot exceed one half of this value.

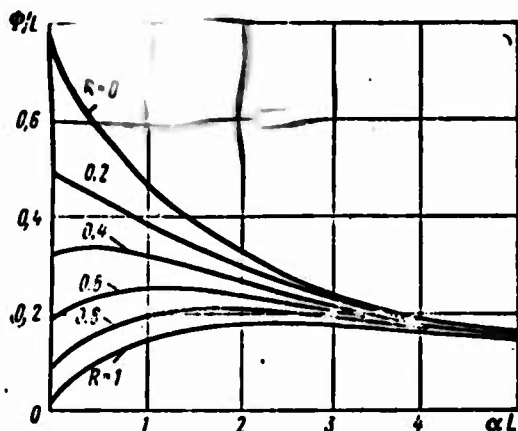


Fig. 7. Dependence of the function  $\Phi/L$ , characterizing the role of radiation in a flat layer of a medium, on  $\alpha L$  with various values of the coefficient of reflection  $R$ .

Since in the majority of cases  $n^2 \approx 2$ , Biot's criteria in the form

$$Bi = \frac{4\sigma T^2 L}{\lambda} \quad (35)$$

may be used for evaluation of the upper limit of the possible influence of radiation transfer in a flat layer.<sup>1</sup> It is worth emphasizing the strong nature of the temperature dependence of this criterion ( $\sim T^3$ ) under conditions typical for changes in heat conductivity of boundary fluids ( $\lambda \sim 0.1-0.3 \text{ W/(m}\cdot\text{deg)}$ ;  $L \sim 1 \text{ mm}$ ). At room temperatures the percentage of heat exchange by radiation should not exceed a few percent. However, at higher temperatures, in particular at temperatures close to the critical points, the role of radiation can be considerably more substantial, especially because the conditions of the transparency in this area passing from the gas to the liquid state, can be especially unfavorable ( $\alpha L \sim 1$ ). It is known that an important role can be played by radiation for high temperatures melts (glasses, slags). It can be just as great in solid nonmetallic substances, as was already many times pointed out in the discussion of the problem of thermal conductivity of semiconductors at high temperatures. There is no basis to anticipate any effect of radiation on heat transfer in solids and liquid metals.

The importance of the problem of heat transfer by radiation in liquids forces us to pay it even more attention. Let us examine the form of the dependence of effective heat conductivity of a definite substance ( $\alpha$  is fixed) on the thickness of the liquid layer.

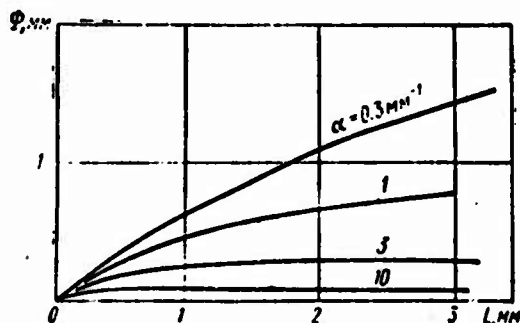


Fig. 8. Dependence of the function of  $\Phi$  on the thickness of the layer  $L$  with various values of the coefficient of absorption  $\alpha$ .

<sup>1</sup>The probability limit of the influence of this effect for  $(1-R) < 0.1$  (metallic walls)  $\sim \frac{1}{4} Bi \pi^2 \approx \frac{1}{2} BL$ .



As was already noted, the character of this dependence may, generally speaking, be different for various liquids in conformance with the form of the dependence  $\alpha(\nu)$ . For the hypothetical "gray" medium the investigated dependence will, however, be directly transferred by function  $\Phi$ . The corresponding curves are depicted in Fig. 8 (for  $R = 0$ ). For a judgement on the order of the value of change of the measured coefficient of heat conductivity let us take into account that in the investigated case

$$\frac{\Delta\lambda}{\lambda} = \frac{4}{3} \frac{Bi \pi^2}{L[\mu M]} \Phi[\mu M]. \quad (36)$$

For room temperatures and a value typical for limited liquids  $\lambda \approx 0.15 \text{ W/(m}\cdot\text{deg)}$ ,  $\frac{Bi}{L} = 0.04 \text{ mm}^{-1}$ , and  $\frac{\Delta\lambda}{\lambda} \approx 5\% \cdot \Phi\pi^2$ . It follows here from Fig. 8, that for distances of 0.5-1 mm, typical for the experiments on measurements of heat conductivity, the percentage of transfer of radiation may lie in the range from 0.5 to  $3\pi^2\%$  (for black walls and  $\alpha$  from 0.3 to  $10 \text{ mm}^{-1}$ ). For temperatures of  $\sim 200^\circ\text{C}$  the effect will amount to between 2 to  $14\pi^2\%$ .

It is significant that for  $\alpha \approx 1-0.3 \text{ mm}^{-1}$  the effect of radiation may be noted according to the change of effective heat conductivity with the change in thickness of the layer of the radiated liquid within the limits of fractions of a millimeter up to 1-2 mm. This fact in principal discloses the possibility for the experimental evaluation of the role of radiation. At present there is known, unfortunately, only one systematic experimental investigation of such kind. In the first of a series of works Fritz and Poltz [45] described an experimental apparatus, based on the use of the method of a flat layer, which permitted the making of measurements at various thicknesses of the layers - from 0.5 to 5 mm. However, the conditions for conducting the experiments were not satisfactory enough: for layers of 1.5 mm there was observed a noticeable convective mixing, and there was a systematic, although not large, dependence of the results on the drop in temperatures even for layers of  $\sim 0.5 \text{ mm}$ . In a subsequent experimental work [47] Poltz used a perfected device to study the dependence of the effective

thermal conductivity on the thickness of a layer for six liquids. In the new device convective shifting was not observed with a layer thickness of up to 2 mm and the effect of a gradient was eliminated with layers of low thickness. The basic result of the work is the clarification of the monotonic dependence of the variable values of heat conductivity on the thickness of a layer in the region from 0.5 to 2 mm for four liquids with a relatively small coefficient of absorption: benzene, toluene, carbon tetrachloride, and paraffin oil. This dependence amounts to 3-4%. For water and methyl alcohol no such dependence was detected. The author connected the observed effect with the role of heat transfer by radiation. A calculation estimate of this effect for toluene (3.7% with  $t = 25^{\circ}\text{C}$ ) was in conformance with the measured value of excess heat conductivity.

In a subsequent work of this cycle Poltz and Jugel [48] supplemented the results found with the data of measurements, obtained on the same apparatus for benzene, toluene, M-xylol, carbon tetrachloride, liquid paraffin, nitrobenzene, and isopropyl alcohol at several temperatures in the range from 10-25 to 55-80°C (with four values of a layer thickness from 0.5 to 2 mm).

The investigation conducted by Poltz and coauthors undoubtedly is of great interest as the work where serious attention was paid to radiation heat transfer in a liquid and shows that this effect can not at all be always disregarded. At the same time several defects of the work should be taken into consideration. Thus, from the four experimental points referring to the thickness of layers from 0.5 to 2 mm, in our opinion, only the first three can be taken into consideration, since the last point, referring to the thickness 2 mm, is on the boundary of the conditions, where mixing of the liquid occurs, and the problem of the degree of reliability of the results for this point can hardly be solved without ambiguity. Consequently, the basic results are based on measurements with layers 0.5, 1, and 1.5 mm and the studied effect amounts to 2-3%.

Under such conditions of special value is the proof of the absence of effects, which may distort the result of measurements. Included among such factors is the radiant heat removal through the liquid layer (an additional experiment would be desirable at a different temperature of the guard rings). Also worthy of consideration is the problem of the correctness of the account given for the role of the glass plates dividing the layer. Finally, it would be desirable to conduct experiments at various pressure drops. The aforesaid does not mean that it is necessary to put in doubt the effect found by Poltz and his coauthors. It is a question of the degree of reliability of the obtained quantitative results. Let us note in connection with this that in the work of Ziebland [51] no systematic differences were detected at various values of the thermal conductivity of toluene, obtained with clearances of 0.26 and 0.76 mm.

Let us further pay attention to the fact that the experimental data of Poltz have been compared so far with the experimental data only for toluene and that these calculations are also not completely free from criticism. We have already noted that the character of the dependence  $\lambda^*$  on the layer thickness, generally speaking, depends on the form of the function  $\alpha(v)$  and in the general case the calculations should be made from formula (30). With Poltz [48] the calculations were made for a "gray" medium, and as the average value of the coefficient of absorption

$$\bar{\alpha} = \frac{\int_0^{\lambda} \alpha dv}{\int_0^{\lambda} \frac{1}{v} dv} \quad (37)$$

was taken.

The use of just such a value is not correct, since in conformance with (30) with averaging it is necessary to use not Planck's function, but a derivative of it. Furthermore, keeping in mind the order of the

value of the coefficient of absorption in the investigated case, it would follow to average not the reverse value of the coefficient of absorption, but rather to average  $\alpha$  directly in conformance with formulas (24) and (25). Let us also note that the degree of blackness of the radiation of the wall in contact with the liquid may be, generally speaking, other than that in a vacuum.

All this makes it desirable to conduct more detailed calculations of the radiation transfer, based on consideration of the spectra of absorption of infrared radiation.

The suggested material refers to the case of a flat layer of the medium. No less important for the practice of investigating heat conductivity of gases and liquids is the case of a cylindrical layer, corresponding to the conditions of the experiment with methods of coaxial cylinders and, especially, a heated wire. The analysis of the distortion of the process of heat transfer due to radiation of the medium in a cylindrical layer was taken up by a single work, written very recently by L. A. Pigal'skaya. Below the basic results of this work are stated.<sup>1</sup>

Just as for the case of a flat layer, the initial equation is the equation of transfer of radiant energy. The desired value of the intensity of radiation is examined here as a function of two angles, determining the direction of the ray and the distance  $r$  from the axis. The boundary conditions on the surfaces of the cylindrical layer  $r = \rho$  and  $r = R$  presuppose a mirror reflection, characterized by the coefficients of reflection  $R_1$  and  $R_2$  averaged with respect to angles.

To find the distribution of temperatures an equation analogous to (13) is used. In order to simplify the problem we use the case

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<sup>1</sup>The authors would like to express their appreciation to L. A. Pigal'skaya for the material which she furnished.

where the difference in temperatures on the surfaces is sufficiently small, which is equivalent to the first assumption on page 14 of this book. The solution of the problem of the distribution of temperatures and of the value of the heat flow is by the method of successive approximations, and as the zero approximation the logarithmic distribution of temperature undisturbed by radiation is assumed [such a method of solution is equivalent to writing (20) for a flat layer]. An analytical investigation can be successfully used only with small coefficients of absorption. Here for the specific heat flow in the first approximation the formula

$$q = -\frac{\Delta T}{r \ln \frac{R}{r}} \left\{ \lambda + \pi L \int_0^1 \frac{dx}{x} \left\{ F_1(R_1, R_2) \Phi_1(x) - \frac{\pi L}{x} \times \right. \right. \\ \times [\Phi_1(x) F_2(R_1, R_2) + \Phi_2(x) F_3(R_1, R_2) + \Phi_3(x) F_4(R_1, R_2) + \\ \left. \left. + \Phi_4(x) F_5(R_1, R_2)] \right\} dx \right\}, \quad (38)$$

is obtained, where

$$L = R - r; \quad \xi = r/R; \quad F_1 = \frac{R_1 + R_2 - R_1 R_2 - 1}{1 - R_1 R_2}; \\ F_2 = 1; \quad F_3 = \frac{R_2 - R_1}{(1 - R_1 R_2)^2}; \\ \Phi_1 = \frac{\xi \ln \xi}{1 - \xi}; \quad \Phi_2 = (1 - \xi)^{-2} (6\xi \sqrt{1 - \xi^2} + \\ + \pi \xi^3 + 3 \arcsin \xi - 4\xi^2 \arccos \xi + \arccos \xi + \frac{\pi(1 - \xi^2)}{\ln \xi} - \frac{\pi}{2}); \\ \Phi_3 = \frac{\ln \xi}{(1 - \xi)^2} (2\xi \sqrt{1 - \xi^2} + 2 \arcsin \xi); \quad \Phi_4 = \pi \xi^2; \\ \Phi_5 = (1 - \xi)^2 (6\xi \sqrt{1 - \xi^2} + 4 \arcsin \xi - \pi \xi^2 - 4\xi^2 \arccos \xi + \\ + 2 \arccos \xi - \pi).$$

At the limit when  $\xi \rightarrow 1$  this formula, as should be expected, is transferred to an analogical relationship for a flat layer, and when  $R_1 = R_2$ , to formula (24).

The first term in the equality (38) characterizes the heat transfer by molecular heat conductivity, and the following ones describe the role of radiation. Of these, the term containing the derivatives  $F_1 \Phi_1$  corresponds to the known expression for heat flow,

transferred by radiation, in a cylindrical layer of a transparent medium, while the remaining terms take into account the natural radiation of the medium and the absorption of total radiation.

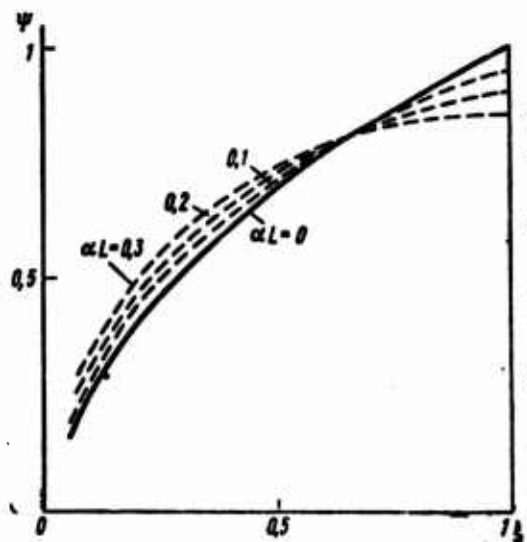


Fig. 9. The dependence of function  $\Psi$ , characterizing the role of radiation in a cylindrical layer of a medium, limited by absolutely black walls, on the relationship of the radii  $\xi = \rho/R$  with various values of the parameter  $\alpha L$  (the continuous line describes an absolutely transparent medium).

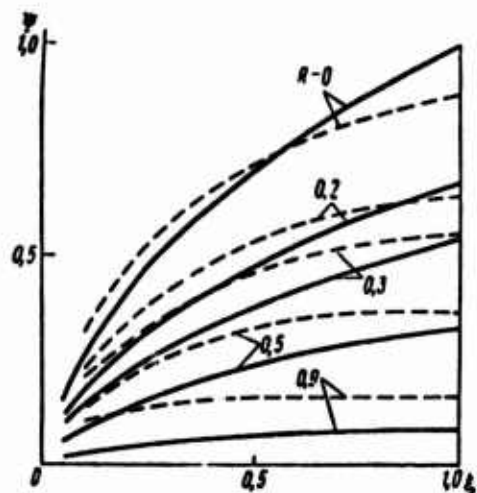


Fig. 10. The dependence of the function  $\Psi$  on the parameter  $\xi$  with various values of the coefficient of reflection of the walls and  $\alpha L = 0.2$  (the continuous lines describe an absolutely transparent medium).

For an analysis of the obtained dependence L. A. Pigal'skaya examines the dimensionless value  $\Psi$ , placed into the figure brackets of expression (38). [For the case of a flat layer the value  $\Psi$  is equivalent to  $\frac{4}{3} \frac{\phi}{L}$  in formula (31) under conditions of smallness of  $\alpha L$ ].

The dependence of  $\Psi$  on the geometrical characteristics of  $\xi$  with absolutely black walls is depicted in Fig. 9. In the case of a flat layer, when  $\xi \rightarrow 1$ , the process of absorption of radiation of the walls predominates over the process of natural radiation, and the presence of the medium leads to a reduction in the heat flow. For geometry characteristic for the method of a heated filament ( $\xi \ll 1$ ), the heat flows of radiation from the walls is noticeably less, as a result of which the natural radiation of the medium plays a significantly greater role, if the absorption of radiation from the walls, and, as a result, the presence of the medium increases the heat flow. With  $\xi = \xi_0 \approx 0.6$  the resulting heat flow proves to be independent of the absorption power of the medium (for the investigated case of low absorptions).

The dependence of function  $\Psi$  on  $\xi$  for walls with a uniform coefficient of reflection ( $R_1 = R_2 = R_{1,2}$ ) when  $\alpha L = 0.2$  - Fig. 10 - shows how in proportion to the increase in the coefficient of reflection, i.e., the reduction in the radiation of the walls, the role of natural radiation of the medium increases. Point  $\xi_0$  here shifts to the right and with  $R_{1,2} = 0.29$  reaches a limiting value of  $\xi_0 = 1$ . For higher values of  $R_{1,2}$  the natural radiation of the medium exceeds the decrease of the radiation of the walls as a result of absorption, and the total effect is positive for all values of  $\xi$ . Under conditions corresponding to the experiments according to the method of a heated filament ( $R_{1,2} > 0.9$ ) the role of radiation is quantitatively similar to the case of a flat layer (the total heat transfer is increased).

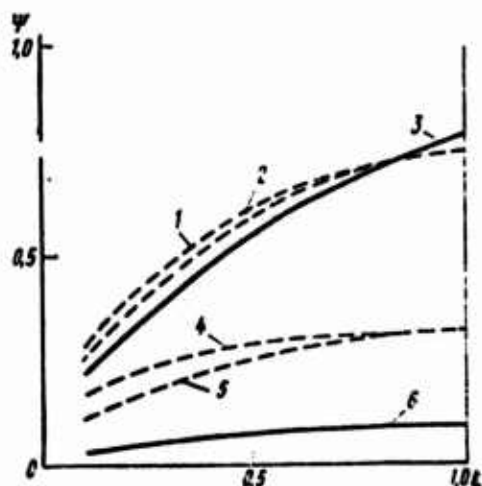


Fig. 11. Dependence of function  $\Psi$  on the parameter  $\xi$  for walls with various coefficients of reflection.

The effect of the coefficient of reflection of the walls is illustrated in Fig. 11, which depicts the dependence of  $\Psi$  on  $\xi$  for  $R_1 = 0.2$ ;  $R_2 = 0$  (curve 1;  $\alpha L = 0.2$ );  $R_1 = 0$ ;  $R_2 = 0.2$  (curve 2;  $\alpha L = 0.2$ ) and  $R_1 = 0$ ;  $R_2 = 0.9$  and  $R_1 = 0.9$ ;  $R_2 = 0$  (curves 4 and 5, respectively;  $\alpha L = 0.2$ ); the latter case most closely approaches the conditions of the experiment with a heated filament in a glass or quartz capillary tube. Continuous lines 3 and 6 describe an absolutely transparent medium. From Fig. 11 one can draw the conclusion that the value of the heat flow is strongly affected by the coefficient of reflection of this surface, the area of which is greater. The influence of the sign  $\Delta R = R_1 - R_2$  naturally is reduced with an increase in  $\xi$ , i.e., in proportion to the approximation to a flat layer, in which both surfaces are equivalent.

On the whole, the picture of heat transfer by radiation in a cylindrical layer proves to be much more complex, than in a flat layer, even for poorly-absorbing media. Further investigations of this problem for practically important cases (in particular, for  $\xi \ll 1$  and  $\alpha L \approx 1$ ) are absolutely essential.

Everything examined allows us to draw the following conclusions on the role of heat transfer by radiation in liquids.



The theoretical approach and quantitative experimental evaluations of the influence of this effect leads to the conclusion that the transfer of heat by radiation under conditions of change in the coefficient of heat conductivity (thickness of layers of 0.5-1 mm) at room temperatures may somewhat distort the results; however, in most cases this distortion lies within the limits of accuracy of the experiment (1-3%). At higher temperatures the effect may become much more substantial, especially in the range of temperatures of  $\sim 200^{\circ}\text{C}$  and higher.

In connection with this, the problem of the degree of reliability of experimental data on heat conductivity of liquids, especially at sufficiently high temperatures, is very complex, and all the more so if we are speaking of sample liquids.

The most detailed examination of the role of heat transfer by radiation was conducted by us for toluene, for which we not only evaluated the possible limit of the role of the radiation component of the flow, but also made an attempt to isolate the purely molecular heat conductivity by introducing corrections into the results obtained by individual authors. For the remaining liquids we were forced at best to make only evaluations of the probable limit of the radiation transfer. For dense gases we did not introduce a correction for the role of radiation of the medium due to the absence of necessary information.

More thorough judgements on the role of heat transfer by radiation can be made only after conducting regular, systematic experimental and theoretical investigations, in particular, investigations of the spectra of infrared absorption of a large class of substances in a wide range of temperatures with the purpose of making theoretical calculations for the value of radiation transfer.

### Concerning New Methods for Measuring the Heat Conductivity of Gases and Liquids

There is no need to give a description of all the basic methods of measuring heat conductivity of gases and liquids. The best known stationary methods - of a flat horizontal layer, of coaxial cylinders and of a heated filament - are examined in a number of monographs and articles, in particular, in the books of N. V. Tsederberg [10], B. S. Petukhov [53], and Tyrrel [54]. A discussion of many problems of the technology of the experiment, and of the important parts of the experimental apparatus for investigating using the method of a flat horizontal layer may be found in works [23, 55, 56], using the method of coaxial cylinders - [57-59], and using the method of a heated filament - [21, 30]. In this text these methods are examined only in connection with the evaluation of the quality of experimental results obtained by various authors. Let us examine in more detail the new methods, mainly nonstationary ones, which have been developed only very recently and which are partially already being used for measurements of heat conductivity of gases and liquids.

Let us examine certain problems related to stationary methods, since the greatest quantity of experimental data existing in the literature has been obtained by these methods.

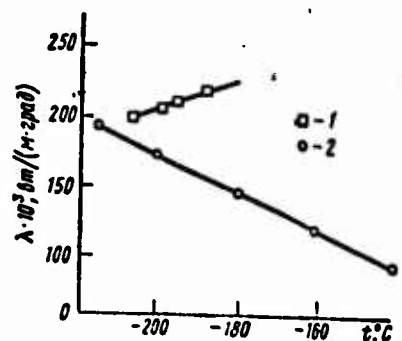
The method of a flat horizontal layer is fundamentally ideal for the exclusion of natural convection, if sufficiently strict isothermicity along the entire surface of the measured plates is guaranteed. This may be achieved with the aid of protective heaters. In the majority of investigations these conditions were observed to a sufficient degree. However, in certain works there were unaccounted for boundary effects and the phenomenon of natural convection related with them in the investigated layer of liquid. This led to large errors, even to an inaccurate temperature dependence of the thermal conductivity. Such phenomena were encountered in the experiments of Hamman [60] on the determination of heat conductivity of oxygen and nitrogen (Fig. 12). The results of these experiments were analyzed in detail by N. V. Tsederberg [10] and Ziebland [61].

A similar occurrence happened in the experiments of Bates [10] in the investigation of the thermal conductivity of ethyl alcohol (Fig. 13). The experiments of Bates are critically examined in work [62]. Ye. P. Borovik [10] in measuring the thermal conductivity of nitrogen by the method of a flat horizontal layer detected a dependence of the effective values of the thermal conductivity of  $\lambda$  on  $\Delta t$ , which testified to the convective transfer of heat in the layer of studied liquid. For the elimination of the effect of convection Ye. P. Borovik made measurements with various  $\Delta t$  and extrapolated the experimental values of  $\lambda'$  to  $\Delta t \rightarrow 0$ . It should be noted that in all of these works the width  $\delta$  of the investigated layer of liquid was comparatively great: in the Borovik's apparatus  $\delta = 2.1$  mm, in Bates' apparatus — 6.3 mm and in Hamman's apparatus — 12 mm. In the majority of works in which convective heat transfer was not observed the measured values of thermal conductivity proved to be independent of  $\Delta t$  when  $\delta = 0.2-1$  mm. Thus, one of the important conditions in method of a flat horizontal layer is a low value for  $\delta$ .

The method of coaxial cylinders also requires isothermic conditions along the length of the measured section, since for determining the heat conductivity we use the formula obtained for infinitely long cylinders. In some works isothermicity was guaranteed by using protective heating devices on the ends, and in others — when the measured section amounted to a small part of sufficiently long cylinders, by means of a special fitting for substances with known heat conductivity heat leakages from the ends of the measured section were determined (in this form the method was used as a relative one).

Fig. 12. Experimental data of various authors on the thermal conductivity of oxygen: 1 — Hamman [60]; 2 — Other authors [29, 124].

Designation:  $\text{BT}/(\text{M} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ .



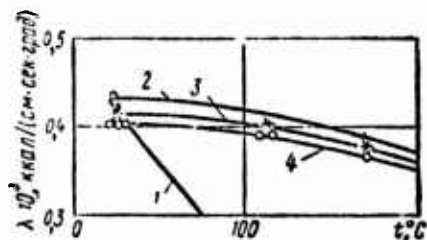


Fig. 13. Experimental data of various authors on the heat conductivity of ethyl alcohol: 1 - Bates [10]; 2, 3, 4 - Kerzhentsev [62] with  $p = 150; 100$  and  $1-15$  atm, respectively.

Designation:  $\text{ккал}/(\text{см} \cdot \text{сек} \cdot \text{град}) = \text{kcal}/(\text{cm} \cdot \text{s} \cdot \text{deg})$ .

The method of coaxial cylinders was employed in the basic investigations on heat conductivity of many liquids and gases [57-59], including those with very precise measurements of heat conductivity of water and water vapor. An interesting construction of a measurement apparatus, based on the method of coaxial cylinders, was recently proposed by Leidenfrost [63]. The ends of the measurement cylinders were connected with spherical surfaces, which facilitated the solution of the problem, connected with end effects.

A deficiency in the devices, based upon methods of a flat horizontal layer and coaxial cylinders, is the great inertia and size.

The heated filament method proved to be very attractive for experimenters. The measuring cell possesses comparatively low inertia. Moreover, the correction for heat removal from the ends of the fine heater ( $d = 0.1$  mm) is very small, and it can be easily taken into account by a calculation method or experimentally, having carried out experiments with two measurement tubes of varying length. The method was used for measuring thermal conductivity of many gases and liquids, and very accurate experimental data were obtained on the thermal conductivity of a significant number of gases and liquids, including water and water vapor.

In recent years the heated filament method has received further development. Blais and Mann [26], D. L. Timrot and A. S. Umanskiy [64] modified this method for the purpose of measuring the thermal conductivity of gases in the region of high temperatures (above  $1300^\circ\text{K}$ ),

in which the application of the usual method of a heated filament was complicated by the difficulty of the prolonged maintenance of strict constancy of the temperature of the wall of the measuring tube and a sufficiently precise measurement of a small difference in temperatures in the layer of the studied gas at these temperatures.

The idea of this modified method is embodied in the study of the dependence of the heat flow  $q$  on temperature  $t$ , which is transferred from the wire through the investigated gas by thermal conductivity in a radial direction.

Using the known solution for the equation for thermal conductivity

$$q = \frac{2\pi}{\ln(d_2/d_1)} \int_{t_{cr}}^t \lambda dt \quad (39)$$

and assuming that the heat flow  $q$  and the heat conductivity of the gas  $\lambda$  are functions of the temperature, that the temperature of the wall is maintained strictly constant (at room temperature), and that the portion of heat transferred by radiation from the wire is small, the authors obtained the expression

$$\lambda_t = \frac{\ln d_2/d_1}{2\pi} \frac{dq(t)}{dt}, \quad (40)$$

where  $\lambda_t$  is the gas thermal conductivity value, relative to the temperature of the filament;  $dq/dt$  is determined by differentiation of the equation  $q = f(t)$ , composed on the basis of experimental data. Thus, in this method only  $q = f(t)$  is studied and there is no need to measure the difference in temperatures in the layer, which is an advantage of this method.

With this method authors [26, 64] measured the thermal conductivity of helium and hydrogen up to temperatures of  $\sim 2000^\circ\text{K}$  at atmospheric pressure. The authors estimate the error of the experiments at 5%. Divergences between data of [26] and [64] reach 12% for helium, and 25% for hydrogen at  $T = 2000^\circ\text{K}$ .

It should be noted that structurally the devices are made differently, in particular, in [26] the measuring tube is positioned vertically, and in [64] - horizontally; in [64] the wall of the measuring tube was thermoregulated more carefully, and the technology of conducting the experiment was different. It would undoubtedly be advantageous to refine and perfect this method, in particular, to make measurements of the thermal conductivity of a gas in one and the same measuring tube in the horizontal and vertical positions. Apparently, it would be good to thoroughly analyze from a quantitative view point the effect of the inconstancy of the temperature of the wall on the results of measurement of thermal conductivity.

Kannuluik and Carman [65], in order to reduce the correction for the temperature jump between the heated filament and studied gas, employed as the heater, placed along the axis of the measurement tube, a platinum wire of large diameter  $d = 1.5$  mm, having modified the heated filament method, in which a fine wire with a diameter  $d = 0.1$  mm is ordinarily used as the heater. Corrections for heat removal from the ends of the heater and for radiation from the heater sharply increased; as a result of large corrections for radiation the authors were forced to limit temperature measurements to  $300^{\circ}\text{C}$ . The total of these corrections at elevated temperatures amounted to approximately 50% of the overall heat flow, and for gases with low thermal conductivity (Kr, Xe) reached as high as 70-80%. Naturally, the use of the heated filament method in the form as employed in the work of Kannuluik and Carman, especially for gases with low thermal conductivity, is not advisable.

In connection with the need for obtaining experimental data for many liquids, gases, and gas mixtures during the last few years widespread application of nonstationary methods has begun. These comparatively quick methods were previously most frequently employed for the measurement of the thermal conductivity of hard nonmetallic solids.

The theory of the most widespread of these nonstationary methods, which in our own literature is called the method of a regular thermal regime of class I is expounded in detail in the books of G. M. Kondrat'yev [66, 67]. The largest quantity of experimental data at elevated temperatures and pressures was obtained using a variant of the same method developed by I. F. Golubev [68].

The device of I. F. Golubev consists of two coaxial cylinders, between which the investigated layer of material (a bicalorimeter) is placed. For the elimination of end losses there are compensation cylinders, the diameter of which is the same as in the internal working cylinder. A difference in temperatures in the investigated layer is determined from the indications of the triple-soldered differential thermocouple. The coefficient of thermal conductivity is calculated using the expression

$$\lambda = \frac{cR_1m}{F} \ln \frac{r_2}{r_1}, \quad (41)$$

where  $c$  is the total specific heat of the internal cylinder;  $r_1$  is the exterior radius of this cylinder;  $F$  is its lateral surface;  $r_2$  is the internal radius of the external cylinder; and  $m$  is the rate of cooling.

The rate of cooling is determined from the known formula

$$m = \frac{\ln \Delta T_1 - \ln \Delta T_2}{\Delta \tau}, \quad (42)$$

where  $\Delta T_1$  and  $\Delta T_2$  are the drop in temperature in the measured layer at the beginning and the end of the process of cooling for the time interval  $\Delta \tau$ .

In the derivation of equation (41) it is assumed that the temperature on the internal surface of the external cylinder is constant in time. From the expressions introduced in work [68] it also follows that the temperature of the metal through the thickness of the internal cylinder is taken as identical everywhere, i.e., not depending on the radius.

In calculating the coefficient of the thermal conductivity from equation (41) a number of corrections, examined in detail in the corresponding work, are introduced.

The investigated method was employed by I. F. Golubev and Ya. M. Naziyev in the investigation of n-hexane, n-heptane, and n-octane [69]. Then I. F. Golubev and coworkers measured the heat conductivity of air, methane, ammonia, and other substances at pressures of up to 500-600 bar, including the supercritical region.

The possible error of the results is estimated by the authors at 1%. However, a comparison of the data of I. F. Golubev and coworkers with the results of other investigators in a number of works shows significantly more divergences. This, possibly, is connected with certain defects of the methods adopted in work [68] for measuring and processing their results:

a) the boundary condition  $t = \text{const}$  is not observed; thus, up to the beginning of cooling of the inner cylinder the temperature of the inner surface of the outer cylinder increases somewhat during the period of heating (2-3 min).

b) the introduction of the correction for heating of the exterior cylinder, based only on its total specific heat, is strictly valid only for cylinders manufactured from materials possessing very high thermal conductivity.

c) the change in temperature of the thermostat for the time for conducting the experiment is not taken into consideration.

According to the data of A. A. Gylmanov [70] changes in the temperature of the thermostat for the time of the experiment by 0.01 deg vary the cooling rate (or what is the same, the measured value of the thermal conductivity) on the average by 1%.



Moreover, when using the given method in the supercritical region it is necessary to keep in mind that in this region the properties of materials vary very strongly in proportion to the change in temperature, while the theory of a regular regime [66] was developed on the assumption of constancy of the thermophysical properties. Let us also note that in the supercritical region a continuous state is achieved very slowly and the use of nonstationary methods may produce distorted results.

The method of a regular regime has a number of advantages in comparison with stationary methods (the short length of time for conducting the experiments, the relative simplicity of construction of the apparatus, etc.), however, as can be seen from the aforesaid, it requires further refining.

The nonstationary method of a heated filament belongs to the class of nonstationary methods for measuring heat conductivity of liquids. It is used in works [71-74], and the theory of it is similarly expounded by Horrocks and McLoughlin [74].

In contradistinction to the stationary method of a heated filament in the nonstationary variant the change in temperature of the thread is determined as a function of the time elapsed from the start of heating (or - in another variant - the change of temperature in the investigated liquid at a certain distance from the thread). Because of the study of the quickly occurring process, measurements are made under conditions when convective flows do not manage to develop. Because of this the necessity arises for centering the filament in the narrow capillaries, and the construction of the measuring cell becomes much simpler. An advantage of the method is also the speed with which measurements can be carried out. The first successful experiments and, in particular, those fulfilled by the differential variant of the method [75] permit us to think that further development and perfection of the method will lead to the creation of a sufficiently simple and precise method.

In another examined group of nonstationary methods heat conductivity of a medium is determined, by studying the continuous pulsation of the temperature of a low-inertia metallic sensor (a wire, foil), placed into the investigated medium and heated by alternating current. A special feature of this method is the possibility of using radiotechnological measurement means. One of the basic advantages is the simplicity of the measuring cell. The placement of the sensor in the medium may be to a significant degree arbitrary, since convective shifting of the medium in the volume has practically no effect on the indications of the sensor due to the small width of the layer, effective at these measurements (the temperature wave is almost completely absorbed at a distance of the order of fractions of a millimeter). Another advantage of the method is the small role played by heat removal by radiation from the sensor under conditions of measurement of the heat conductivity of gases at high temperature (only the change in radiation during pulsation of the temperature is important).

The idea of the method and its first realization belong to L. P. Filippov [76]. As the sensor a strip of foil, inserted into the investigated liquid, was used. The amplitude of pulsation of the temperature of the foil during its heating by ac current with all other conditions being equal depends only on the coefficient of heat activity of the liquid

$$b = \frac{\lambda}{\sqrt{a}} = \sqrt{i c_p \rho}, \quad (43)$$

where  $a$  is the thermal diffusivity;  $c_p$  is the specific heat; and  $\rho$  is the density. The procedure in this variant is thus, actually the method of measuring the coefficient of thermal activity; the coefficient of thermal conductivity can thus be found, if we know the value of the volumetric specific heat  $c_p \rho$ .

To measure the amplitude of pulsation of the temperature of the foil a circuit consisting of an ac bridge, into one arm of which a sensor is connected, is employed. The bridge was balanced at the heating frequency  $\omega$  (tens-hundreds of Hz). The pulsation of the

temperature of the sensor, occurring with doubled frequency  $2\omega$ , and the resistance pulsation connected with it led to the occurrence in the bridge diagonal of a voltage of tripled frequency  $3\omega$ , proportional to the amplitude of the temperature pulsation. The signal of voltage  $3\omega$  is separated, amplified, and measured using a radiotechnological circuit. The measurement procedure was relative. Direct results of the experiment were reproduced with a divergence in fractions of a percent, and the maximum error of the values of the coefficient of thermal activity with consideration of the error of calibration amounted to 3%.

The method has been used for conducting a series of scientific-research works, in particular, in Hungary [33, 77]. Recently this method has been developed in the works of I. I. Novikov and F. G. El'darov [78]. Details of the theory and of the experiment can be found in work [33]. There also is described one more direction of development of the experiment — the measurement of the specific heat of a wire under conditions, when the pulsation of the temperature of the wire is determined by the thermal inertia of the sensor.

A sensor in the form of a wire was also used by American authors [79, 80] for measuring the thermal conductivity of gases. The measuring scheme is analogous to that of L. P. Filippov.

The theory of the method for the sensor in the form of a cylinder is more complex than for a sensor-foil, since in general the result depends not on one variable  $b$ , as in a flat layer, but on two — on  $b$  and on the thermal diffusivity  $a$ . In order to obtain values of the coefficient of thermal conductivity from experimental data, in the considered work measurements were made with a constant ratio  $c'_{pQ}/c_{pQ}$ , where  $c'_{pQ}$  is the volumetric specific heat of the gas, and  $c_{pQ}$  is the volumetric specific heat of the sensor. This made it necessary to select the gas pressure specially at each temperature, in order to fulfill the given condition.

Measurements [79, 80] are relative ones (only the temperature dependence of the thermal conductivity was studied); the maximum error was estimated at 2-3%. There is a basis for thinking, however, that this estimate is somewhat understated, at least in the area of high temperatures. The fact is that the variants of experimental data in the examined work exceed the cited value and go as high as 4.5%. Here there still remains unclarified the question of systematic errors. Their value must depend on the relative value of the thermal inertia of the sensor. Unfortunately, the corresponding estimates cannot be made, since in this publication the most essential thing was not mentioned - the frequencies at which the measurements were made. One can only assert that, all other conditions being equal, the role of error, caused by the thermal inertia of the sensor, must be greater for gases with lower thermal conductivity.

In conclusion, we should say a few words on the perspectives of development of methods of periodic heating. There is reason for thinking that these methods have a great future, since apart from the above formulated advantages this group of methods has one more important quality - it enables us to conduct experiments of a complex nature, which ensures our obtaining a whole set of fundamental thermal physical parameters (thermal conductivity, thermal diffusivity, specific heat, and the coefficient of thermal activity) using one measurement system. This capability is related with the mentioned fact of the dependence of the pulsations of temperature of the wire sensor on two thermophysical characteristics. A concrete analysis of the ways of conducting the complex experiment is described in the book [33].

Finally, it is important to turn our attention to one more important peculiarity of the examined method of measurement - to the capability of varying the effective width of the investigated layer of the medium by means of changing the frequency of pulsations. The conducted measurements with various effective layers may play a very significant role in the investigation of the influence of the process of radiation.

Of the other methods of measuring the thermal conductivity of gases, developed in recent years, we should mention the method of a laminar regime, employed by Westenberg and de Haas [81].

The essence of this method consists in the following. A linear heat source of finite length (the wire) is situated perpendicular to a laminar uniform gas flow, having a velocity  $u$ . Under the condition of consistency of the coefficient of thermal conductivity  $\lambda$  and specific heat  $c_p$  a rise in temperatures behind the linear heat source at any distance from it  $r^2 = x^2 + y^2$  is expressed by the formula

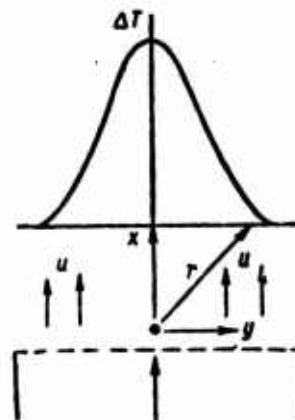
$$\Delta T = [q/(4\pi u c_p \lambda r)] \exp [u c_p (x - r)/2\lambda], \quad (44)$$

where  $q$  is the specific power of the heat source;  $\rho$  is the gas density. Expression (44) is obtained for the case, when the linear heat source is situated along the axis  $z$ , the gas flow is directed along the axis  $x$  (Fig. 14). If we measure  $\Delta T$  at points where  $y = 0$ , so that  $x = r$ , then from formula (44) we get

$$\lambda = (q^2/4\pi u c_p \rho) (1/x \Delta T_{\max}^2), \quad (45)$$

where  $\Delta T_{\max}$  is the maximum rise in temperature in the direction  $x$ . As follows from formula (45), with constant  $q$  and  $u$  the value of  $\frac{1}{x} \Delta T_{\max}^2$  must be constant at various values of  $x$ .

Fig. 14. On the laminar flow method.



Another variant for conducting measurements of thermal conductivity is possible. The measurement of  $\Delta T$  at various distances  $r_n$  in one transverse cross section  $x = \text{const}$  allows us to determine  $\lambda$  without knowing the specific power of the heat flow. In this case besides the relative measurements of  $\Delta T_n$ , it is necessary to know the velocity of the gas flow  $u$ .

A third method for measuring thermal conductivity is a combination of the two mentioned variants. In this case the velocity of the gas flow is excluded from the measurements, however, just as in the first case,  $\Delta T$  and  $q$  are determined.

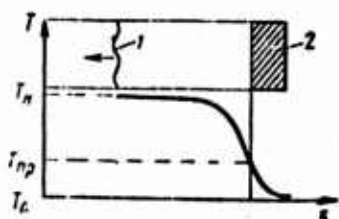


Fig. 15. Schematic representation of the temperature field of a reflected shock wave: 1 - reflected wave; 2 - end of the tube.

At high temperatures the second variant appears to be most suitable, where there is no need to know  $q$  and the absolute values of  $\Delta T$ , the measurement of which at high temperatures is complicated due to the consideration of correction for radiation.

This variant was also used by the authors of work [81] for measuring the thermal conductivity of  $N_2$ ,  $O_2$ ,  $CO_2$  up to  $T \approx 1100^\circ K$  at atmospheric pressure. The results of the experiments agree satisfactorily with the most reliable literature data. However, the authors point out that at high temperatures, especially for  $CO_2$ , a great divergence of the experimental points was observed. The authors explain this by the insufficient stability of the stream. This method is not simple, since it requires the creation of a stationary gas flow and sufficiently precise measurement of its parameters. Apparently, additional study should be made for certain

systematic questions, in particular, for the problem of the possibility of disturbing the laminar stream during nonisothermic flow, which is especially important at elevated gas pressures.

During the last few years, to obtain experimental data on thermal conductivity of gases at very high temperatures (up to 8000°K), the method of a shock tube was employed [82]. This is based on the employment of the process of heat transfer by the end wall of a shock tube by a hot gas. In solving the equation of the thermal conductivity for the gas behind the front of a shock wave it is suggested that the gas is a semi-infinite medium (the one-dimensional case) and is situated in thermal contact with a semi-infinite solid wall (Fig. 15). The heat is transferred by radiation and by convection.

The equation of thermal conductivity for the semi-bounded medium with boundary conditions of the fourth class has a simple solution, if one assumes that the coefficient of heat conductivity of the gas varies according to exponential law, i.e.,

$$\lambda = \lambda_{np} (T/T_{np})^b, \quad (46)$$

where the subscript "np" refers to the parameters of the gas being the shock wave.

Using formula (46), one obtains a relationship, which connects the temperature of the gas right after heating  $T_n$ , the temperature of the gas (of the wall) after the arrival of the shock wave  $T_{np}$ , the subscript b and a certain dimensionless parameter  $q_{np}$ ,

$$\frac{T_n}{T_{np}} = f(b, q_{np}), \quad (47)$$

where

$$q_{np} = \sqrt{2/\pi} K \frac{T_{np} - T_c}{T_c};$$

$$K = \frac{(\lambda \rho c)_c}{(\lambda \rho c)_{np}}$$

The parameters with the subscript "c" refer to the end wall up to the arrival of the shock wave.

Expression (47) can be obtained in explicit form only with certain values of parameter  $b$ . When  $b = 1$  it has the simplest form:

$$\frac{T_n}{T_{np}} = 1 + \sqrt{\pi/2} \cdot q_{np}. \quad (48)$$

In this way, the experiment is reduced to the determination of the superscript  $b$ . It is found by the method of least squares from plotting curves of the dependence (47). The thermal physical properties of the gas and wall with temperatures  $T_{np}$ ,  $T_c$  (practically, room temperatures) are considered to be unknown. The gas temperature and pressure after heating  $T_H$  and  $p_H$  are calculated from the equation of energy preservation, just as for an ideal gas.

Using this method, experimental data were obtained mainly for monatomic gases, and also for air and nitrogen. The error of the results of the experiments amounts to 20-30%. At the same time the method of a shock tube until now appeared to be practically the only one for determining experimental data on the thermal conductivity of gases at very high temperatures.



## CHAPTER II

### ANALYSIS OF THE EXPERIMENTAL DATA. RECOMMENDED VALUES OF THERMAL CONDUCTIVITY

#### Helium

The thermal conductivity of helium at atmospheric pressure was studied by various authors in a wide range of temperatures. The basic works are cited in Table 1. As can be seen from them, a comparatively large number of them were dedicated to measurements within a range of low temperatures 80-300°K.

In this temperature interval the most reliable data appear to be those of Johnston and Grilly [85]. The authors of [85] made careful measurements by the heated filament method, and paid special attention to the analysis of the conditions of the experiment. With these results there is good correspondence to the data of Eucken [83], Kannyluk [65], Barua [92] and others. The results of their experiments are shown in Fig. 16. The averaged curve is closest to the data of Johnston and Grilly [85]. Divergences of the experimental data of various authors from the curve do not exceed ~2%, which also defines the accuracy of the recommended values in the considered interval of temperatures.

Table 1. Basic investigations of the thermal conductivity of helium.

Author	Year	Liter- ature source	Method	Temperature, °K	Pressure, bar
Eucken	1911; 1913	[83]	Heated filament	52-373	1
Ubbink, de Haas	1943	[84]	"	89-278	1
Johnston, Grilly	1946	[85]	"	80-380	1
Lenoir, Commings	1951	[86]	Coaxial cylinders	316	1-210
Kannyluik, Carman	1952	[65]	Heated filament	90-580	1
Tsederberg, Popov	1958	[87]	"	273-673	10-500
Zaytseva	1959	[88]	"	273-873	1
Blais, Mann	1960	[26]	"	1200-2200	1
Johannin, Wilson	1962	[89]	Coaxial cylinders	308-629	1-230
Vargaftik, Zimina	1965	[90]	Heated filament	273-1273	1
Collins, Greif	1966	[82]	Shock tube	1600-6700	1
Timrot, Umanskiy	1966	[64]	Heated filament	400-2400	1
Saxena, Saxena	1966	[91]	"	313-388	1
Mukhopadhyay, Barua	1967	[92]	"	90-473	1
Strivastava, Gupta	1967	[93]	"	314-473	1
Gandhi, Saxena	1967	[94]	"	303-363	1
Freud, Rothberg	1967	[95]	Coaxial cylinders (relative)	298	1-3300

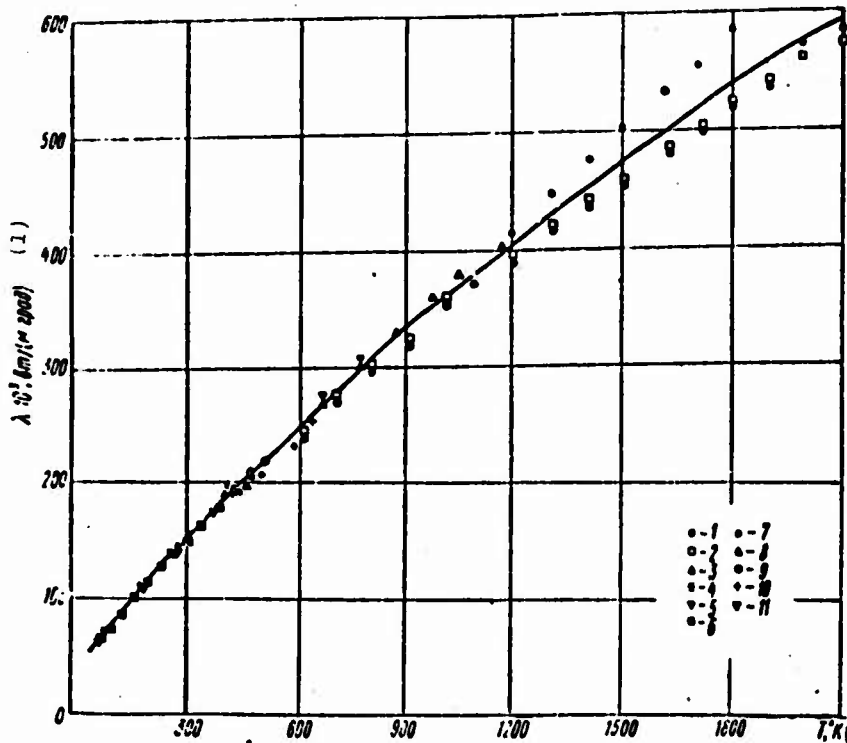


Fig. 16. Dependence of the thermal conductivity of gaseous helium on the temperature when  $p = 1$  atm according to the data of: 1 - Blais and Mann, [26]; 2 - Collins and Greif [82]; 3 - Vargaftik and Zimina [90]; 4 - Kannyluik and Carman [65]; 5 - Zaytseva [88]; 6 - Johnston and Grilly [85]; 7 - Barua, et al. [92]; 8 - Gupta, et al. [93]; 9 - Timrot and Umanskiy [64]; 10 - Johannin and Wilson [89]; 11 - Eucken [83].

KEY: (1)  $\lambda \cdot 10^3$ , (W/m·deg).

Just as for the majority of gases, heat conductivity is most completely studied in the higher range of temperatures: 300-1000°K. One can note the good correspondence of the results obtained by various authors. One exception is the data of Kannyluik and Carman, which in this temperature range are significantly lower. A similar picture can also be observed for other gases, whose heat conductivity was measured by these authors. The inadequate reliability of the data of Kannyluik and Carman in the cited range of temperatures can be explained by the large error in determining the correction for radiation, which reached as high as 20%. Here the total of all the errors reached as high as 30%.

There is good correspondence for the results of N. B. Vargaftik and N. Kh. Zimina; those of L. S. Zaytseva; those of D. L. Timrot and A. S. Umanskiy; and those of Collins and Greif at temperatures of up to  $\sim 1000^{\circ}\text{K}$ . The average curve in this temperature region, as seen from Fig. 16, passes between the data of Vargaftik and Zimina, and also of Zaytseva, on the one hand, and Timrot, Umanskiy and Collins and Greif on the other. The error of the recommended values, which are represented in Table 2, for this range of temperatures may be estimated at 2%. These values can be recommended as standard in measurements of the thermal conductivity of substances, in particular for gases and liquids with high thermal conductivity.

Table 2. Recommended values of the thermal conductivity of gaseous helium at atmospheric pressure.

$T, ^{\circ}\text{K}$	$\lambda \cdot 10^3$ $\text{вт}/(\text{м} \cdot \text{град})$	$T, ^{\circ}\text{K}$	$\lambda \cdot 10^3$ $\text{вт}/(\text{м} \cdot \text{град})$	$T, ^{\circ}\text{K}$	$\lambda \cdot 10^3$ $\text{вт}/(\text{м} \cdot \text{град})$
70	57.9	260	138	650	264
80	63.2	270	142	700	278
90	67.6	280	145	750	291
100	72.0	290	148	800	304
110	76.4	300	151	850	317
120	81.6	310	154	900	330
130	86.0	320	157	950	342
140	90.5	330	160	1000	354
150	94.5	340	163	1100	379
160	98.8	350	166	1200	405
170	103	360	170	1300	430
180	107	370	173	1400	455
190	111	380	176	1500	479
200	115	390	181	1600	502
210	120	400	184	1700	523
220	124	450	201	1800	543
230	127	500	218	1900	562
240	130	550	235	2000	579
250	134	600	250		

Designation:  $\text{вт}/(\text{м} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ .

In the range of even higher temperatures there are the data of N. B. Vargaftik and N. Kh. Zimina [90], D. L. Timrot and A. S. Umanskiy [64], Blais and Mann [26], and Collins and Greif [82]. Up to temperatures  $\sim 1200^{\circ}\text{K}$  the difference in the results of these authors lies within the limits of 3%, which also defines the error of the recommended values for the interval  $T = 1000\text{--}1200^{\circ}\text{K}$ . Within the range of higher temperatures up to  $2000^{\circ}\text{K}$  there is good correspondence between the data of D. L. Timrot and A. S. Umanskiy, and Collins and

Greif — the divergence does not exceed 3%. The data of Blais and Mann are high in comparison with the results of the cited authors; the difference reaches as high as 12%. Such a divergence may be explained (as was noted in Chapter I) by insufficiently careful consideration of end effects, and by the insufficiently strict adherence to the constant temperature of the wall of the measured cylinder in the work of Blais and Mann. The curve in the temperature range of 1200 to 2000°K was plotted close to the data of D. L. Timrot and A. S. Umanskiy, and Collins and Greif. The error of the recommended values in the temperature range 1500–2000°K amounts to 3–5%.

For the temperature interval 2000–6000°K there are up to this time only the experimental data of Collins and Greif [82] (Table 3). As was mentioned in Chapter I, the possible error of these data, obtained by the shock tube method, amounts to 10–20%.

Table 3. The thermal conductivity of helium at high temperatures and at atmospheric pressure according to the data of Collins and Greif [82].

$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$	$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$	$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$
2000	563	3500	826	5000	1050
2500	657	4000	907	5500	1180
3000	745	4500	970	6000	1200

Designation:  $\text{вт/(м} \cdot \text{град)} = \text{W/(m} \cdot \text{deg)}$ .

The thermal conductivity of helium at elevated pressures was studied by N. V. Tsederberg and V. N. Popov [87], Johannin and Wilson [89], Lenoir and Commings [86], and Freud and Rothberg [95]. The results of these measurements have been generalized in the coordinates of excess thermal conductivity-density and are shown in Fig. 17. The averaging curve plotted passes between the data of Lenoir and Commings, Johannin, N. V. Tsederberg and V. N. Popov.

The maximum divergence in the results of the various authors from this curve does not exceed 2%. The averaging curve in this interval of density 0–0.06 g/cm<sup>3</sup> can be described by the formula

$$\Delta\lambda = a\rho + b\rho^2, \quad (49)$$

where  $a = 0.344$ ,  $b = 0.863$ ; and  $\rho$  is expressed in  $\text{g/cm}^3$ . According to the tabulated data, when  $p = 1$  bar and with the excess thermal conductivity determined according to formula (49), the table of recommended values for the thermal conductivity of gaseous helium was compiled with temperatures of 270-1500°K and pressures of 1-300 bar. The error of the data cited in Table 4 at elevated pressures can be estimated at 3% up to 1000°K and 4% up to 1500°K in the entire pressure range.

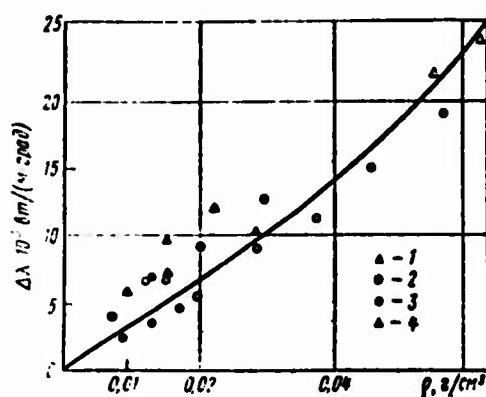


Fig. 17. The dependence of excess thermal conductivity of helium on the density according to the data of: 1 - Johannin and Wilson [89]; 2 - Lenoir and Commings [86]; 3 - Tsederberg and Popov [87]; 4 - Freud and Rothberg [95].

Designations:  $\text{BT}/(\text{m} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ ;  $\text{r}/\text{cm}^3 = \text{g}/\text{cm}^3$ .

Let us plot the values of the thermal conductivity of liquid helium on to the absorption lines, taken by us from the work of the National Bureau of Standards (USA) [96]:

$T, ^\circ\text{K}$	$\lambda \cdot 10^3$ $\text{BT}/(\text{m} \cdot \text{град})$	$T, ^\circ\text{K}$	$\lambda \cdot 10^3$ $\text{BT}/(\text{m} \cdot \text{град})$
2.3	18.1	3.0	21.4
2.4	18.5	3.5	23.8
2.6	19.5	4.0	26.2
2.8	20.5	4.2	27.1

Designation:  $\text{BT}/(\text{m} \cdot \text{град}) =$   
 $= \text{W}/(\text{m} \cdot \text{deg}).$

Table 4. Recommended values of thermal conductivity of gaseous helium as a function of temperature and pressure.

T, °K	(1) $\lambda \cdot 10^3, \text{ mW/(m} \cdot \text{cm} \cdot \text{deg)}, \text{ при } p, \text{ бар}$						
	1	50	100	150	20	250	300
270	142	144	147	150	153	156	159
280	145	148	151	153	156	159	162
290	148	151	153	156	159	161	164
300	151	154	158	158	161	164	167
310	154	157	160	162	165	167	170
320	157	160	162	164	167	169	172
330	160	162	165	167	170	172	175
340	163	165	167	169	172	174	177
350	166	168	170	172	174	176	179
400	184	186	188	180	182	184	188
450	201	203	205	207	209	211	213
500	218	220	221	223	224	226	228
550	235	236	238	239	240	242	244
600	250	251	252	254	255	257	259
650	264	265	266	267	269	271	273
700	278	279	280	281	282	283	285
750	291	292	293	294	295	296	297
800	304	305	306	307	308	309	311
850	317	318	319	320	321	322	323
900	330	331	331	332	333	334	335
950	342	343	344	345	345	346	347
1000	354	355	356	357	357	358	359
1100	379	380	381	381	382	383	384
1200	405	406	406	407	408	408	409
1300	430	430	431	431	432	433	434
1400	455	455	456	456	457	457	458
1500	479	479	480	480	481	482	483

KEY: (1)  $\lambda \cdot 10^3$ , W/(m·deg), with p, bar.

Neon

The most careful investigation has been made for the thermal conductivity of neon gas at atmospheric pressure by the heated filament method. The basic works are shown in Table 5.

Kannyluik and Carman [65] measured the thermal conductivity in the temperature range from 90 to 579°K; the measured wire in their apparatus was very fine, and its diameter measured 1.5 mm.

L. S. Zaytseva [88] in the measurement of thermal conductivity in the temperature interval from 413 to 803°K paid special attention to consideration of the temperature jump between the central heater and the gas.

Table 5. Basic research of the thermal conductivity of neon.

Author	Year	Liter- ature source	Method	Temperature, °K	Pressure, bar
Curie, Lepape	1931	[97]	Heated filament	273	1
Kannyluik, Carman	1952	[65]	" "	90-579	1
Zaytseva	1958	[88]	" "	413-803	1
Löchtermann	1963	[98]	Flat layer	25-516	Of saturated liquid
Sengers, Bolk, Stigter	1964	[99]	" "	298-348	1-2600
Saxena	1966	[91]	Heated filament	323-723	1
Gandhi, Saxena	1967	[94]	" "	303-363	1
Strivastava, Gupta	1967	[93]	" "	303-473	1
Vargaftik, Yakush	1968	[100]	" "	310-1073	1



The results of Saxena, Gandhi and Strivastava [91, 93, and 94] were obtained using different variants of the heated filament method.

The measurements were made at various pressures, in order to take into account the correction for the temperature jump between the heater and the gas. In work [91] it was demonstrated that at the highest temperatures of the described experiments ( $T = 623$  to  $723^{\circ}\text{K}$ ), in the transition from one pressure value to another the temperature regimes were unstable, and the variation of points reached as high as 10%. The authors therefore think that the obtained data for this temperature region should be viewed as tentative. At lower temperatures the error of the results obtained in work [91] may be estimated as equal to 2%. Naturally, the experimental data of these authors with  $T > 623^{\circ}\text{K}$  were not taken into account in the compilation of the tables of the recommended values of thermal conductivity.

Recently, N. B. Vargaftik and L. D. Yakush [100] made measurements of thermal conductivity in a sufficiently wide temperature range - from  $303$  to  $1073^{\circ}\text{K}$ . In order to be confident of the correctness of their consideration of the correction for radiation from the heater, and this is especially important at elevated temperatures, in the experiments they used two measurement tubes of different diameter. In the first series of experiments the inner diameter of the quartz tube was  $D = 4.07$  mm, and in the second series -  $2.97$  mm. Divergences of the results of both series lie within the limits of 1.5% in the entire investigated temperature range.

For the thermal conductivity of neon gas at atmospheric pressure and  $T = 273$ - $1073^{\circ}\text{K}$  the method of least squares produced the following equation

$$\lambda = a + bT + cT^2 + dT^3 [\text{W}/(\text{m} \cdot \text{deg})], \quad (50)$$

where  $a = 0.87 \cdot 10^{-2}$ ;  $b = 1.547 \cdot 10^{-4}$ ;  $c = 7.63 \cdot 10^{-8}$ ;  $d = 26.32 \cdot 10^{-12}$ ;  $T$  is expressed in  $^{\circ}\text{K}$ .

Divergences of the experimental data from the calculated data according to equation (50) are shown in Fig. 18. The experimental data of L. S. Zaytseva lie somewhat above the rest, approximately by 2%. The data of Kannyluik and Carman at the highest temperatures, which occurred in their experiments (473-573°K), are lower - the divergence reaches as high as 3.7%. Such a deviation is characteristic for the results of the experiments of Kannyluik and Carman even with other gases at the same temperature, since the corrections for heat removal and radiation exceeded 50% (the problem is discussed in Chapter 1 in connection with the method under consideration). Data of the remaining authors can be described by this equation, and deviations from the calculated values lie within the limits of 2%.

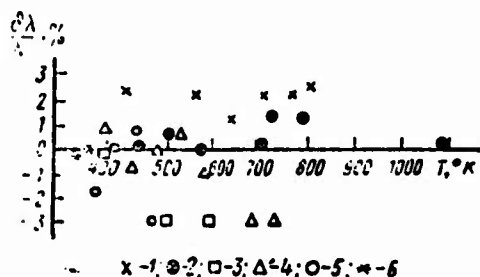


Fig. 18. Divergences of the experimental values of thermal conductivity of neon from the values calculated by the recommended equation: 1 - Zaytseva [88]; 2 - Vargaftik, Yakush [100]; 3 - Kannyluik, Carman [65]; 4 - Saxena, V., Saxena, M., Saxena, S. [91]; 5 - Strivastava, Gupta [93]; 6 - Gandhi, Saxena, S. [94].

According to equation (50) Table 6 was compiled for the values of thermal conductivity for the temperature range from 273 to 1073°K with intervals of 50 degrees at  $p = 1$  bar. The error of these data may be estimated at 2%. This same table shows the values of thermal conductivity below 273°K - to  $T = 90^\circ\text{K}$ . They were taken from works [59] and are the only ones in this temperature range.

Table 6. Thermal conductivity of neon gas at atmospheric pressure.

$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{BT}/(\text{m} \cdot \text{град})$	$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{BT}/(\text{m} \cdot \text{град})$	$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{BT}/(\text{m} \cdot \text{град})$	$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{BT}/(\text{m} \cdot \text{град})$
90	20,5	350	54,6	650	84,3	950	109,4
125	26,8	400	60,1	700	88,6	1000	113,4
175	33,6	450	65,3	750	92,9	1050	117,5
225	39,9	500	70,3	800	97,1	1100	121,6
273	45,8	550	75,1	850	101,2		
300	48,9	600	79,7	900	105,3		

Designation:  $\text{BT}/(\text{m} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ .

At high pressures Sengers and his colleagues measured the thermal conductivity using the flat horizontal layer method [99] with the same apparatus, which was previously used by Sengers together with Michels to determine the thermal conductivity of argon [101]. In their apparatus the clearance between the plates was  $\delta = 1.27 \text{ mm}$ , and the temperature difference in the gas layer  $\Delta T = 0.3\text{--}0.4 \text{ deg}$ . The thermal conductivity of neon was measured on three isotherms:  $298.15$ ;  $323.15$  and  $348.15^\circ \text{K}$  with pressures from 1 to 2600 atm. In work [99] graphs were made at the coordinates  $\lambda - p$  and  $\lambda - \rho$ . These experimental data were represented by us in Fig. 19 in the generalized coordinates  $\Delta\lambda = \lambda - \lambda_1 = f(\rho)$ , and the values of  $\lambda_1$  are taken from the experimental data, given in work [100]. From Fig. 19 it is clear that in the range  $\rho = 0\text{--}500 \text{ kg/m}^3$   $\Delta\lambda$  depends univalently on the density. At higher values of  $\rho$  there is a certain stratification in the isotherms.

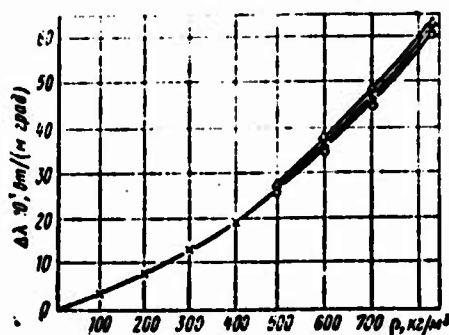


Fig. 19. Dependence of excess thermal conductivity of neon on the density.

Designations:  $\text{BT}/(\text{m} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ ;  $\text{кг}/\text{м}^3 = \text{kg}/\text{m}^3$ .

From the method of least squares we formulated an equation for  $\Delta\lambda = f(\rho)$  up to values  $\rho = 500 \text{ kg/m}^3$ :

$$\lambda = \lambda_1 + a\rho + b\rho^2 + c\rho^3 \text{ [W/(m}\cdot\text{deg)]}, \quad (51)$$

where  $a = 34.33 \cdot 10^{-2}$ ;  $b = 2.255 \cdot 10^{-4}$ ;  $c = 0.354 \cdot 10^{-6}$ .

Divergences of the experimental data from equation (51) for all three isotherms are within the limits of 1%. Equation (51) can be recommended for calculations of the thermal conductivity of neon gas at a density of up to  $500 \text{ kg/m}^3$ .

The stratification of  $\Delta\lambda$ , observable when  $\rho > 500 \text{ kg/m}^3$ , has an insignificant effect on  $\lambda$ . As Fig. 19 shows, the maximum differences in the values of  $\Delta\lambda$  amount to  $2 \cdot 10^{-3} \text{ W/(m}\cdot\text{deg)}$ , and here  $\lambda \approx 100 \cdot 10^{-3} \text{ W/(m}\cdot\text{deg)}$ . Thus, the stratification in the cited temperature range has relative little effect on the value of  $\lambda$ ; the relationship is  $\Delta\lambda/\lambda \approx 2\%$ . It is possible that the stratification is connected with some systematic experimental errors. Since this appeared in experiments in a relatively narrow temperature range (298–348°K), we recommend the values of thermal conductivity for  $\rho > 500 \text{ kg/m}^3$  only for the cited three isotherms. The recommended values of thermal conductivity are given in Table 7.

Table 7. Recommended values of thermal conductivity of neon gas as a function of temperature and pressure.

(1) p, bar	(2) $\lambda \cdot 10^3$ , $\frac{\text{erg}}{\text{cm} \cdot \text{sec} \cdot \text{deg}}$ , при T, °K			(1) p, bar	(2) $\lambda \cdot 10^3$ , $\frac{\text{erg}}{\text{cm} \cdot \text{sec} \cdot \text{deg}}$ , при T, °K		
	298.15	323.15	348.15		298.15	323.15	348.15
1	0.0188	0.0516	0.0542	900	0.0753	0.0768	0.0744
100	0.0516	0.0543	0.0566	1000	0.0784	0.0795	0.0801
200	0.0545	0.0569	0.0591	1200	0.0844	0.0850	0.0854
300	0.0574	0.0596	0.0615	1400	0.0904	0.0905	0.0907
400	0.0603	0.0624	0.0642	1500	0.0932	0.0933	0.0933
500	0.0633	0.0653	0.0668	1600	0.0960	0.0960	0.0959
600	0.0663	0.0682	0.0694	1800	0.1017	0.1015	0.1012
700	0.0693	0.0710	0.0721	2000	0.1072	0.1074	0.1065
800	0.0723	0.0739	0.0748	2500	0.1215	0.1213	0.1196

KEY: (1) p, bar; (2)  $\lambda \cdot 10^3$ , W/(m·deg), when T, °K.

Undoubtedly, of interest is the further investigation of the thermal conductivity of neon at high pressures in a range expanded into the regions of high and low temperatures.

Only one work [98] is dedicated to the study of the thermal conductivity of neon in the liquid phase. The measurements were done using the flat horizontal layer method. A description is given in brief, and the results of the experiment are given only in graphic form. It is clear from this graph that the heat conductivity at temperatures from 25 to 28°K fall monotonically in proportion to the increase in temperature; in the range from 28 to 30°K the dependency of the thermal conductivity on the temperature becomes more pronounced. Let us give the thermal conductivity values taken from the graph:

$T, ^\circ K$	$\lambda \cdot 10^3,$ $erg/(m \cdot sec \cdot grad)$	$T, ^\circ K$	$\lambda \cdot 10^3,$ $erg/(m \cdot sec \cdot grad)$
25	117	28	112
26	115	29	108
27	113	30	92

Designation:  $erg/(m \cdot grad) =$   
 $= W/(m \cdot deg).$

This abrupt change in the thermal conductivity begins relatively far from the critical temperature ( $T_{kp} = 44.9^\circ K$ ) with values of the reduced temperature of  $\tau = \frac{T}{T_{kp}} \approx 0.7$ . With other liquids at these values of  $\tau$  there is a monotonic dependence of the thermal conductivity on the temperature. In work [98] they do not give the pressure at which the experiments were conducted. It is only said that the experimental data referred to liquid neon on the saturation line. This does not eliminate the possibility of the presence of a gas phase during elevated temperatures of the experiment, which also could lead to the understating of the thermal conductivity. The further study of the thermal conductivity of neon in the liquid phase, especially at elevated temperatures — up to temperatures close to critical — would undoubtedly be interesting.

## Argon

Argon belongs to the class of those few gases, the thermal conductivity of which at atmospheric pressure has been studied most completely in a broad temperature range (90-2000°K), as Table 8 shows. A significant number of experimental results on thermal conductivity at atmospheric pressure are given in Fig. 20. In accordance with the criteria for selecting the material given in the forward, we did not take into consideration the data of Weber [102], Dikins [103], Rosenbaum [109], Freud, et al., [25], and Uhlir [104]. The results of N. V. Tsederberg, et al. [107], and Zarkova and Stepanov [110] were not taken into account, since they were obtained during the checking of the experimental equipment. Results of the works of Schäfer and Reiter [31], and of Schottky [24] at temperatures above 600°K were taken with corrections for the temperature jump in accordance with the work of N. V. Vargaftik and N. Kh. Zimina [32].

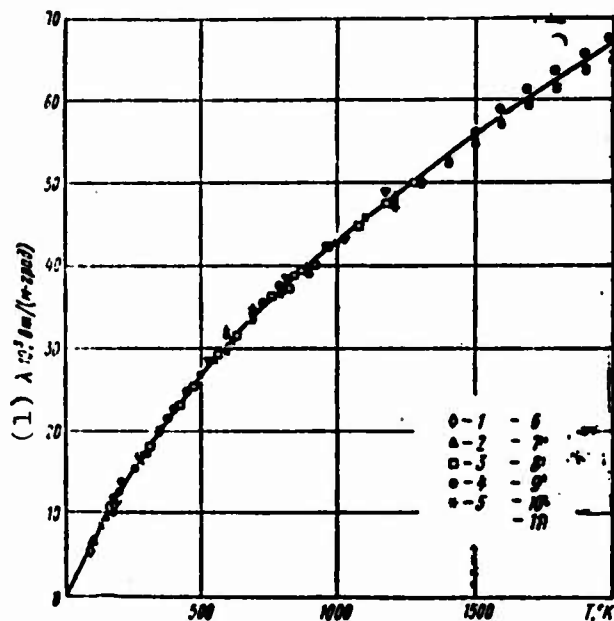


Fig. 20. The dependence of the thermal conductivity of argon gas on the temperature at atmospheric pressure according to the data of: 1 - Lenoir and Commings [86]; 2 - Ziebland and Barton [5]; 3 - Vargaftik, Zimina [32]; 4 - Zaytseva [88]; 5 - Schäfer, Reiter [31]; 6 - Collins, Minard [82]; 7 - Timrot, Umanskiy [64]; 8 - Foyes [105]; 9 - Gupta, et al. [93]; 10 - Vines [27]; 11 - Rosenbaum [109].

KEY: (1)  $\lambda \cdot 10^3$ , W/(m·deg).

Table 8. Basic research on the thermal conductivity of argon.

Author	Year	Liter- ature source	Method	Temperature, °K	Pressure, bar
Eucken	1911 1913	[83]	Heated filament	90-373	1
Weber	1917	[102]	"	273-293	1
Dikins	1934	[103]	"	273-293	1
Lenoir, Cummings	1951 1953	[86]	Coaxial cylinders	314, 326	1-217
Kannuluik, Carman	1952	[65]	Heated filament	273-573	1
Schottky	1952	[24]	"	373-773	1
Uhlir	1952	[104]	Coaxial cylinders	90-194	1-96
Rotman, Bromley	1954 1955	[58]	The same	273-1073	1
Keyes	1954 1955	[105]	"	104-523	1-100
Michels, et al.	1956	[106]	Flat layer	273-348	1-2400
Schäfer, Reiter	1957	[31]	Heated filament	273-1373	1
Ziebland, Barton	1958	[59]	Coaxial cylinders	94-196	1-124
Zaytseva	1959	[88]	Heated filament	316-788	1
Vines	1960	[27]	Coaxial cylinders	533-1033	1
Tsederberg, et al.	1960	[107]	Heated filament	203-663	1-500
Ikenberg, et al.	1963	[108]	Coaxial cylinders	91-234	1-500
Michels, et al.	1963	[101]	Flat layer	273-348	1-2400
Vargaftik, Zimina	1964	[32]	Heated filament	373-1200	1
Rosenbaum	1966	[109]	Coaxial cylinders	283-322	1-700
Zarkova, Stepanov	1966	[110]	Heated filament	1000-2200	1

Table 8 Cont'd.

Author	Year	Liter- ature source	Method	Temperature, °K	Pressure, bar
Timrot, Umanskiy	1966	[64]	The same, modified	600-2100	1
Collins, Minard	1966	[82]	Shock tube	1500-5000	1
Strivastava, Gupta	1967	[93]	Heated filament	353-473	1
Freud, Rothberg	1967	[95]	Coaxial cylinders (relative)	298	1-3000



As follows from Fig. 20, in the low temperature region from 90-300°K there is relatively good agreement among one another for the data of Eucken [83], Kannuluik and Carman [65], Ziebland and Barton [59], and Keyes [105]. The greatest divergence between them does not exceed 3.5%. Thoroughly studied is the temperature region between 300-600°K, where the maximum difference does not exceed 2%. A much smaller number of works will fall into the region of higher temperatures. The data obtained in them by N. V. Vargaftik and N. Kh. Zimina [32], L. S. Zaytseva [88], Vines [27], Rotman [58], and also the corrected data of Schäfer and Reiter [31], Schottky [24], have good correspondence with one another, the maximum divergence being ~3%.

In the high temperature region there are the data of Collins and Minard [82], who measured the thermal conductivity of argon by the shock tube method with  $T = 1500-5000^\circ\text{K}$ . Let us introduce these unique experimental data (with  $p = 1$  bar), since they may be of interest for technical calculations:

$T, ^\circ\text{K}$	$\lambda \cdot 10^3$ $\text{erg}/(\text{cm} \cdot \text{grad})$	$T, ^\circ\text{K}$	$\lambda \cdot 10^3$ $\text{erg}/(\text{cm} \cdot \text{grad})$
1500	56	3500	102
2000	68	4000	110
2500	80	4500	118
3000	91	5000	131

Designation:  $\text{erg}/(\text{cm} \cdot \text{grad}) =$   
 $= \text{W}/(\text{m} \cdot \text{deg}).$

For the temperature region above 1400°K there are also the data of D. L. Timrot and A. S. Umanskiy [64], obtained by a modified heated filament method. All the data of the enumerated authors were processed by computer in order to obtain an analytical dependence<sup>1</sup> for the thermal conductivity of argon on the temperature:

$$\lambda = 0,615 \cdot 10^{-3} + 0,0656 \cdot 10^{-3}T - 0,0331 \cdot 10^{-6}T^2 + \\ + 0,0124 \cdot 10^{-9}T^3 - 0,00207 \cdot 10^{-12}T^4. \quad (52)$$

<sup>1</sup>The calculations of the coefficients, just as for a number of other gases, were made by N. G. Sokolova, an engineer of the Calculation Laboratory of the Kazan Chemical-Technical Institute, to whom the authors express their deep gratitude.

Equation (52) describes well the temperature region of 200-2000°K (error ~1.5%) and is significantly worse for the segment between 90-200°K, which apparently is connected with the abrupt change in the thermal conductivity activity in this region. Graphic averaging was conducted for the interval of 90-200°K.

In the interval of 600-1400°K the data of Rotman diverge by ~3%, and above 1400°K the average line passes close to the data of D. L. Timrot and A. S. Umanskiy.

Considering the thorough study of the thermal conductivity of argon in the wide temperature range of 200-1400°K, and also its inertness, easy accessibility, the ease of purification, and the lack of danger in using it, etc., argon can be recommended as a sample substance in checking and calibrating experimental equipment for measuring the thermal conductivity of gases.

The recommended data on the thermal conductivity of argon at atmospheric pressure, calculated according to formula (52) for  $T = 200-2000^{\circ}\text{K}$  and obtained graphically for  $T = 90-200^{\circ}\text{K}$ , are shown in Table 9. The error comprises 2.5% for 90-200°K, 1.5% for 200-600°K, 2% for 600-1400°K, and 3-4% for 1400-2000°K.

Table 9. Recommended values of the thermal conductivity of argon gas at atmospheric pressure.

$T, ^{\circ}\text{K}$	$\lambda \cdot 10^3$ $\text{sr}/(\text{m} \cdot \text{grad})$	$T, ^{\circ}\text{K}$	$\lambda \cdot 10^3$ $\text{sr}/(\text{m} \cdot \text{grad})$	$T, ^{\circ}\text{K}$	$\lambda \cdot 10^3$ $\text{sr}/(\text{m} \cdot \text{grad})$
90	6.00	300	17.7	750	35.8
100	6.60	310	18.2	800	37.4
110	7.20	320	18.6	850	39.1
120	7.80	330	19.2	900	40.6
130	8.40	340	19.6	950	42.2
140	9.00	350	20.0	1000	43.6
150	9.60	360	20.5	1050	45.0
160	10.3	380	21.3	1100	46.3
170	10.9	400	22.2	1150	47.6
180	11.5	420	23.0	1200	48.9
190	12.0	440	23.9	1250	50.2
200	12.6	460	24.8	1300	51.4
210	13.1	480	25.7	1350	52.6
220	13.6	500	26.6	1400	53.7
230	14.1	520	27.5	1500	56.0
240	14.7	540	28.3	1600	58.3
250	15.2	560	29.1	1700	60.5
260	15.7	580	29.9	1800	62.6
270	16.2	600	30.7	1900	64.7
280	16.7	650	32.4	2000	66.7
290	17.2	700	34.1		

Designation:  $\text{sr}/(\text{m} \cdot \text{grad}) = \text{W}/(\text{m} \cdot \text{deg})$ .

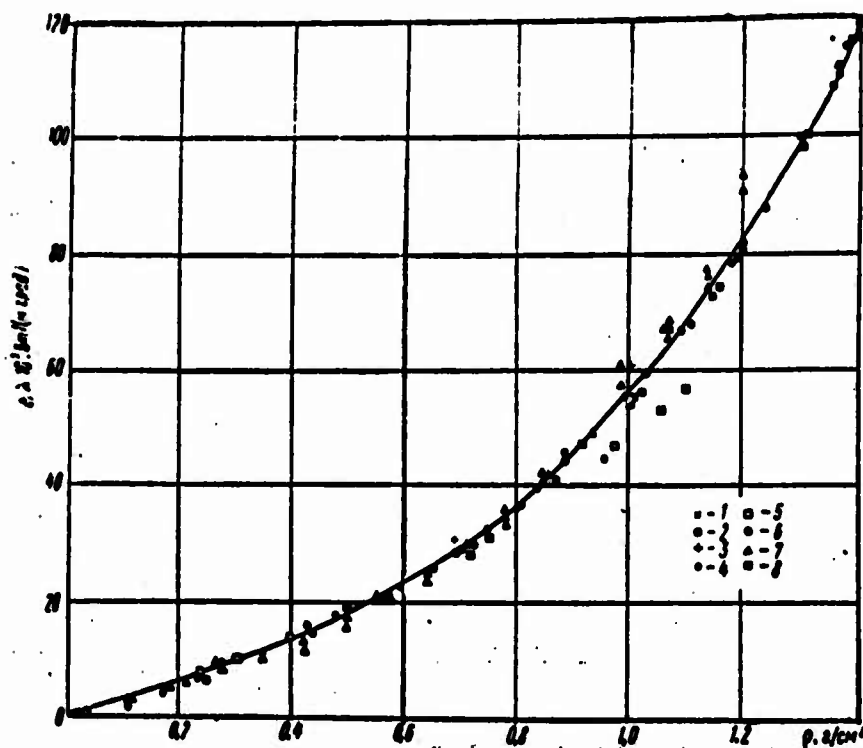


Fig. 21. Dependence of the excess thermal conductivity of argon on the density according to the data of: 1 - Keyes [105]; 2 - Uhlir [104]; 3 - Freud, Rothberg [95]; 4 - Rosenbaum [109]; 5 - Tsederberg, et al. [107]; 6 - Ikenberry, et al. [108]; 7 - Michels, et al. [101]; 8 - Ziebland, Barton [59].

Designations:  $\kappa/(\text{m} \cdot \text{град}) = W/(\text{m} \cdot \text{deg})$ ;  $\rho/\text{cm}^3 = \text{g}/\text{cm}^3$ .

The thermal conductivity of argon is also rather well studied at elevated pressures. As follows from Table 8, the most complete investigation is for the region  $T = 90\text{--}500^\circ\text{K}$  with  $T = 1\text{--}600$  bar. At certain temperatures measurements were made as high as 2400–3000 bar.

The experimental data for the thermal conductivity from the works cited in Table 8 were worked out at coordinates of excess thermal conductivity-density and are shown in Fig. 21. Excluded from consideration are only the earlier data of Michels and coauthors [106]: in the opinion of the authors themselves, these data are erroneous. It is clear from the graph that the majority of experimental points are grouped around an averaging curve. The greatest variation occurs in the region of high densities: above all the others are the data of Michels, et al. [101]; while the data of N. V. Tsederberg [107]

Table 10. Recommended values of the thermal conductivity of argon as a function of temperature and pressure.

T, °K	(1) $\lambda \cdot 10^3$ , $\text{cal}/(\text{m} \cdot \text{sec} \cdot \text{deg})$ , from R. G. Sp															
	1	10	20	30	40	50	60	70	80	90	100	150	200	250	300	350
90	6.00	121	122	123	124	—	125	—	126	—	127	129	132	135	—	—
100	6.60	109	110	111	112	—	113	—	114	—	116	118	122	125	136	138
110	7.20	96.2	97.1	98.2	99.3	—	100	—	101	—	104	107	110	114	125	128
120	7.80	86.4	87.4	88.5	89.4	89.4	90.5	91.4	92.3	93.3	94.4	96.3	102	106	117	120
130	8.40	9.50	—	73.4	74.3	75.9	77.6	78.8	80.0	81.0	82.0	86.5	90.8	94.9	108	114
140	9.00	10.1	11.3	13.0	14.3	17.3	—	—	—	—	—	—	81.9	86.7	98.0	111
150	9.60	10.4	11.5	13.1	14.5	15.9	17.7	19.8	22.4	25.6	29.2	33.5	38.4	44.1	51.4	60.8
160	10.3	10.8	11.7	13.3	14.6	16.1	17.3	18.9	20.7	22.8	25.2	28.4	32.9	39.0	46.4	55.8
170	10.9	11.5	12.3	13.6	14.9	16.6	17.5	18.5	20.0	21.5	23.3	26.5	31.2	38.3	46.9	56.4
180	11.5	12.0	12.7	14.0	15.2	16.6	17.2	18.4	19.4	20.4	21.7	24.8	29.4	36.6	45.3	55.0
190	12.0	12.5	13.2	14.4	15.6	17.3	18.0	18.7	19.9	20.6	21.3	25.1	30.3	37.5	46.4	56.2
200	12.6	13.0	13.6	14.8	16.0	17.8	18.6	19.2	20.5	21.0	21.7	25.8	31.2	38.3	47.2	57.0
220	13.6	14.1	14.6	15.8	17.0	18.8	19.3	19.9	20.5	21.0	21.6	25.9	31.9	39.0	48.0	57.8
240	14.7	15.1	15.5	16.7	17.9	19.6	20.1	20.6	21.1	21.6	22.1	26.2	32.9	40.0	49.0	58.6
260	15.7	16.1	16.5	17.7	18.9	20.4	20.8	21.7	22.8	23.6	24.4	28.4	34.2	41.3	50.2	59.0
280	16.7	17.1	17.4	18.6	19.8	21.3	21.6	22.0	22.7	23.6	24.4	28.4	34.2	41.3	50.2	59.0
300	17.7	18.0	18.3	19.5	20.7	22.0	22.3	22.7	23.4	24.1	24.7	28.7	34.6	41.7	50.6	59.4
320	18.6	—	19.3	—	20.0	21.3	21.6	22.0	22.8	23.6	24.4	28.7	34.6	41.7	50.6	59.4
350	20.0	—	20.7	—	21.3	22.6	22.9	23.4	24.7	25.4	25.9	29.3	35.3	42.4	51.3	60.2
400	22.2	—	22.9	—	23.4	24.7	25.0	25.5	26.6	27.1	27.6	30.3	36.3	43.4	52.3	61.0
450	24.6	—	25.0	—	25.5	26.6	26.9	27.4	28.3	28.8	29.3	31.9	37.9	45.0	53.9	62.6
500	26.6	—	27.0	—	27.4	28.3	28.6	29.0	29.6	30.1	30.6	32.8	38.8	46.0	54.9	63.6
550	28.6	—	29.0	—	29.4	29.6	29.8	30.2	30.9	31.4	31.9	33.5	39.5	46.7	55.6	64.3
600	30.7	—	30.9	—	31.2	31.4	31.6	31.9	32.6	33.0	33.5	34.9	40.9	48.1	57.0	65.8
650	32.4	—	32.7	—	33.0	33.1	33.3	33.6	34.3	34.7	35.0	36.5	42.5	49.7	58.6	67.0
700	34.1	—	34.4	—	34.6	34.7	34.9	35.3	36.0	36.4	36.8	38.3	44.3	51.5	60.4	68.6
750	35.8	—	36.0	—	36.3	36.4	36.6	36.9	37.7	38.0	38.4	39.7	45.7	52.9	61.8	70.0
800	37.4	—	37.6	—	38.0	38.2	38.4	38.7	39.5	39.8	40.1	41.4	47.4	54.6	63.5	71.6
850	39.1	—	39.2	—	39.5	39.6	39.7	40.0	40.8	41.1	41.6	42.8	48.8	56.0	64.9	73.0
900	40.6	—	40.7	—	41.0	41.0	41.2	41.8	42.5	42.8	43.0	44.3	50.3	57.5	66.4	74.6
950	42.0	—	42.2	—	42.4	42.5	42.6	43.0	43.7	44.0	44.3	45.6	51.6	58.8	67.7	76.2
1000	43.6	—	—	—	—	43.9	44.0	44.4	45.0	45.2	45.5	46.6	52.6	59.8	68.7	77.2
1100	46.3	—	—	—	—	46.5	46.5	46.8	47.4	47.7	47.9	48.9	54.9	62.1	71.0	79.6
1200	48.9	—	—	—	—	49.2	49.2	49.5	50.0	50.3	50.6	51.6	57.6	64.8	73.7	82.2
1300	51.4	—	—	—	—	51.4	51.4	51.7	52.2	52.5	52.7	53.7	59.7	66.9	75.8	84.3
1400	53.7	—	—	—	—	53.7	53.7	54.0	54.5	54.8	55.1	56.1	62.1	69.3	78.2	86.7

KEY: (1)  $\lambda \cdot 10^3$ , W/(m·deg), with p, bar.

show an understated course with the increase in density. The results of other authors in the entire density range investigated by them correspond well among themselves.

The averaging curve (see Fig. 21) is well described by the equation cited in work [106],

$$\lambda \cdot 10^{-5} = 195p + 494p^2 - 483p^3 + 337p^4 \text{ [W/(m} \cdot \text{deg)]}, \quad (53)$$

which is also correct for the density interval of 0-1.4 g/cm<sup>3</sup>.

From equations (52) and (53) a table was compiled for the dependence of the thermal conductivity of argon on the temperature and pressure in the interval 90-1400°K and 1-600 bar (Table 10). The error of the cited data amounts to 3-4% for the entire interval.

The thermal conductivity of liquid argon at the saturation line, calculated from equations (52) and (53), is shown in Table 11.

Table 11. Thermal conductivity of liquid argon at the saturation line.

$T, ^\circ K$	$\lambda \cdot 10^5$ $\text{вт/(м} \cdot \text{град)}$	$T, ^\circ K$	$\lambda \cdot 10^5$ $\text{вт/(м} \cdot \text{град)}$	$T, ^\circ K$	$\lambda \cdot 10^5$ $\text{вт/(м} \cdot \text{град)}$
90	121	115	91,0	135	65,1
95	114	120	85,8	140	58,2
100	108	125	78,6	145	48,3
105	102	130	71,5	150	38,0
110	97,2				

Designation:  $\text{вт/(м} \cdot \text{град)} = \text{W/(m} \cdot \text{deg)}$ .

### Krypton

The fundamental works on the study of the thermal conductivity of krypton are cited in Table 12. The greatest number of experiments were conducted at pressures close to atmospheric. In the works of L. S. Zaytseva [88] and N. V. Vargaftik, L. V. Yakush [100] the correction for the temperature jump was carefully taken into account. Even with high temperatures it is comparatively small, since krypton has a high molecular weight.

Table 12. Basic research on the thermal conductivity of krypton.

Author	Year	Liter- ature source	Method	Temperature, °K	Pressure, bar
Curie, Lepape	1931	[97]	Heated filament	273	1
Kannuluik, Carman	1952	[65]	"	195-579	1
Keyes	1955	[105]	Coaxial cylinders	123-273	0.3-11
Schäfer, Reiter	1957	[31]	Heated filament	273-1373	1
Zaytseva	1958	[88]	"	313-798	1
Ikenberry, Rice	1963	[108]	Coaxial cylinders	125-311	25-500
Grambhir, Saxena	1966	[111]	Heated filament	308-363	1
Gupta	1966	[112]	"	312-473	1
Vargaftik, Yakush	1967	[100]	"	318-1153	1

Schäfer and Reiter conducted measurements at  $p = 250$  and  $500$  mm Hg. The curve shown in work [31] shows that the heat conductivity values with  $p = 500$  mm Hg lie somewhat higher than with  $p = 250$  mm Hg, — this is connected with the temperature jump, which is dependent on the pressure. The authors of [100] introduced a correction for the temperature jump into the experimental data of work [31], which with  $T = 1153^\circ\text{K}$  amounted to only 1.2%. The results of the experiments of [31, 100] in the range of high temperatures correspond well with each other.

On the basis of these data according to the method of least squares the authors of [100] formulated the equation

$$\lambda = a + bT + cT^2 + dT^3 \text{ [W/(m}\cdot\text{deg)]}, \quad (54)$$

where  $a = 0.1917 \cdot 10^{-2}$ ;  $b = 2.742 \cdot 10^{-4}$ ;  $c = -12.56 \cdot 10^{-10}$ ;  $d = -186.9 \cdot 10^{-16}$ ;  $T - \text{ }^\circ\text{K}$ .

Figure 22 shows the divergences of the experimental data from data calculated according to equation (54). The divergences basically lie within the limits of 2%. The greatest divergences are in the experimental data of [65, 112] — up to 3%. In this work there was too high a correction for the heat removal from the end and for radiation, especially for krypton, the thermal conductivity of which is relatively small (a critique of this method is given in Chapter I).

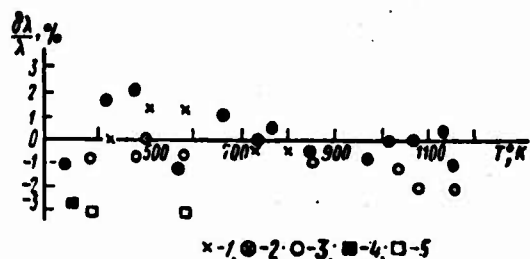


Fig. 22. Divergences of the data of various authors from the recommended values of the thermal conductivity of krypton: 1 — Zaytseva [88]; 2 — Vargaftik, Yakush [100]; 3 — Schäfer, Reiter [31]; 4 — Gupta [112]; 5 — Kannuluik, Carman [65].

The recommended values for the thermal conductivity are cited in Table 13, and their error is estimated at 2%.

Table 13. Recommended values of the thermal conductivity of krypton gas at atmospheric pressure.

$T, ^\circ K$	$\lambda \cdot 10^3$ вт/(м·град)	$T, ^\circ K$	$\lambda \cdot 10^3$ вт/(м·град)	$T, ^\circ K$	$\lambda \cdot 10^3$ вт/(м·град)	$T, ^\circ K$	$\lambda \cdot 10^3$ вт/(м·град)
125	4,20	400	12,6	700	19,8	1000	26,2
175	5,85	450	13,8	750	21,0	1050	27,2
225	7,20	500	15,1	800	22,1	1100	28,1
273	8,85	550	16,3	850	23,2	1150	29,0
300	10,0	600	17,5	900	24,2	1200	29,8
350	11,3	630	18,7	930	25,2		

Designation: вт/(м·град) = W/(m·deg).

At high pressures there exists only the data of Ikenberry and Rice [108]. Unfortunately, at the present time there are no published values for the density of krypton for this same range of temperatures and pressures, and therefore we have not managed to generalize these experimental data in the form adopted by us  $\Delta\lambda = f(p)$ . Table 14 shows the values of thermal conductivity of krypton at various pressures and temperatures, taken directly from the work of Ikenberry and Rice [108].

For the liquid phase Keyes [105] obtained (in 1955) three experimental points, referring to saturation lines: at temperatures of 162, 143.4 and 123.1°K these values of thermal conductivity amount to, respectively: 0,044, 0,075; 0,088 W/(m·deg).

For the gas phase at low temperatures (up to  $T = 123^\circ K$ ) there are the experimental data of Kannuluik and Carman [65] and Keyes [105] at atmospheric pressure. On the basis of these data the smoothed out values for the thermal conductivity with  $T < 273^\circ K$  were obtained; they are shown in Table 13.



Table 14. Thermal conductivity of krypton at various temperatures and pressures according to the data of Ikenberry and Rice [108].

$T, ^\circ K$	$p, \text{ бар}$	$\lambda \cdot 10^3$ $\text{Вт/(м} \cdot \text{град)}$	$T, ^\circ K$	$p, \text{ бар}$	$\lambda \cdot 10^3$ $\text{Вт/(м} \cdot \text{град)}$
125,46	25,5	88,0	175,32	203,3	67,2
125,46	50,9	88,9	175,34	305,7	72,7
125,45	101	91,2	175,26	406,7	77,6
125,45	202,7	95,2	175,25	506,6	82,0
125,45	303,3	98,7			
125,47	306,7	99,0	200,26	51,1	41,2
125,54	337,7	102,7	200,28	101,5	46,2
125,62	407,7	131	200,30	203,3	54,3
125,60	507,3	132,8	200,28	304	60,9
			200,29	406	66,3
			200,28	506,6	71,0
150,35	25,8	71,1			
150,35	50,6	73,7	235,43	50,3	10,68
150,35	101,5	75,7	235,44	76,2	17,02
150,35	204	81	235,46	101,3	27,45
150,35	304,7	85,7	235,45	131,5	32,2
150,32	406	90	235,47	202,7	39,6
150,32	507,3	93,6	235,46	306,7	47,2
			235,47	405	52,9
175,34	25,8	54,2	235,50	505,3	58,1
175,34	51,7	56,5			
175,34	100,8	60,4			

Designation:  $\text{Вт/(м} \cdot \text{град)} = \text{W/(m} \cdot \text{deg)}$ .

### Xenon

Works on the study of thermal conductivity of xenon are enumerated in Table 15. From Tables 12 and 15 it is clear that xenon was studied basically by the same authors and using the same experimental apparatus as for krypton. On the basis of the existing experimental data at atmospheric pressure the equation in [100] was formulated:

$$\lambda = a + bT + cT^2 + dT^3 \text{ [W/(m} \cdot \text{deg)]}, \quad (55)$$

where  $a = 0,06715 \cdot 10^{-2}$ ;  $b = 1,829 \cdot 10^{-4}$ ;  $c = -43,4 \cdot 10^{-10}$ ;  $d = 180,1 \cdot 10^{-16}$ ;  $T$  — in  $^\circ K$ .

Divergences of experimental data from this equation are shown in Fig. 23; they do not exceed 2%. An exception is the results of Kannuluik and Carman at elevated temperatures, where deviations run as high as 3%, just as for krypton. The reasons are the same. From equation (55) a table of values of the thermal conductivity of xenon gas with  $p = 1$  bar (Table 16) was compiled. The error of these data is estimated at 2%.

Table 15. Investigation of the thermal conductivity of xenon.

Author	Year	Liter- ature source	Method	Temperature, °K	Pressure, bar
Curie, Lepape	1931	[97]	Heated filament	273	1
Kannululk, Carman	1952	[65]	"	200-579	1
Keyes	1955	[105]	Coaxial cylinders	172-200	0.5-125
Zaytseva	1958	[88]	Heated filament	323-773	1
Ikenberry, Rice	1963	[108]	Coaxial cylinders	170-235	25-500
Gandhi, Saxena	1967	[94]	Heated filament	303-363	1
Vargaftik, Yakush	1968	[100]	"	298-1179	1

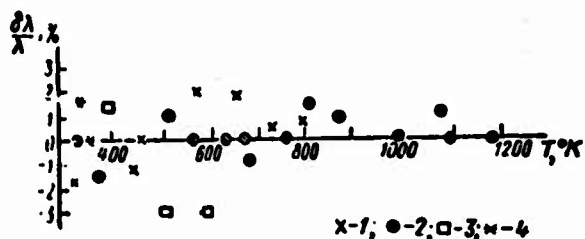


Fig. 23. Divergences of the data of various authors from the recommended values of the thermal conductivity of xenon: 1 - Zaytseva [88]; 2 - Vargaftik, Yakush [100]; 3 - Kannuluik, Carman [65]; 4 - Gandhi, Saxena [94].

Table 16. Recommended values of the thermal conductivity of xenon gas at atmospheric pressure.

$T, ^\circ K$	$\lambda \cdot 10^3, \frac{\text{erg}}{\text{cm} \cdot \text{sec} \cdot \text{deg}}$	$T, ^\circ K$	$\lambda \cdot 10^3, \frac{\text{erg}}{\text{cm} \cdot \text{sec} \cdot \text{deg}}$	$T, ^\circ K$	$\lambda \cdot 10^3, \frac{\text{erg}}{\text{cm} \cdot \text{sec} \cdot \text{deg}}$	$T, ^\circ K$	$\lambda \cdot 10^3, \frac{\text{erg}}{\text{cm} \cdot \text{sec} \cdot \text{deg}}$
175	3.34	450	8.2	750	12.7	1050	17.2
225	4.33	500	9.0	800	13.5	1100	17.9
273	5.2	550	9.7	850	14.2	1150	18.7
300	5.8	600	10.5	900	14.9	1200	19.5
350	6.6	650	11.2	950	15.6		
400	7.4	700	12.0	1000	16.4		

Designation:  $\text{erg}/(\text{cm} \cdot \text{grad}) = \text{W}/(\text{m} \cdot \text{deg})$ .

The experiments carried out by Keyes [105] at  $T = 273^\circ K$  and various pressures from 1 to 10 bar show that with an increase in pressure by 1 bar the value of thermal conductivity increases by 0.7%.

At low temperatures and a pressure close to atmospheric there are the experimental data of [65]. On the basis of these experiments smoothed out data, which are cited in Table 16, were compiled.

The thermal conductivity with sufficiently high pressures - up to 500 atm - and low temperatures was studied by Ikenberry and Rice [108]. Unfortunately, just as for krypton, there are no tables for the values of the density for this region of temperatures and pressures, and therefore we cannot generalize the experimental data according to the relationship  $\Delta\lambda = f(\rho)$ . Table 17 shows these values, taken directly from work [108].

Table 17. Thermal conductivity of xenon at various temperatures and pressures according to the data of Ikenberry and Rice [108].

$T, ^\circ K$	$p, \text{бар}$	$\lambda \cdot 10^3$ $\text{вт}/(\text{м} \cdot \text{град})$	$T, ^\circ K$	$p, \text{бар}$	$\lambda \cdot 10^3$ $\text{вт}/(\text{м} \cdot \text{град})$
170,24	51,1	70,5	210,20	26	54,8
170,24	98,7	71,9	210,20	51,9	55,6
170,24	203,7	74,8	210,21	96,6	57,6
170,30	304,3	106,5	210,23	201,4	61,8
170,29	314	108	210,22	304	65,4
170,30	406,3	107,5	210,16	405,3	68,5
170,30	504,5	107,7	210,16	506	71,2
190,44	24,8	62,1	235,08	26	45,7
190,43	53,6	63,1	235,05	52,07	46,3
190,42	95,4	64,7	235,06	101,5	49,0
190,41	204	68,3	235,02	197,8	53,9
190,42	305,7	71,5	235,03	304,3	57,7
190,41	406	74,3	235,03	405,7	61,2
190,41	501,4	76,7	235,04	501,1	64,3

Designations:  $\text{вт}/(\text{м} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ ; бар = bar.

For the liquid phase Keyes (in 1955) [105] obtained two experimental points:  $\lambda = 0.0585 \text{ W}/(\text{m} \cdot \text{deg})$  with  $T = 200.3^\circ \text{K}$  and  $p = 5.5 \text{ atm}$  and  $\lambda = 0.0705 \text{ W}/(\text{m} \cdot \text{deg})$  with  $T = 172^\circ \text{K}$  and  $p = 1.3 \text{ atm}$ .

### Hydrogen

A summary of the works on the study of the thermal conductivity of hydrogen was made in Table 18. The greater part of them [25, 113-118] is dedicated to the study of the thermal conductivity of hydrogen at atmospheric pressure. As follows from Table 18, and also from the graph (Fig. 24), on which the majority of experimental points obtained by various authors are plotted, the most complete study is for the region of temperatures 80-500°K, where the most varied methods are employed. In the region of low temperatures, just as for other gases, one should note the work of Johnston and Grilly [85]. The reliability of these data was repeatedly confirmed by later investigations [115], [119]. The greatest divergence in this temperature range is observed between the data of Gregory, Marshall [114], D. L. Timrot, A. S. Umanskiy [64], on the one hand, and the data of Schäfer, Geier [25], on the other. With  $T = 500^\circ \text{K}$  the divergence amounts to ~10%.

Table 18. Research on the thermal conductivity of hydrogen.

Author	Year	Literature source	Method	Temperature, °K	Pressure, bar
Schleiermacher	1888	[113]	Heated filament	273-373	1
Eucken	1911 1913	[83]	"	82-373	1
Dikins	1934	[103]	"	273-293	1
Gregory, Marshall	1935	[114]	"	300-590	1
Vargaftik, Parfenov	1938	[115]	"	300-750	1
Johnston, Grilly	1946	[85]	"	85-374	1
Stolyarov, et al.	1950	[116]	"	288-573	1-500
Lenoir, Commings	1951	[86]	Coaxial cylinder	315.8	1-207
Blais, Mann	1950	[26]	Heated filament, modified	1200-2200	1
Schäfer, Geier	1961	[25]	The same	273-1473	1
Golubev, Kal'sina	1964	[117]	Bicolorimeter (reg- ular thermal regime of the 1st class	78-293	1-500
Timrot, Umanskiy	1966	[64]	Heated filament, modified	400-2000	1
Hamrin, Thodos	1966	[118]	Coaxial cylinder	275-347	1-660
Mukhopadhyay, Barua	1967	[92]	Heated filament	90-473 260-473	1 1

As the graph shows, in proportion to the rise in temperature the correspondence of the data of the different investigators deteriorates. The measurement results of Blais, Mann [26], N. B. Vargaftik, I. D. Parfenov [115] have a higher temperature coefficient than the data of Schäfer, Geier [25] and D. L. Timrot, A. S. Umanskiy [64] the divergence between which with  $T = 700^\circ\text{K}$  reaches as high as 15%. Above this temperature there are the data of only three works: Schäfer, Geier [25] — up to  $1300^\circ\text{K}$ , Blais, Mann [26] and D. L. Timrot, A. S. Umanskiy [64] — up to  $2000^\circ\text{K}$ . The divergence between the data of works [26] and [64], in spite of the use of the very same modified method of a heated filament, substantially exceed the author's estimate of the error at 5-6% and amounts to  $\sim 20\%$  with  $T = 2000^\circ\text{K}$ . The latter circumstance is witnessed by the necessity for a careful analysis of the possible sources of errors of the given method.

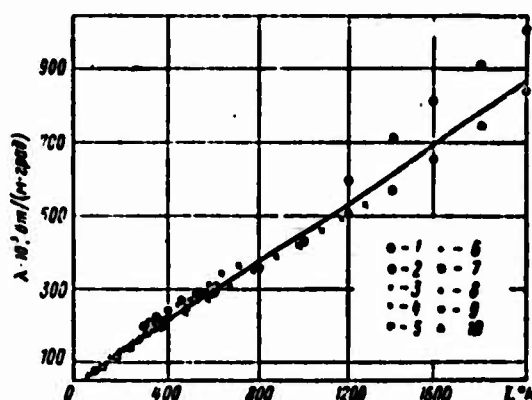


Fig. 24. Dependence of the thermal conductivity of hydrogen gas on the temperature at atmospheric pressure according to the data of: 1 — Blais and Mann [26]; 2 — Timrot and Umanskiy [64]; 3 — Schäfer and Geier [25]; 4 — Vargaftik and Parfenov [115]; 5 — Gregory and Marshall [114]; 6 — Johnston and Grilly [85]; 7 — Golubev and Kal'sina [117]; 8 — Barua, et al. [92]; 9 — Hamrin and Thodos [118]; 10 — Stolyarov, et al. [116].

Designation:  $\text{BT}/(\text{m} \cdot \text{град}) = W/(\text{m} \cdot \text{deg})$ .

Averaging up to  $T = 500^\circ\text{K}$  was done with consideration of the equal validity of all the selected works in this temperature range. At high temperatures a somewhat smaller value was given to the data of Blais and Mann, inasmuch as their work was subjected to

the critique of [64] (the authors of work [26] in the measurements did not consider end heat removal from the filament, heating of the exterior wall of the measuring cylinder, and other things). The data of Schäfer and Geier [25] are apparently low, just as for other gases (Ar, N<sub>2</sub>, CO<sub>2</sub> and others). In all probability, also somewhat low are the data of D. L. Timrot and A. S. Umanskiy [64], since in general, beginning with T = 400°K (see Fig. 34), they have a reduced temperature pattern. The averaging curve in the region of high temperatures passes between the data of Blais and Mann, on the one hand, and those of Schäfer and Geier, and D. L. Timrot and A. S. Umanskiy on the other, differing from the data of the latter authors by 5% at a temperature of 2000°K.

Considering such a difference in the experimental data at a temperature above 500°K, one notes that the formulation of a more careful experiment in this temperature region is very desirable. In conformance with the analysis made, the error of the recommended values for thermal conductivity at atmospheric pressure, cited in Table 19, amounts to 4-5% up to T = 500°K and 8-10% up to T = 2000°K.

Table 19. Recommended values for the thermal conductivity of normal hydrogen gas at atmospheric pressure.

T, °K	$\lambda \cdot 10^3$ вт/(м · град)	T, °K	$\lambda \cdot 10^3$ вт/(м · град)	T, °K	$\lambda \cdot 10^3$ вт/(м · град)
80	53,2	250	157	700	342
90	60,1	260	162	750	360
100	67,0	270	167	800	378
110	74,3	280	172	850	396
120	81,5	290	178	900	412
130	87,8	300	183	950	430
140	94,6	310	187	1000	448
150	101	320	191	1100	468
160	107	330	196	1200	528
170	113	340	200	1300	568
180	119	350	204	1400	610
190	125	400	226	1500	655
200	131	450	247	1600	697
210	137	500	266	1700	742
220	142	550	285	1800	786
230	147	600	305	1900	835
240	152	650	323	2000	878

Designation: вт/(м · град) = W/(m · deg).

There are very few works on the study of the thermal conductivity of hydrogen at elevated temperatures (see Table 18). One immediately notices that high temperature measurements are lacking. The results of investigations enumerated in Table 18 were worked out at the coordinates of excess thermal conductivity-density and are shown in Fig. 25. The majority of the experimental values are mainly grouped around the average curve. An exception is the data of Ye. A. Stolyarov, et al. [116] at high densities, which produce a noticeably reduced pattern in proportion to the increase in density. In the averaging the data of work [116], beginning with  $\rho = 0.02 \text{ g/cm}^3$ , were not taken into consideration. All other works were taken as correct. According to the results of processing (Fig. 25) and from the data on thermal conductivity at atmospheric pressure (Table 19) tables were compiled for the values of the thermal conductivity in the most thoroughly studied temperature range of 80-600°K and pressure range of 1-600 bar (Table 20). The inaccuracy of the recommended data is 5% up to a temperature of 400°K and 6% from 400 to 600°K.

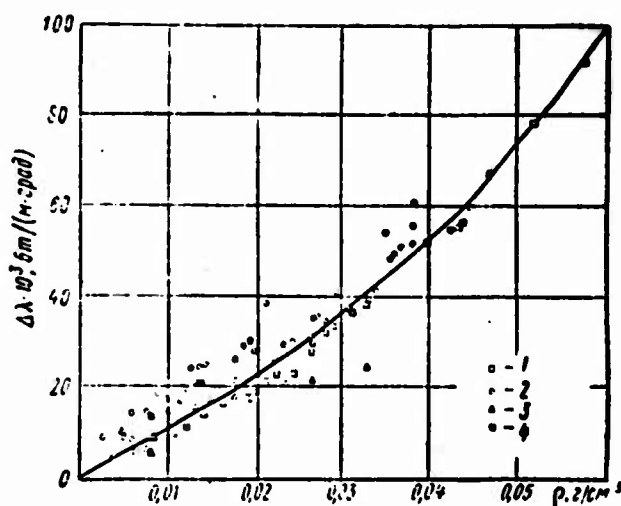


Fig. 25. The dependence of the excess thermal conductivity of hydrogen on the density according to the data of: 1 - Golubev, Kal'sina [117]; 2 - Hamrin, Thodos [118]; 3 - Stolyarov, et al. [116]; 4 - Lenoir, Commings [86].

Designations:  $\text{BT}/(\text{m} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ ;  $\text{г}/\text{см}^3 = \text{g}/\text{cm}^3$ .



Table 20. Recommended values of the thermal conductivity of hydrogen gas at various pressures.

(1) $\lambda \cdot 10^3$ , $\sigma_T / (\lambda \cdot \sigma_{\text{ср}})$ , mm p. Gap																						
$\lambda$	1	10	20	30	40	50	60	70	80	90	100	150	200	270	300	350	400	450	500	550	600	
80	53.2	55.8	60.0	63.2	66.0	69.8	74.7	78.8	81.8	85.3	90.2	108	119	128	138	147	156	165	174	184	194	
90	60.1	63.2	66.1	69.2	72.3	75.1	78.0	81.3	84.7	88.0	91.4	108	119	128	138	147	156	165	174	184	194	
100	67.0	70.7	74.6	78.5	82.3	86.1	89.8	92.6	95.6	98.6	104	115	125	134	143	152	161	170	179	188	196	
110	74.3	77.6	80.9	84.2	87.5	90.8	94.1	96.8	99.7	104	106	118	128	137	146	154	162	171	179	188	196	
120	81.5	84.8	88.1	91.4	94.7	98.0	101.3	104	110	111	113	122	131	140	149	157	165	174	182	190	198	
130	87.8	91.1	94.4	97.7	101.0	104.3	107.6	110	115	116	117	126	135	145	153	161	169	177	185	192	199	
140	94.6	97.9	101.2	104.5	107.8	111.1	114.4	117.7	121.0	121	122	130	138	146	154	162	170	178	186	194	200	
150	101	103	105	108	110	112	115	118	120	121	122	130	138	146	154	162	170	178	186	194	200	
160	107	109	110	112	113	115	116	118	120	121	122	130	138	146	154	162	170	178	186	194	200	
170	113	115	116	118	119	120	121	123	124	125	126	134	141	148	156	164	172	180	188	196	203	
180	119	121	122	123	125	126	127	129	129	130	131	138	145	153	160	167	174	181	188	196	203	
190	125	127	128	129	130	132	133	134	135	136	137	144	150	157	164	171	177	183	189	197	204	
200	131	132	134	135	136	137	139	140	141	142	143	149	156	163	168	173	178	184	189	194	200	
210	137	138	139	141	142	143	144	145	147	148	149	154	160	166	172	177	183	188	193	199	205	
220	142	143	144	145	147	148	149	150	151	152	151	158	164	170	176	181	186	192	198	205	209	
230	147	148	149	150	151	152	151	155	156	157	158	163	168	173	178	183	188	193	199	205	209	
240	152	153	154	155	156	157	158	159	160	161	162	167	173	178	183	189	194	199	204	209	214	
250	157	158	159	160	161	162	163	164	165	167	168	172	177	181	186	191	196	201	205	209	214	
260	162	163	164	165	166	167	168	169	170	171	172	177	181	185	189	193	197	202	207	211	216	
270	167	168	169	170	171	172	173	174	175	176	177	181	185	189	193	197	201	205	208	212	216	
280	172	173	174	175	176	177	178	179	180	181	182	186	190	194	198	202	206	210	214	218	221	
290	178	179	180	181	182	183	184	185	186	187	188	192	195	199	203	206	210	214	218	221	224	
300	183	184	185	186	187	188	189	190	191	192	193	197	201	204	208	212	216	220	224	227	230	
350	204	205	206	207	208	209	209	210	211	212	213	217	221	224	227	231	235	238	241	244	247	
400	226	227	228	229	230	231	232	233	234	235	236	240	244	247	250	253	256	259	262	265	268	
450	247	248	249	250	251	252	253	254	255	256	257	261	265	268	271	274	277	280	283	286	289	
500	266	267	268	269	270	271	272	273	274	275	276	280	284	287	290	293	296	299	302	305	308	
550	285	286	287	288	289	290	291	292	293	294	295	300	304	307	310	313	316	319	322	325	328	
600	305	306	307	308	309	310	311	312	313	314	315	320	324	327	330	333	336	339	342	345	348	

KEY: (1)  $\lambda \cdot 10^3$ , W/(m·deg), with p, bar.

The thermal conductivity values of liquid hydrogen are shown in Table 21, compiled from the data recommended by the National Bureau of Standards of the USA [96].

Table 21. The thermal conductivity of liquid hydrogen according to the data of the National Bureau of Standards of the USA.

$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт}/(\text{м} \cdot \text{град})$	$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт}/(\text{м} \cdot \text{град})$	$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт}/(\text{м} \cdot \text{град})$
16	108	21	120	26	132
17	111	22	123	27	134
18	113	23	125	28	137
19	116	24	127	29	139
20	118	25	129	30	141

Designation:  $\text{вт}/(\text{м} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ .

### Nitrogen

The thermal conductivity of nitrogen has been studied most completely. An enumeration of the basic works is given in Table 22. As can be seen from the table, a significant number of works are dedicated to thermal conductivity at atmospheric pressure. The experiments embrace a large temperature region (80-1400°K). In the low temperature region of 80-300°K there is good correspondence between the measurements of the following authors: Eucken [83], I. F. Golubeva and M. V. Kal'sina [117], Keyes [105], Ziebland and Barton [29]; however, in the low temperature part of the interval the maximum difference reaches up to 5%. Most completely studied is the region  $T = 300\text{-}800^\circ\text{K}$ , where the results of almost all the investigators correspond well with one another — the maximum divergence does not exceed 3%. In processing the data in this temperature interval the work of Stopps [28] was excluded from consideration, since it was published in the form of a very brief report, from which it is impossible to establish the reasons for the large scattering of points. The results of Schäfer and Reiter [31] were taken with a correction for the temperature jump in correspondence with the work of N. B. Vargaftik and N. Kh. Zimina [30]. In the very high temperature

Table 22. Basic research on the thermal conductivity of nitrogen.

Author	Year	Literature source	Method	Temperature, °K	Pressure, bar
Eucken	1911	[83]	Heated filament	90-240	1
Vargaftik	1937	[120]	"	313-333	1-30
Vargaftik, Zimina	1964	[32]	"	320-1134	1
Borovik	1947	[121]	Flat layer	126-170	1-100
Stopps	1949	[28]	Heated filament	273-1373	1
Stolyarov, et al.	1950	[116]	"	288-323	1-500
Frank	1951	[22]	"	300-800	1
Lenoir, Commings	1951	[86]	Coaxial cylinder	314-322	1-205
Michels, et al.	1952	[122]	Flat layer	298-322	1-2500
Schottky	1952	[24]	Heated filament	373-773	1
Uhlir	1953	[104]	Coaxial cylinder	77-121	6-67
Filippov	1953	[123]	Flat layer, relative	373-573	1
Keyes	1954	[105]	Coaxial cylinder	90-523	1-145
Rothman	1954	[58]	The same	330-1045	1
Nattall, Ginnigs	1957	[23]	Flat layer	323-773	1-100
Schäfer, Reiter	1956	[31]	Heated filament	273-1373	1
Johannin	1958	[89]	Coaxial cylinder	348-973	1-1600
Ziebland, Barton	1958	[29]	The same	85-200	1-135
Vines	1960	[27]	The same	513-1173	1
Westenberg, de Haas	1962	[81]	Laminar flow	300-1000	1
Golubev, Kal'sing	1964	[117]	Regular regime of the first class	80-273	1-500
Misic, Thodor	1965	[124] (sic)	Coaxial cylinder	295-323	1-300
Freud, Rothberg	1967	[95]	Coaxial cylinders (relative)	298	1-3500

region of 800-1400°K the maximum difference between the data of N. B. Vargaftik and N. Kh. Zimina [30], Rothman [58], Johannin [89], Westenberg and de Haas [81], and Schäfer and Reiter [31] does not exceed 4%.

The results of all the works taken into consideration (Fig. 26) were processed by computer. An equation obtained as a result of the processing

$$\lambda = 0,825 \cdot 10^{-3} + 0,959 \cdot 10^{-4}T - 0,428 \cdot 10^{-7}T^2 + 0,250 \cdot 10^{-11}T^3 + 0,815 \cdot 10^{-14}T^4 \text{ [W/(m} \cdot \text{deg)]}, \quad (56)$$

describes the temperature dependence of thermal conductivity in the range of 200-1200°K. Averaging for  $T = 80-200^\circ\text{K}$  and  $1200-1400^\circ\text{K}$  was carried out graphically on the same grounds as for argon.

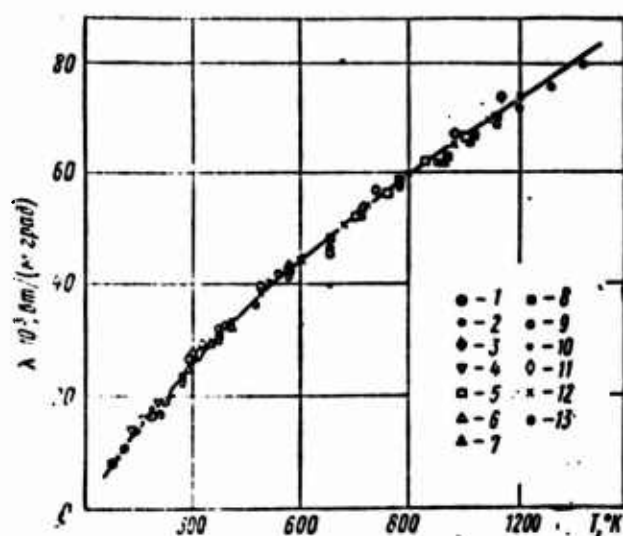


Fig. 26. The dependency of the thermal conductivity of nitrogen on the temperature with pressure  $p = 1$  bar according to the data of: 1 - Golubev and Kal'sina [117]; 2 - Schäfer and Reiter [25]; 3 - Vines [27]; 4 - Ziebland and Barton [29]; 5 - Rothman [58]; 6 - Johannin, et al. [89]; 7 - Stolyarov, et al. [116]; 8 - Vargaftik, Zimina [32]; 9 - Filippov [123]; 10 - Eucken [83]; 11 - Lenoir, Commings [86]; 12 - Westenberg, de Haas [81]; 13 - Keyes [105].

Designation:  $\text{Вт}/(\text{м} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ .

The inaccuracy of the recommended data (Table 23) amounts to 2.5% in the temperature range of 80-300°K; 1.5% for T = 300-800°K; and 2% for T = 800-1400°K.

Table 23. Recommended values of the thermal conductivity of nitrogen gas at atmospheric pressure.

T, °K	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$	T, °K	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$	T, °K	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$
80	7.82	310	26.6	720	50.9
90	8.63	320	27.3	740	51.9
100	9.58	340	28.7	760	52.9
110	10.48	350	29.3	780	53.9
120	11.3	360	30.1	800	54.8
130	12.0	370	30.7	820	55.8
140	13.0	380	31.4	840	56.8
150	13.9	390	32.0	860	57.8
160	14.8	400	32.7	880	58.8
170	15.7	420	34.0	900	59.7
180	16.6	460	36.5	920	60.7
190	17.5	480	37.7	940	61.7
200	18.3	500	38.9	960	62.7
210	19.1	520	40.1	980	63.7
220	20.0	540	41.2	1000	64.7
230	20.6	560	42.4	1050	67.3
240	21.4	580	43.5	1100	70.0
250	22.2	600	44.6	1150	71.9
260	22.9	620	45.7	1200	75.8
270	23.7	640	46.7	1250	78.4
280	24.4	660	47.7	1300	81.0
290	25.2	680	48.8	1350	84.2
300	25.9	700	49.8	1400	87.4

Designation:  $\text{вт/(м} \cdot \text{град)} = \text{W/(m} \cdot \text{deg)}$ .

On the strength of the fact that the thermal conductivity of nitrogen in the temperature range of 300-1200°K has been studied comparatively reliably, the introduced tabulated data, just as the data for argon, may be recommended as reference materials in the calibration and checking of equipment for measuring the heat conductivity of gases.

In the region of elevated pressures the most complete measurements at low temperatures are those of N. B. Vargaftik [120], Ziebler [121], Barton [59], Ye. A. Stolyarov [116], I. F. Golubev and N. V. [117], and Keyes [105], and at moderate and high temperatures — the data of Johannin [89].

The data processed at coordinates  $\Delta\lambda = f(\rho)$  are presented in Fig. 27. In view of the fact that the results of Michels [122] were clearly erroneous, which was subsequently pointed out by the authors themselves [101], these data were not considered in the processing. It is clear from Fig. 27 that the results of the majority of authors can be well grouped together around a smooth curve, in the plotting of which the data of all the authors were accepted as equivalent. The maximum divergence from this curve, with the exception of the region close to critical ( $T = 110-150^\circ\text{K}$  and  $\rho = 0.18-0.45 \text{ g/cm}^3$ ), does not exceed 5%. This region is excluded from examination for the reasons given in the introduction. The average curve can be satisfactorily described by equations (106) in the density interval  $\rho = 0-0.7 \text{ g/cm}^3$

$$\Delta\lambda = 307 \cdot 10^{-8} \rho + 158 \cdot 10^{-8} \rho^2 - 227 \cdot 10^{-8} \rho^3 + 235 \cdot 10^{-8} \rho^4, \quad (57)$$

where  $\Delta\lambda$  is in  $10^{-8} \text{ kW/(m.deg)}$ ;  $\rho$  is in  $\text{g/cm}^3$ .

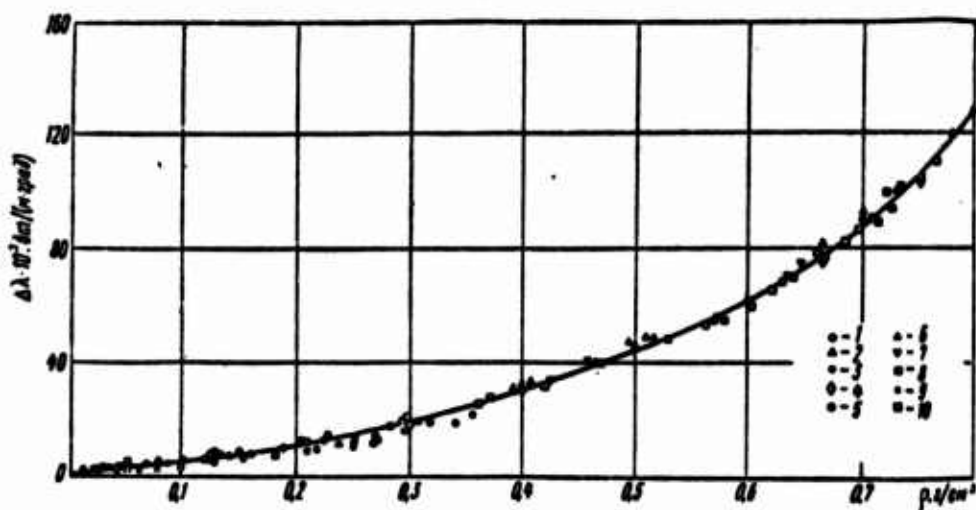


Fig. 27. Dependency of excess thermal conductivity of nitrogen on the density from the data of: 1 - Keyes [105]; 2 - Johannin [89]; 3 - Stoylarov, et al. [116]; 4 - Lenoir, Commings [86]; 5 - Misic, Thodos [124] (sic); 6 - Freud, Rothberg [95]; 7 - Ziebland and Barton [29]; 8 - Uhlir [104]; 9 - Nuttall, Ginnigs [23]; 10 - Golubev, Kal'sina [117].

Designations:  $\text{вт/(м·град)} = \text{W/(m.deg)}$ ;  $\text{г/см}^3 = \text{g/cm}^3$ .

Table 24. Recommended values of the thermal conductivity of gaseous and liquid nitrogen as a function of temperature and pressure.

T, °K	$\lambda, 10^3 \text{ W/(m-deg)}, \text{ with } p, \text{ bar}$																		
	1	10	20	30	40	50	60	70	80	90	100	150	200	250	300	350	400	450	500
80	7.82	138	139	140	141	142	143	—	144	—	146	154	162	167	171	175	179	183	188
90	8.63	113	114	—	116	—	119	—	121	—	123	132	140	146	151	157	163	169	174
100	9.58	95.2	97.4	—	99.3	—	102	—	105	—	107	114	119	124	130	137	144	150	156
110	10.48	11.9	78.3	—	83.5	—	87.2	—	90.0	—	93.2	99.1	105	110	116	122	128	134	140
120	11.30	12.5	14.7	63.2	68.4	—	73.1	—	77.3	—	80.4	87.2	94.3	100	105	110	115	119	124
130	12.0	13.3	14.9	—	—	—	57.0	—	65.4	—	69.3	79.4	87.5	93.4	99.6	101	105	110	114
140	13.0	14.1	15.4	17.4	—	—	—	—	—	—	—	69.3	78.4	84.2	90.5	95.4	100	103	106
150	13.9	14.9	16.0	17.6	19.7	—	—	—	—	—	—	60.5	69.4	76.3	82.4	88.2	93.6	97.3	101
160	14.8	15.7	16.7	18.0	19.6	21.8	—	—	—	—	—	52.8	62.3	70.2	76.3	81.4	86.1	91.2	95.4
170	15.7	16.5	17.4	18.5	19.9	21.6	23.6	25.9	28.6	31.2	34.1	47.3	56.2	64.4	70.5	76.4	81.2	86.3	91.2
180	16.6	17.3	18.1	19.1	20.3	21.7	23.3	25.0	27.2	29.3	32.0	43.2	52.4	59.3	65.4	71.6	76.4	80.3	84.5
190	17.5	18.1	18.8	19.7	20.8	22.2	23.3	24.9	26.5	28.3	30.2	40.4	48.3	55.5	61.3	67.2	71.4	76.5	80.4
200	18.3	18.9	19.6	20.4	21.3	22.4	23.6	24.9	26.3	27.8	29.4	38.5	45.2	52.4	58.1	63.3	68.2	72.7	76.5
220	20.0	20.5	21.1	21.8	22.5	23.4	24.3	25.4	26.4	28.2	29.2	35.4	42.1	48.3	53.4	58.5	62.4	66.6	70.3
240	21.4	22.0	22.5	23.2	23.8	24.5	25.3	26.0	27.0	28.4	29.0	34.3	40.2	45.1	50.2	54.1	58.5	62.4	66.5
260	22.9	23.5	23.9	24.5	25.0	25.7	26.4	27.0	28.0	28.7	29.5	33.9	38.5	43.5	47.4	51.6	55.5	59.4	62.7
280	24.4	24.9	25.3	25.8	26.3	26.9	27.5	28.0	28.8	29.5	30.2	34.0	37.4	41.7	45.6	49.4	52.8	55.7	59.7
300	25.9	26.2	26.6	27.1	27.5	28.0	28.6	29.2	29.7	30.3	31.0	34.4	37.6	40.7	44.8	47.7	51.8	54.9	57.8
320	27.3	—	27.9	—	28.3	—	29.7	—	30.8	—	31.9	35.2	37.9	40.7	43.6	47.5	50.3	53.1	56.2
350	29.3	—	29.9	—	30.6	—	31.4	—	32.3	—	33.3	36.1	39.0	42.2	43.8	46.7	49.8	52.2	54.7
400	32.7	—	33.0	—	33.6	—	34.3	—	35.1	—	35.9	38.0	39.9	43.0	44.8	47.1	48.9	51.8	54.2
450	35.8	—	36.0	—	36.8	—	37.2	—	37.8	—	38.2	40.3	42.3	44.4	46.2	48.3	50.2	52.4	54.3
500	38.9	—	38.0	—	39.5	—	40.0	—	40.6	—	41.2	43.2	44.6	46.0	47.6	49.6	51.3	53.2	55.2
550	41.7	—	41.8	—	42.3	—	42.8	—	43.2	—	43.8	45.4	47.3	48.4	49.5	50.5	52.7	53.8	55.4
600	44.6	—	44.8	—	45.2	—	45.6	—	45.0	—	46.3	47.5	48.9	50.1	51.8	53.4	54.4	55.6	57.1
650	47.2	—	47.3	—	47.7	—	48.1	—	48.5	—	48.8	49.8	51.3	52.5	53.7	54.9	56.1	57.3	58.4
700	49.9	—	50.2	—	50.4	—	50.6	—	50.8	—	51.2	52.4	53.6	54.6	55.6	56.8	57.9	58.8	59.9
750	52.4	—	52.6	—	52.8	—	53.0	—	53.3	—	53.6	54.8	55.8	56.9	58.0	58.9	60.0	60.9	62.0
800	54.8	—	55.2	—	55.5	—	55.7	—	56.0	—	—	56.6	57.6	58.8	60.0	60.9	62.0	63.0	63.9
850	57.2	—	57.5	—	57.7	—	57.9	—	58.2	—	—	59.8	60.6	61.5	62.0	62.9	63.8	64.9	65.8
900	59.7	—	60.0	—	60.2	—	60.4	—	60.6	—	—	61.8	62.8	63.7	64.6	65.5	66.4	67.3	68.2
950	62.2	—	62.4	—	62.6	—	62.8	—	63.0	—	—	64.2	65.1	66.0	66.9	67.8	68.7	69.6	70.5
1000	64.7	—	64.9	—	65.1	—	65.3	—	65.5	—	—	66.6	67.5	—	69.3	—	71.1	—	72.2
1100	70.0	—	70.2	—	70.4	—	70.6	—	70.8	—	—	71.0	71.9	—	73.0	—	74.4	—	75.3
1200	75.8	—	76.0	—	—	—	76.4	—	76.5	—	—	76.6	77.8	—	78.6	—	79.5	—	80.2
1300	81.0	—	81.2	—	—	—	81.6	—	81.8	—	—	82.2	83.0	—	83.8	—	84.9	—	85.8
1400	87.0	—	87.2	—	—	—	87.4	—	87.5	—	—	87.7	88.5	—	89.4	—	90.4	—	91.3
197	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
183	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
168	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
151	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
133	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
123	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
114	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
109	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
103	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
97.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
92.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
88.4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
83.6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
77.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
72.6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
69.4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
65.8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
62.7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
61.2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
59.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
57.9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
57.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
58.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
58.8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
59.6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
61.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
62.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
64.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
66.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
67.8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
70.0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
72.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
73.4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
76.4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
81.3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
86.6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
92.1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

The dependence of the thermal conductivity of nitrogen on the temperature and pressure was calculated according to formulas (56) and (57); the recommended values are given in Table 24 for the temperature interval of 80-1400°K and for the pressure interval of 1-600 bar. The inaccuracy of these data is 4% for the gas phase; 5-6% for the liquid phase. On the saturation line the thermal conductivity of liquid nitrogen, calculated according to equations (56) and (57), is shown below:

$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$	$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$
90	112	110	80.2
95	104	115	70.4
100	95.5	120	62.8
105	88.0		

Designation:  $\text{вт/(м} \cdot \text{град)} =$   
 $= W/(m \cdot \text{deg}).$

### Oxygen

The thermal conductivity of oxygen at atmospheric pressure, as follows from Table 25 and Fig. 28, has been studied relatively little. Basically, the temperature interval of 80-300°K has been investigated. The results of measurements of various authors correspond comparatively well with one another. The maximum difference, which occurs only in individual cases, amounts to ~5%. In the region of moderate and high temperatures the divergences in the values of the two existing works: Westenberg and de Haas [81] and Schäfer and Geier [25] lie within the limits of 1% in the entire temperature range.

Fig. 28. Dependence of the thermal conductivity of oxygen on the temperature at pressure  $p = 1$  bar, according to the data of:

- 1 - Westenberg and de Haas [81];
- 2 - Schäfer and Geier [25];
- 3 - Johnston and Grilly [85];
- 4 - Mukhopadhyay and Barua [92];
- 5 - Ziebland and Barton [29];
- 6 - Keyes [105].

Designation:  $\text{вт/(м} \cdot \text{град)} =$   
 $= W/(m \cdot \text{deg}).$

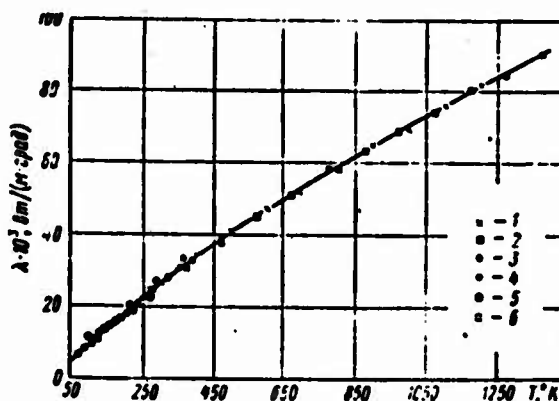




Table 25. Investigations of the thermal conductivity of oxygen.

Author	Year	Liter- ature source	Method	Temperature, °K	Pressure, bar
Eucken	1911	[83]	Heated filament	80-373	1
Weber	1917	[102]	The same	273	1
Gregory, Martin (sic)	1928	[114]	The same	273-320	1
Kannuluik, Martin	1934	[65]	The same	273	1
Dikins	1934	[103]	The same	273	1
Nothdurft	1937	[125]	The same	273-320	1
Johnston, Grilly	1946	[85]	The same	87-376	1
Borovik	1947	[121]	Parallel plates	156	25-97
Ziebland, Burton	1955	[29]	Coaxial cylinders	79-200	1-136
Keyes	1955	[105]	The same	97-273	1-10
Tsederberg, Timrot	1958	[124]	Heated filament	83-298	60-100
Geler, Schäfer	1961	[25]	The same	273-1373	1
Westenberg, de Haas	1963	[81]	Laminar flow	300-1200	1
Mukhopadhyay, Barua	1967	[92]	Heated filament	90-473	1
Ivanova, Tsederberg, Ponov	1967	[126]	The same	83-343	100-500

Table 26. Recommended values of the thermal conductivity of oxygen gas at atmospheric pressure.

$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$	$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$	$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$
80	7.40	220	20.0	600	47.3
90	8.40	230	20.8	650	50.0
100	9.25	240	21.7	700	52.8
110	10.2	250	22.6	750	56.2
120	11.0	260	23.4	800	58.9
130	11.9	270	24.1	850	62.1
140	12.8	280	25.5	900	64.9
150	13.8	290	25.8	950	68.1
160	14.7	300	26.6	1000	71.0
170	15.6	350	29.8	1100	75.8
180	16.6	400	33.0	1200	81.9
190	17.7	450	36.3	1300	87.1
200	18.3	500	41.2	1400	92.3
210	19.2	550	44.1		

Designation:  $\text{вт/(м} \cdot \text{град)} = \text{W/(m} \cdot \text{deg)}$ .

In the region of low temperatures the results of Westenberg and de Haas, and also those of Schäfer and Geier, correspond well with the data of other researchers.

In connection with what has been said, averaging was carried out, considering the data of all the authors as equivalent. The inaccuracy of the recommended values of thermal conductivity, cited in Table 26, amounts to 2.5% in the temperature interval of 80–300°K, 3% in the interval from 300–600°K, and 4% in the interval from 600–1400°K. Let us note that at temperatures above 500°K it would be very desirable to have experimental investigations on the thermal conductivity of oxygen.

Only a few works have been dedicated to the study of thermal conductivity of oxygen at elevated temperatures (see Table 25). The most complete and reliable are the data of Ziebland and Barton [29], who measured the thermal conductivity with  $p$  up to 136 atm in the liquid and gas region, those of N. V. Tsederberg and D. L. Timrot [124] – with  $p$  up to 100 atm and the latter work of Z. A. Ivanova, N. V. Tsederberg, and V. N. Popov [126] – with  $p$  up to 500 atm. The results of these three works, although obtained by various methods, have a divergence of only 5–6%.

Table 27. Recommended values of the thermal conductivity of gaseous and liquid oxygen as a function of temperature and pressure.

T. °K	$\lambda \cdot 10^6 \cdot W / (m \cdot deg)$ with p. bar																				
	1	10	20	30	40	50	60	70	80	90	100	150	200	250	300	350	400	450	500	550	600
80	161	162	163	—	164	—	165	—	—	—	167	170	172	175	177	179	181	183	185	187	189
90	147	148	149	—	150	—	151	—	—	—	154	157	159	162	164	166	168	170	172	174	176
100	9.25	134	135	—	136	—	138	—	—	—	142	144	147	150	153	155	157	159	161	163	165
110	10.2	120	121	—	123	—	125	—	—	—	128	131	135	138	141	143	146	149	152	155	157
120	11.0	12.2	108	—	100	—	110	—	—	—	113	115	117	121	125	128	132	135	137	140	143
130	11.9	13.0	95.9	—	97.4	—	99.6	—	—	—	102	106	109	113	116	120	124	127	130	133	135
140	12.8	13.7	15.4	80.6	83.5	85.4	87.6	89.5	91.3	93.8	95.6	99.4	104	108	112	115	118	121	124	127	130
150	13.8	14.7	16.0	18.2	21.0	22.9	24.8	27.0	29.8	32.8	36.0	39.3	42.6	46.0	49.4	52.8	56.2	59.6	63.0	66.4	69.8
160	14.7	15.5	16.7	18.4	20.9	23.0	25.1	27.4	29.6	31.9	34.2	36.5	38.8	41.1	43.4	45.7	48.0	50.3	52.6	54.9	57.2
170	15.6	16.4	17.4	18.8	20.7	22.8	24.7	26.6	28.4	30.3	32.2	34.1	36.0	37.9	39.8	41.7	43.6	45.5	47.4	49.3	51.2
180	16.6	17.2	18.1	19.3	21.0	22.8	24.7	26.6	28.4	30.3	32.2	34.1	36.0	37.9	39.8	41.7	43.6	45.5	47.4	49.3	51.2
190	17.4	18.0	18.9	19.9	21.3	22.9	24.7	26.6	28.4	30.3	32.2	34.1	36.0	37.9	39.8	41.7	43.6	45.5	47.4	49.3	51.2
200	18.3	18.9	19.7	20.6	21.8	23.0	24.7	26.6	28.4	30.3	32.2	34.1	36.0	37.9	39.8	41.7	43.6	45.5	47.4	49.3	51.2
220	20.0	—	21.2	—	22.9	—	25.2	—	28.0	—	30.9	33.8	36.7	39.6	42.5	45.4	48.3	51.2	54.1	57.0	59.9
240	21.7	—	22.8	—	24.2	—	25.4	—	29.0	—	31.0	33.8	36.6	39.4	42.2	45.0	47.8	50.6	53.4	56.2	59.0
260	23.4	—	24.3	—	25.6	—	27.2	—	30.0	—	32.0	34.8	37.6	40.4	43.2	46.0	48.8	51.6	54.4	57.2	60.0
280	25.0	—	25.8	—	27.0	—	28.4	—	31.0	—	32.6	35.4	38.2	41.0	43.8	46.6	49.4	52.2	55.0	57.8	60.6
300	26.6	—	27.4	—	28.4	—	29.6	—	33.6	—	34.8	38.0	40.7	43.5	46.3	49.1	51.9	54.7	57.5	60.3	63.1
350	29.8	—	30.8	—	31.6	—	32.6	—	40.0	—	39.0	43.0	45.8	48.6	51.4	54.2	57.0	59.8	62.6	65.4	68.2
400	33.0	—	34.0	—	34.8	—	35.8	—	43.6	—	40.8	46.0	48.8	51.6	54.4	57.2	60.0	62.8	65.6	68.4	71.2
450	36.3	—	37.3	—	38.2	—	39.1	—	48.0	—	44.3	50.0	52.8	55.6	58.4	61.2	64.0	66.8	69.6	72.4	75.2
500	41.2	—	41.4	—	41.8	—	42.7	—	52.3	—	46.6	53.8	56.6	59.4	62.2	65.0	67.8	70.6	73.4	76.2	79.0
550	44.1	—	44.4	—	44.9	—	—	—	—	—	49.2	56.8	59.6	62.4	65.2	68.0	70.8	73.6	76.4	79.2	82.0
600	47.3	—	—	—	47.8	—	—	—	—	—	52.7	60.1	62.9	65.7	68.5	71.3	74.1	76.9	79.7	82.5	85.3
650	50.0	—	—	—	51.4	—	—	—	—	—	54.8	61.3	64.1	66.9	69.7	72.5	75.3	78.1	80.9	83.7	86.5
700	52.8	—	—	—	53.6	—	—	—	—	—	58.3	62.3	65.1	67.9	70.7	73.5	76.3	79.1	81.9	84.7	87.5
750	56.2	—	—	—	57.1	—	—	—	—	—	61.3	64.8	67.3	69.8	72.3	74.8	77.3	79.8	82.3	84.8	87.3
800	58.9	—	—	—	59.8	—	—	—	—	—	63.8	67.0	69.5	72.0	74.5	77.0	79.5	82.0	84.5	87.0	89.5
850	62.1	—	—	—	—	—	—	—	—	—	66.2	69.1	71.6	74.1	76.6	79.1	81.6	84.1	86.6	89.1	91.6
900	64.9	—	—	—	—	—	—	—	—	—	68.1	70.5	72.9	75.3	77.7	80.1	82.5	84.9	87.3	89.7	92.1
950	68.1	—	—	—	—	—	—	—	—	—	69.3	71.3	73.3	75.3	77.3	79.3	81.3	83.3	85.3	87.3	89.3
1000	71.0	—	—	—	—	—	—	—	—	—	71.8	72.6	73.4	74.2	75.0	75.8	76.6	77.4	78.2	79.0	79.8
1100	75.8	—	—	—	—	—	—	—	—	—	76.6	77.6	78.1	78.9	79.6	80.4	81.1	81.9	82.6	83.3	84.1
1200	81.9	—	—	—	—	—	—	—	—	—	82.6	83.1	83.6	84.1	84.7	85.2	85.7	86.3	86.8	87.4	88.0
1300	87.1	—	—	—	—	—	—	—	—	—	87.9	88.5	89.0	89.5	90.0	90.5	91.0	91.6	92.1	92.6	93.1
1400	92.3	—	—	—	—	—	—	—	—	—	82.8	93.3	93.8	94.3	94.8	95.3	95.9	96.4	96.9	97.3	97.8

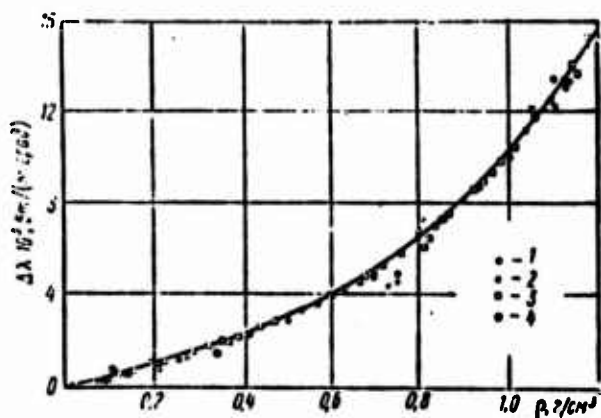


Fig. 29. The dependence of the excess thermal conductivity of oxygen on the density according to the data of: 1 - Ivanova, Tsederberg, and Popov [126]; 2 - Borovik [121]; 3 - Ziebland and Barton [29]; 4 - Keyes [105].

Designation:  $\lambda/(m \cdot \text{град}) = W/(m \cdot \text{deg})$ ;  $\rho/\text{cm}^3 = g/\text{cm}^3$ .

The results of all the authors who measured the thermal conductivity at elevated pressures were processed at coordinates of excess thermal conductivity-density and are shown in Fig. 29. The greater part of the experimental points are grouped around a smooth curve; one exception is a few points of works [121, 126] with densities of  $\sim 0.7 \text{ g/cm}^3$ , lying below the averaging curve by 8%. We should note that the generalizing curve can be described by the equations given in works [106, 126]. Values calculated by these equations with large densities coincide, practically speaking; at low densities the divergence does not exceed 4%.

According to the recommended data on the thermal conductivity at atmospheric pressure (see Table 26) and from the curve described by the equation taken from work [106], for  $\rho = 0-1.2 \text{ g/cm}^3$

$$\Delta\lambda = 255 \cdot 10\rho + 193 \cdot 10^2\rho^2 - 433 \cdot 10^3\rho^3 + 478 \cdot 10^4\rho^4 - 156 \cdot 10^5\rho^5, \quad (58)$$

where  $\rho$  is in  $\text{g/cm}^3$ , and  $\Delta\lambda$  can be expressed by  $10^{-8} \text{ kW/(m} \cdot \text{deg)}$ , and tables were compiled for the dependence of the thermal conductivity of oxygen on the temperature in the range of 80-1400°K and for pressures of 1-600 bar (Table 27). The table does not include the

region around critical, which embraces the temperature interval of 140-150°K and the density range of 0.25-0.57 g/cm<sup>3</sup>. The inaccuracy of the recommended data, cited in Table 28, amounts to 5% in the entire temperature and pressure range.

According to the data of Table 27 and equation (58) the table of recommended values for the thermal conductivity of liquid oxygen was also compiled on the saturation line (Table 28).

Table 28. Recommended values of the thermal conductivity of liquid oxygen on the saturation line.

$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт}/(\text{м} \cdot \text{град})$	$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт}/(\text{м} \cdot \text{град})$	$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт}/(\text{м} \cdot \text{град})$
90	148	115	115	135	88,6
95	142	120	109	140	82,0
100	135	125	102	145	72,8
105	129	130	95,1	150	65,3
110	122				

Designation:  $\text{вт}/(\text{м} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ .

### Air

Air is one of the gases recommended by us as a reference substance. There are completely reliable data on the thermal conductivity of air. Therefore it is understood why it, just like water, is widely used as a reference material for control and calibration of experimental equipment.

The thermal conductivity of air at atmospheric pressure and room temperature has been measured by very many investigators. In a well known report Hilsenrath and Touloukian [127] made a detailed review of all these works. Table 29 includes only the basic studies of the thermal conductivity of air, embracing the relatively wide temperature range from 82 to 1373°K. In the majority of works the heated filament method was employed.

Table 29. Basic research on the thermal conductivity of gaseous air at atmospheric pressure.

Author	Year	Liter- ature source	Method	Temperature, °K
Eucken	1911	[83]	Heated filament	82-273
Sherrat, Griffiths	1939	[128]	" "	333-583
Vargaftik, Oleshchuk	1946	[129]	" "	317-1069
Taylor, Johnston	1946	[130]	" "	87-376
Stopps	1949	[28]	" "	273-1273
Kannulnik, Carman	1951	[131]	" "	90-491
Zaytseva	1956	[132]	" "	319-761
Vines	1960	[27]	Coaxial cylinders	513-1173
Tarziminov	1960	[133]	Heated filament	303-835
Geler, Schäfer	1961	[25]	" "	273-1373

In generalizing the experimental data we eliminated the results of Stopps [28] as insufficiently reliable (there is a large correction for heat removal from the ends of the measuring section, there is a noticeable scattering of the experimental points, and there is a significant correction for radiation and other factors). The data of Geier and Schäfer [25] were also not taken into consideration, since the correction for the temperature jump was not introduced completely correctly [30]. Refinement of the correction value was not managed due to the absence in work [25] of the essential primary data.

The experimental data of all the remaining authors in the temperature range of 200-1000°K can be well described by the equation

$$\lambda = 0,0012 + 0,0808 \cdot 10^{-3}T + 0,0321 \cdot 10^{-6}T^2 - 0,0942 \cdot 10^{-9}T^3 + 0,0468 \cdot 10^{-12}T^4 \text{ [W/(m.deg)]}, \quad (59)$$

where T is in °K.

The coefficients of equations (59) were determined by the method of least squares on an electronic digital computer.

Table 30 shows the recommended values for the thermal conductivity of air at atmospheric pressure, which were calculated from equations (59) for the temperature region of 200-1000°K. For segments T = 80-200°K and 1000-1200°K the thermal conductivity was determined graphically.

Figure 30 shows the divergence in percentages for the experimental data from the tabulated data of thermal conductivity. The scattering of points of various authors basically does not exceed 2%, which undoubtedly bears witness to the sufficient reliability of the data on thermal conductivity of air with p = 1 bar.

The inaccuracy of the recommended data of thermal conductivity amounts to 2% in the range of T = 80-250°K; 1% - for 250-400°K; 1.5% - for 400-800°K; and 2% - for 800-1200°K.

Table 30. Recommended values of the thermal conductivity of gaseous air at atmospheric pressure.

$T, ^\circ K$	$\lambda \cdot 10^3$ $вт/(м \cdot град)$	$T, ^\circ K$	$\lambda \cdot 10^3$ $вт/(м \cdot град)$	$T, ^\circ K$	$\lambda \cdot 10^3$ $вт/(м \cdot град)$	$T, ^\circ K$	$\lambda \cdot 10^3$ $вт/(м \cdot град)$
80	7.5	220	19.6	360	30.8	600	46.9
90	8.4	230	20.4	370	31.5	650	49.7
100	9.3	240	21.2	380	32.3	700	52.4
110	10.2	250	22.1	390	33.0	750	54.9
120	11.1	260	22.9	400	33.8	800	57.3
130	12.0	270	23.8	420	35.2	850	59.6
140	12.9	280	24.6	440	36.6	900	62.0
150	13.8	290	25.4	460	38.0	950	64.3
160	14.7	300	26.2	480	39.4	1000	66.7
170	15.5	310	26.9	500	40.7	1050	69.1
180	16.4	320	27.7	520	42.0	1100	71.5
190	17.2	330	28.5	540	43.3	1150	73.9
200	18.0	340	29.2	560	44.5	1200	76.3
210	18.8	350	30.0	580	45.7		

Designation:  $вт/(м \cdot град) = W/(m \cdot deg)$ .

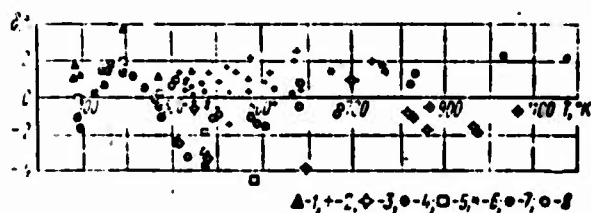


Fig. 30. Divergences of the experimental data of various authors on the thermal conductivity of gaseous air from the recommended values at atmospheric pressure: 1 - Eucken [83]; 2 - Sherratt, Griffiths [128]; 3 - Vargaftik, Oleshchuk [129]; 4 - Taylor, Johnston [130]; 5 - Kannuluik, Carman [131]; 6 - Zaytseva [132]; 7 - Vines [27]; 8 - Tarziminov [133];

The thermal conductivity of air at elevated pressures (up to 200 bar) and  $T = 407^\circ K$  was first measured by I. F. Golubev [134] by the heated filament method.

In 1950 the results of measurements done also by the heated filament method by Ye. A. Stolyarov, V. V. Ipat'yev, and V. P. Teodorovich [116] in the temperature interval of  $284-469^\circ K$  at pressures of 1-400 bar were published. The possible inaccuracy is estimated by the authors as equal to 3%.



In 1963 I. F. Golubev [68] measured the thermal conductivity of air at pressures from 1 to 500 bar in the temperature range from 196 to 426°K by the regular regime method (a cylindrical bicalorimeter). The possible error, in the author's opinion, is 1.1%.

Recently, A. A. Tarziminov and V. S. Lozova [135]<sup>1</sup> used the heated filament method to study the thermal conductivity of air at pressures up to 1000 bar in the temperature region from 298 to 793°K. The possible error of the obtained data, in the authors' estimate, does not exceed 1.5%.

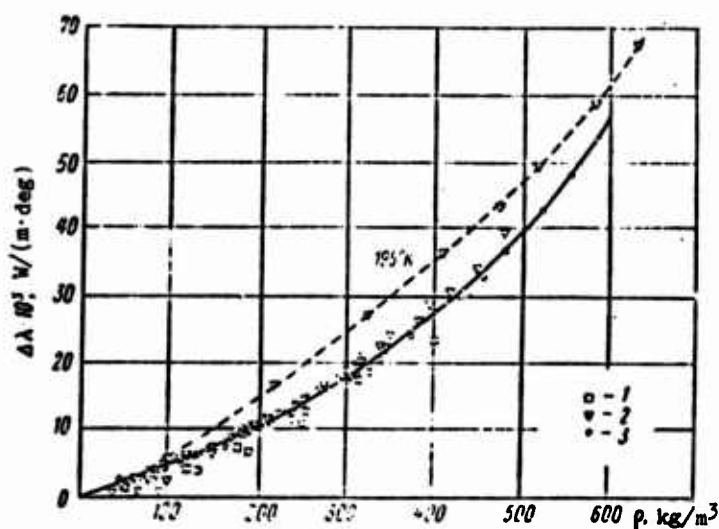


Fig. 31. The dependence of the excess thermal conductivity of air on the density according to the data of: 1 - Stolyarov, et al. [116]; 2 - Golubev [68]; 3 - Tarziminov, Lozova [135].

Figure 31 at the coordinates  $\Delta\lambda - \rho$  shows the experimental data, obtained in works [68, 116, 135]. The experimental points of I. F. Golubev, and also those of A. A. Tarziminov and V. S. Lozova with a small scattering (not greater than 2-3%) are positioned around the averaging curve. An exception is the isotherm of

<sup>1</sup>In work [135] the results of the experiments have been refined, in comparison with the earlier published data [136].

196°K [68], the points of which fall higher - up to 8-10%. It is highly improbable that with such a large distance from the critical temperature there was a significant stratification of the isotherms at the coordinates  $\Delta\lambda - \rho$ . Therefore in the generalization of the data we did not take into account this isotherm.

The experimental results of Ye. A. Stolyarov [116] are systematically positioned lower than the data of the other investigators and have a significant scattering, which probably can be explained by the insufficiently high accuracy of the experiments.

The averaging curve (Fig. 31) was used by us to determine the tabulated data of the thermal conductivity of air at temperatures up to 1000°K in the interval  $p = 300$ -800 bar (Table 31). The possible error of the tabulated data under pressure amounts to 2-3%.

There are no direct experimental data on the thermal conductivity of liquid air. Therefore only indirect methods for its determination were possible.

Table 31. Recommended values of the thermal conductivity of gaseous air as a function of temperature and pressure.

T, °K	(1) $\lambda \cdot 10^3$ , $\text{BTU}/(\text{ft} \cdot \text{sec})$ при p, бар									
	300	350	400	450	500	550	600	650	700	800
1	26,2	30,0	33,8	37,3	40,7	43,9	46,9	49,7	52,4	54,9
50	28,4	31,8	35,4	38,7	42,0	45,0	47,9	50,6	53,2	55,7
100	31,4	34,1	37,3	40,3	43,3	46,2	49,0	51,6	54,1	56,5
150	34,9	36,7	39,4	42,0	44,9	47,6	50,2	52,7	55,2	57,4
200	38,5	39,5	41,8	44,0	46,5	49,0	51,5	53,9	56,2	58,4
250	42,0	42,3	44,1	46,0	48,3	50,5	52,9	55,1	57,3	59,4
300	45,5	45,1	46,4	48,0	50,1	52,2	54,3	56,3	58,4	60,4
350	48,9	47,8	48,6	49,9	51,8	53,7	55,7	57,6	59,6	61,5
400	52,2	50,5	50,9	51,9	53,5	55,2	57,1	58,9	60,8	62,6
450	55,3	53,1	53,1	53,8	55,2	56,7	58,4	60,2	62,0	63,7
500	58,4	55,5	55,2	55,8	56,8	58,2	59,8	61,4	63,1	64,8
550	61,4	58,0	57,3	57,6	58,4	59,7	61,1	62,6	64,2	65,9
600	64,4	60,3	59,4	59,4	60,0	61,1	62,4	63,8	65,3	66,9
650	67,4	62,7	61,5	61,2	61,6	62,5	63,7	65,0	66,4	67,9
700	70,3	65,1	63,6	62,9	63,2	64,0	65,0	66,2	67,5	68,9
750	73,2	67,6	65,6	64,6	64,7	65,4	66,3	67,4	68,6	69,9
800	76,0	70,0	67,6	66,2	66,2	66,8	67,6	68,6	69,7	70,9
850	78,6	72,5	69,6	67,8	67,7	68,2	68,9	69,7	70,8	71,9
900	81,1	74,9	71,6	69,4	69,4	69,2	69,5	70,1	71,9	72,9
950	83,7	77,4	73,6	71,0	70,5	70,8	71,3	72,0	73,0	73,9
1000	86,2	79,8	75,6	72,6	71,8	72,0	72,5	73,2	74,1	74,9

KEY: (1)  $\lambda \cdot 10^3$ , W/(m·deg) with p, bar.

The basic component parts of air, as is known, are nitrogen (75.52 weight %) and oxygen (23.15 weight %).

Therefore, liquid air may be examined, practically speaking, as a mixture of liquid nitrogen and oxygen.

The thermal conductivity of liquid nitrogen and oxygen, as well as their mixtures of various composition was measured by Hamman by the flat layer method [60]. However, Hamman's results for liquid nitrogen and oxygen are higher by 20-30% than the data of the other investigators and have a clearly erroneous temperature pattern. N. V. Tsederberg points out [10] that a possible reason for the exaggerated values of the coefficient of thermal conductivity may be the emergence of convections in Hamman's apparatus.

Let us introduce corrections into the results of Hamman on the basis of more reliable data on the thermal conductivity of nitrogen and oxygen. In conformance [60] with  $T = 73^\circ\text{K}$  the thermal conductivity of nitrogen equals  $0.206 \text{ W}/(\text{m} \cdot \text{deg})$ , and that of oxygen -  $0.208 \text{ W}/(\text{m} \cdot \text{deg})$ , while the actual values are:  $\lambda_{\text{N}_2} = 0.160 \text{ W}/(\text{m} \cdot \text{deg})$  (see Table 23) and  $\lambda_{\text{O}_2} = 0.172 \text{ W}/(\text{m} \cdot \text{deg})$  (see Table 26), i.e., lower by 22 and 18%, respectively.

According to the graph shown by Hamman [60], the thermal conductivity of a nitrogen-oxygen mixture of a composition corresponding to air, with  $T = 73^\circ\text{K}$ , is equal to  $0.200 \text{ W}/(\text{m} \cdot \text{deg})$ . Introducing a correction on the basis of the aforesaid, we determine the value of the thermal conductivity of liquid air with  $T = 73^\circ\text{K}$  as equal to  $0.165 \text{ W}/(\text{m} \cdot \text{deg})$ .

The thermal conductivity of liquid air may be determined also according to the equation suggested by L. P. Filippov and N. S. Novoselova for binary solutions [137]. For  $T = 27^\circ\text{K}$  the calculations produce  $0.161 \text{ W}/(\text{m} \cdot \text{deg})$ , which is in complete correspondence with the value obtained on the basis of Hamman's data.

Thus, for practical calculations see thermal conductivity of liquid air at  $T = 73^{\circ}\text{K}$  may be taken as equal to  $0.163 \text{ W/(m}\cdot\text{deg)}$  with a probable error of 5-6%.

### Carbon Dioxide

A significant number of works (Table 32) have been dedicated to the study of the thermal conductivity of  $\text{CO}_2$ . More than half of them have been done at atmospheric pressure in the temperature range of  $185\text{--}1375^{\circ}\text{K}$ . From Table 32 it is clear that the least studied of all is the region of high temperatures of  $800\text{--}1400^{\circ}\text{K}$ . In processing the initial material we took into account all the most reliable data and excluded works which did not correspond to the prerequisites of selection of the material, set down in the introduction. Thus, we did not consider the work of Stopps [28], just as for nitrogen, and the work of Rothman and Bromley [149], in which the authors introduce averaging results of their former measurements and data from work [28]. The data of Geier and Schäfer [25] in the high temperature region (beginning with  $700^{\circ}\text{K}$ ) were adjusted by us by the introduction of a correction for the temperature jump similar to that used with the data for argon and nitrogen [30, 32].

The selected experimental data at atmospheric pressure are introduced in Fig. 32. A comparison of these values obtained by the same various methods allow us to make the following conclusions. In the low temperature region of  $180\text{--}400^{\circ}\text{K}$  agreement of all the data can be observed with a divergence within the limits of 2-3%. In the temperature range of  $400\text{--}800^{\circ}\text{K}$ , into which a smaller number of works fall, divergences are within the limits of 4%. Above all these fall the data of Ye A. Stolyarov, et al. [116]. In the high temperature region which is the most experimentally complex (above  $800^{\circ}\text{K}$ ) the maximum divergence in the data of various authors reaches as high as 6%.

Table 32. Investigation of the thermal conductivity of carbon dioxide.

Author	Year	Liter- ature source	Method	Temperature, °K	Pressure, bar
Bucken	1911	[83]	Heated filament	195-373	1
Gregory, Marshall	1927	[114]	"	277-285	1
Kannuluik	1934	[65]	"	273	1
Dikins	1934	[103]	"	273-280	1
Sellshopp	1934	[138]	Coaxial cylinders	284-313	1-20
Archer	1935	[139]	"	298-348	1
Sherrat, Griffiths	1939	[128]	Heated filament	339-566	1
Golubev, Kal'sina	1964	[117]	"	293-373	1-500
Vargaftik, Oleshchuk	1946	[129]	"	325-880	1
Johnston, Grilly	1946	[121] (sic)	"	186-380	1
Timrot, Oleshchuk	1948	[140]	"	302-412	20-300
Stopps	1949	[28]	"	273-1373	1
Lambert	1950	[141]	"	339-358	1
Stolyarov, et al.	1950	[116]	"	273-473	1-300
Keyes	1951	[105]	Coaxial cylinders	206-631	1-63
Lenoir, Commings	1951	[86]	"	314-340	1-200
Frank	1951	[22]	Heated filament	197-598	1
Shingarev	1950	[14]	"	263-298	1-200
Filippov	1953	[123]	Flat layer (relative)	273-533	1
Thomas	1954	[142]	Heated filament	314-338	1
Rothman, Bromberg	1954 1955	[58]	Coaxial cylinders	631-1047	1

Table 32 (Cont'd).

Author	Year	Liter- ature source	Method	Temperature, °K	Pressure, bar
Guildner	1958 1962	[143]	Coaxial cylinder	298-348	2-300
Vines	1960	[27]	"	543-1173	1
Robin	1960	[144]	Heated filament	313-453	1
Geier, Schäfer	1961	[25]	"	273-1373	1
Michels, Sengers	1962	[145]	Flat layer	298-348	1-2140
Westenberg, de Haas	1962	[81]	Laminar heat flow	300-1100	1
Amirkhanov, Adamov	1963	[146]	Flat layer	293-304	57-64
Bakker, Brokkau	1964	[147]	Heated filament	478	1
Gilmore	1966	[148]	Coaxial cylinder	348	1-3000
Freud, Rothberg	1967	[95]	Coaxial cylinders (relative)	298	1-1400

On the basis of the averaging curve shown in Fig. 32, Table 33 was compiled for the recommended values of thermal conductivity with rounded values of the temperatures within the interval of 200-1400°K. The error of the recommended values amounts to 1.5% in the interval  $T = 200-400^{\circ}\text{K}$ , 2% - for  $400-800^{\circ}\text{K}$ , and 3% - for  $800-1400^{\circ}\text{K}$ .

A significant part of the works presented in Table 32 were dedicated to the study of thermal conductivity at elevated pressures in the range of low and moderate temperatures. The most complete (with respect to pressures) are the data of Michels, et al. [145], I. F. Golubev and M. V. Kal'sina [117], and Ye. A. Stolyarov, et al. [116].

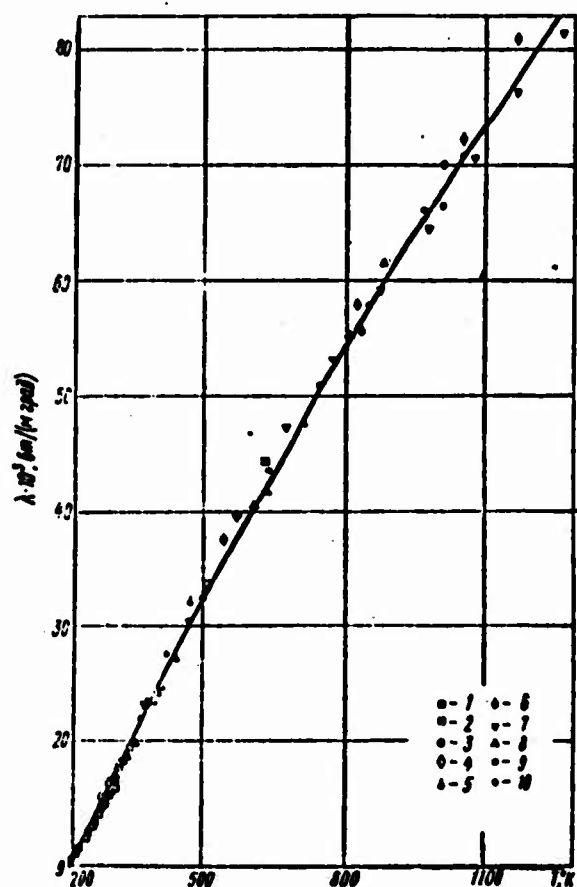


Fig. 32. Dependence of the thermal conductivity of gaseous carbon dioxide on the temperature at atmospheric pressure according to the data of: 1 - Keyes [105]; 2 - Johnston, Grilly [121]; 3 - Westenberg, de Haas [81]; 4 - Shingarev [14]; 5 - Stolyarov, et al. [116]; 6 - Vines [27]; 7 - Schäfer, Geier [25]; 8 - Vargaftik, Oleshchuk [129]; 9 - Rothman [58]; 10 - Filippov [123].

Designation:  $\text{Вт/(м} \cdot \text{град)} = \text{W/(m} \cdot \text{deg)}$ .

Table 33. Recommended values for the thermal conductivity of gaseous carbon dioxide at atmospheric pressure.

$T, ^\circ K$	$\lambda \cdot 10^3$ $вт/(м \cdot град)$	$T, ^\circ K$	$\lambda \cdot 10^3$ $вт/(м \cdot град)$	$T, ^\circ K$	$\lambda \cdot 10^3$ $вт/(м \cdot град)$
200	9.38	330	19.0	650	44.5
210	10.1	340	19.7	700	48.1
220	10.7	350	20.4	750	51.7
230	11.5	360	21.2	800	55.1
240	12.2	370	21.9	850	58.5
250	13.0	380	22.7	900	61.8
260	13.7	390	23.5	950	65.0
270	14.5	400	24.3	1000	68.2
280	15.2	450	28.3	1100	74.3
290	16.0	500	32.5	1200	80.3
300	16.6	550	36.6	1300	86.2
310	17.4	600	40.7	1400	92.1
320	18.3				

Designation:  $вт/(м \cdot град) = W/(m \cdot deg)$ .

The results of measurements were processed at coordinates  $\Delta\lambda - \rho$  and are presented in Fig. 33. The greater part of the experimental data, excluding the circumcritical region, are grouped around a smooth curve. The best correspondence can be observed between the data of Michels [145], Sellshopp [138], R. V. Shingarev [14] and Freud [95]. The greatest divergences occur in the region of high densities. The divergence (not systematic) of the data of I. F. Golubev and M. V. Kal'sina [117] from the data of the above-cited group of works reaches up to 15%. A somewhat smaller divergence occurs in the data of D. L. Timrot and V. G. Oskolkova [140]. The measurement results [117, 140] were critically analyzed in works [14, 36]. In particular, it was shown that certain experiments in works [140] were conducted with values of  $Pr \cdot Gr$  above those permissible, which might have led to the emergence of convection. The corresponding points were not taken into consideration in the processing.

Being guided by the general considerations laid down in the introduction, in the final processing of the results, just as for the other gases, we excluded from consideration the circumcritical region.

The averaging curve (see Fig. 33) can well be described by the equation introduced in work [149]:



$$\Delta\lambda \cdot 10^4 = 0,422\rho + 1,174 \cdot 10^{-3}\rho^2 - 1,772 \cdot 10^{-6}\rho^3 + 1,296 \cdot 10^{-9}\rho^4 \quad [\text{W}/(\text{m} \cdot \text{deg})], \quad (60)$$

where  $\rho$  is given in  $\text{kg}/\text{m}^3$ .

In the evaluations of the authors of [149a] equation (60) is valid in the density interval  $\rho = 0-1 \text{ g}/\text{cm}^3$  with an error of 2%.

According to the values of the thermal conductivity at atmospheric pressure and from equation (60) Table 34 was calculated for the dependency of the thermal conductivity on  $p$  and  $T$  in the most widely studied temperature and pressure intervals:  $T = 220-1400^\circ\text{K}$ ;  $p = 1-600 \text{ bar}$ .

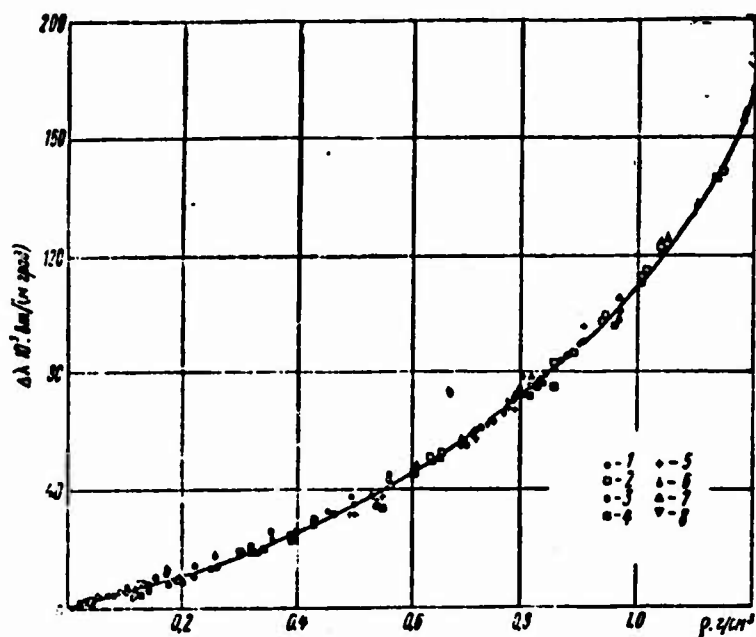


Fig. 33. The dependence of the excess thermal conductivity of  $\text{O}_2$  on the density according to the data of: 1 - Stolyarov et al. [149a]; 2 - Shingarev [14]; 3 - Sellshopp [138]; 4 - Timrot, Oskolkov [149b]; 5 - Golubev, Kal'sina [117]; 6 - Michels, Sengers [145]; 7 - Freud, Rothberg [95]; 8 - Guildner [143].

Designations:  $\text{BT}/(\text{m} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ ;  $\text{г}/\text{см}^3 = \text{g}/\text{cm}^3$ .

Table 34. Recommended values of the thermal conductivity of gaseous and liquid carbon dioxide as a function of temperature and pressure.

T, °K	$\lambda \cdot 10^3$ , W/(m·deg), with p, bar													
	1	10	20	30	40	50	60	70	80	90	100	110	120	130
220	10,70	177	178	179	180	181	182	183	184	185	186	187	188	189
230	11,47	162	163	164	165	166	167	168	169	170	171	172	173	174
240	12,20	—	150	151	152	153	154	155	156	157	158	159	160	161
250	12,55	—	136	137	138	139	141	142	143	144	145	147	148	149
260	13,65	—	—	125	126	127	129	130	131	132	133	134	135	136
270	14,45	15,4	16,3	18,0	115	117	118	119	120	122	123	124	125	126
280	15,20	16,1	17,0	18,6	21,0	104	106	108	110	111	113	114	116	117
290	15,95	16,7	17,7	19,0	21,4	22,0	92	95	98	100	101	103	104	105
300	16,55	17,4	18,4	19,4	21,1	23,0	26,4	—	—	—	90	93	95	97
310	17,40	18,2	19,0	20,2	21,4	23,4	25,6	29,1	34,6	93,8	67,2	74,4	—	—
320	18,05	18,8	19,6	20,8	21,9	23,8	25,4	27,9	31,4	36,4	44,6	54,9	63,5	69,0
330	18,95	19,7	20,5	21,5	22,7	24,2	25,7	27,5	30,2	33,6	37,7	43,2	49,6	56,0
340	19,70	20,4	21,2	22,1	23,2	24,7	25,8	27,4	29,6	32,2	35,3	38,7	42,9	47,4
350	20,4	21,1	21,9	22,7	23,8	25,0	26,1	27,6	29,4	31,4	33,9	36,8	39,6	43,0
360	21,2	21,8	22,6	23,3	24,4	25,4	26,6	28,2	29,5	31,2	33,4	35,5	38,0	40,7
370	21,95	22,6	23,3	24,1	25,0	26,0	27,1	28,3	29,7	31,3	32,9	35,0	37,2	39,3
380	22,75	23,4	24,1	24,8	25,6	25,9	27,6	28,7	30,0	31,4	33,1	34,7	36,6	38,0
390	23,5	24,1	24,8	25,5	26,3	27,2	28,2	29,1	30,3	31,5	33,0	34,5	36,2	37,8
400	24,3	24,8	25,5	26,2	27,0	27,8	28,7	29,7	30,7	31,6	33,2	34,4	36,1	37,2
450	28,3	28,8	29,3	30,0	30,6	31,3	32,0	32,8	33,6	34,4	35,3	36,3	37,1	38,2
500	32,5	33,0	33,5	34,0	34,5	35,1	35,8	36,4	36,9	37,7	38,3	38,4	39,8	40,6
550	36,6	37,1	37,6	38,0	38,5	39,0	39,6	40,1	40,7	41,2	41,7	42,3	43,1	43,6
600	40,7	41,1	41,5	41,9	42,4	42,8	43,3	43,8	44,3	44,8	45,4	45,9	46,3	46,9
650	44,5	44,9	45,2	45,6	46,0	46,4	46,8	47,3	47,7	48,2	48,6	49,1	49,5	49,9
700	48,1	48,4	48,8	49,2	49,5	49,8	50,3	50,7	51,1	51,4	51,7	52,3	52,7	53,2
750	51,7	52,1	52,4	52,7	53,0	53,4	53,7	54,1	54,4	54,8	55,2	55,5	55,9	56,4
800	55,1	55,4	55,7	56,0	56,3	56,6	57,0	57,3	57,6	58,0	58,2	58,6	59,1	59,3
850	58,5	58,8	59,1	59,3	59,6	59,8	60,1	60,4	60,7	61,0	61,4	61,7	62,1	62,4
900	61,8	62,0	62,2	62,5	62,8	63,0	63,3	63,5	63,8	64,1	64,2	64,4	64,9	65,3
950	65,0	65,2	65,4	65,6	65,8	66,0	66,3	66,6	66,9	67,2	67,4	67,8	68,1	68,4
1000	68,2	68,4	68,6	68,7	68,8	68,9	69,2	69,4	69,7	70,0	70,2	70,5	70,9	71,2
1100	74,3	74,6	74,8	75,0	75,2	75,3	75,5	75,8	76,0	76,2	76,5	76,7	76,9	77,2
1200	80,3	80,5	80,7	80,8	81,0	81,2	81,4	81,6	81,8	82,0	82,2	82,4	82,6	82,8
1300	86,2	86,4	86,6	86,7	86,9	87,0	87,2	87,4	87,5	87,7	87,9	88,1	88,3	88,5
1400	92,1	92,3	92,5	92,6	92,8	92,9	93,0	93,2	93,4	93,5	93,7	93,9	94,1	94,4

Table 34 (Cont'd.).

T, °K	$\lambda \cdot 10^3$ , W/(m·deg), with p, bar														
	110	150	160	170	180	190	200	250	300	350	400	450	500	550	600
220	190	191	192	193	194	195	196	198	203	206	208	211	215	218	221
230	175	176	177	178	179	180	182	185	189	193	196	200	203	206	209
240	162	163	164	165	166	167	168	172	176	181	185	189	192	196	200
250	150	151	152	153	154	155	156	160	164	169	173	177	181	185	189
260	137	138	139	140	142	143	144	149	154	158	162	166	170	174	178
270	127	128	130	131	132	133	134	139	144	148	152	156	160	164	168
280	118	119	120	121	123	124	125	129	134	139	143	147	151	155	159
290	107	109	110	112	113	114	115	120	125	130	134	138	142	146	150
300	99	101	102	103	105	107	108	114	119	123	128	132	136	139	142
310	—	91	93	95	97	99	100	106	111	116	120	124	128	132	136
320	73,5	—	—	—	—	—	92	99	107	111	114	118	122	126	130
330	61,2	66,2	70,4	73,4	76,2	—	—	—	—	—	—	—	—	—	—
340	52,3	56,7	64,5	68,1	70,9	75,9	—	—	—	—	—	—	—	—	—
350	46,7	50,3	54,2	57,0	60,4	63,6	66,6	77,6	—	—	—	—	—	—	—
360	43,4	46,4	49,6	52,6	55,6	58,4	60,6	72,4	—	—	—	—	—	—	—
370	41,4	44,0	46,6	48,4	51,8	54,4	56,9	67,6	76,2	—	—	—	—	—	—
380	40,4	42,4	44,6	46,9	49,3	51,5	53,6	63,7	72,4	79,0	—	—	—	—	—
390	39,8	41,6	43,4	45,6	47,4	49,2	51,3	60,1	74,7	75,6	81,5	—	—	—	—
400	38,6	40,9	42,5	44,2	46,0	48,3	49,5	58,1	65,4	62,9	78,5	—	—	—	—
450	39,4	40,5	41,3	42,5	43,4	45,3	46,2	52,2	57,9	63,3	68,3	72,9	77,7	80,9	85,1
500	41,4	42,2	43,2	44,3	45,1	46,0	46,9	51,3	55,9	60,2	64,5	68,3	71,8	75,1	78,7
550	44,3	45,0	45,6	46,4	47,1	47,9	48,6	52,5	56,3	59,7	63,2	66,5	69,8	72,9	75,6
600	47,4	48,1	48,5	49,2	49,7	50,4	51,1	54,3	57,7	60,7	63,6	66,6	69,4	72,1	74,7
650	50,5	50,9	51,4	52,0	52,4	53,1	53,8	56,4	59,4	62,1	64,7	67,3	69,8	72,3	73,5
700	53,7	54,0	54,5	55,0	55,4	55,8	56,3	58,4	61,4	64,0	66,4	68,7	71,0	73,3	75,4
750	56,7	57,2	57,6	58,0	58,4	58,8	59,2	61,4	63,8	66,1	68,5	70,6	72,8	74,4	76,6
800	59,8	60,2	60,5	60,9	61,2	61,9	62,3	64,0	66,0	68,2	70,4	72,2	74,2	76,0	77,9
850	62,8	63,2	63,6	63,9	64,2	64,6	64,9	66,7	68,8	70,6	72,6	74,5	76,7	77,8	79,5
900	65,8	66,0	66,4	66,8	67,2	67,6	67,9	69,4	71,2	72,9	74,7	76,6	78,5	79,8	81,4
950	68,7	69,0	69,3	69,6	69,9	70,2	70,5	72,0	73,6	75,3	77,0	78,7	80,4	81,8	83,4
1000	71,5	71,9	72,2	72,4	72,7	73,0	73,3	74,9	76,4	77,9	79,3	80,8	82,6	83,8	85,5
1100	77,4	77,7	78,0	78,2	78,5	78,8	79,1	80,1	81,2	83,1	84,3	85,8	87,4	88,6	89,8
1200	83,0	83,3	83,5	83,7	84,0	84,3	84,6	85,7	86,8	88,1	89,3	90,7	92,0	93,1	94,4
1300	88,7	88,9	89,2	89,4	89,6	89,8	90,1	91,2	92,3	93,4	94,3	95,4	96,3	97,4	98,3
1400	94,6	94,8	95,0	95,2	95,4	95,6	95,8	96,8	97,9	99,1	100	101	102	103	104

Table 35 shows the data of the thermal conductivity on the absorption line.

In conformance with the errors of determining  $\lambda_{\text{atm}}$  and  $\Delta\lambda$  the error of the recommended tabulated data at elevated pressures amounts to 3.5% for the temperature interval of 220-400°K, 4% for 400-800°K, and 5% for 800-1400°K.

Table 35. Recommended values of the thermal conductivity of liquid carbon dioxide on the absorption line.

$T, ^\circ K$	$\lambda \cdot 10^3$ вт/(м · град)	$T, ^\circ K$	$\lambda \cdot 10^3$ вт/(м · град)	$T, ^\circ K$	$\lambda \cdot 10^3$ вт/(м · град)
218	179	248	137	273	109
223	172	253	131	278	104
228	163	258	125	283	99,2
233	156	263	120	288	93,3
238	149	268	115	293	86,2
243	142				

Designation:  $\text{вт}/(\text{м} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ .

#### Ammonia

The thermal conductivity of ammonia at atmospheric pressure has been studied in a relatively narrow temperature range (200-770°K). The most widely investigated range, as follows from Table 36 and Fig. 34, is the interval 300-600°K. There is good correspondence between the data of various investigators only in the interval 300-400°K, where the greatest divergence does not exceed 2.5%. In proportion to the rise in temperature (see Fig. 34) the thermal conductivity curve stratifies into two branches; on the upper are the data of Keyes [105], Ziebland and Needham [150], and on the lower are those of Schäfer and Geier [25], I. F. Golubev, M. V. Kal'sina [117], and Frank [22]. The maximum divergence between the extremes reaches as high as 8% at high temperatures.

The averaging curve in the low temperature region passes through the data of Eucken [83], and in the temperature interval of 300-400°K — through the middle of the entire mass of points, and in the region of higher temperatures a certain preference was given to the more carefully

Table 36. Investigation of the thermal conductivity of ammonia.

Author	Year	Liter- ature source	Method	Temperature, °K	Pressure, bar
Eucken	1913	[83]	Heated filament	216-273	1
Dikins	1934	[103]	"	273	1
Sellshopp	1934	[138]	Coaxial cylinders	293-373	On the saturation line
Frank	1951	[22]	Heated filament	273-583	1
Kaller, Rob	1955	[49]	"	273	1
Keyes	1956	[105]	Coaxial cylinders	323-523	1-9
Geler, Schäfer	1961	[25]	Heated filament	273-773	1
Golubev, Kal'sina	1964	[117]	Regular regime, first-class bicalorimeter	212-673	1-395
Ziebland, Needham	1962 1965	[150]	Coaxial cylinders	293-450	1-475
Strivastava, Bupta	1966	[93]	Heated filament	353-393	1

carried out measurements of Keyes [105], Ziebland and Needham [150]. On the basis of the averaging-curve a table was compiled for the values of the thermal conductivity of ammonia at atmospheric pressure in the interval  $T = 200-600^\circ\text{K}$  (Table 37). The error of the recommended values amounts to 2% for the interval  $T = 200-400^\circ\text{K}$  and 3% - for  $400-600^\circ\text{K}$ .

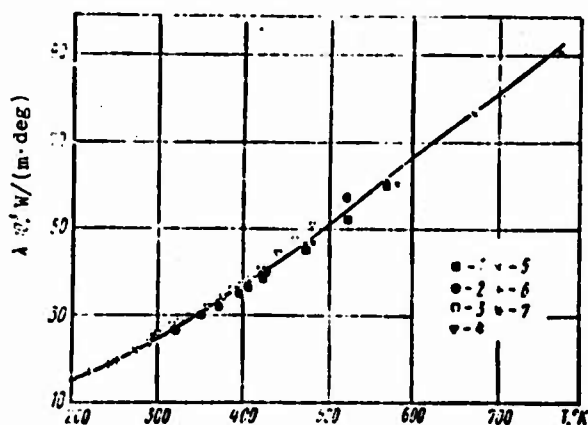


Fig. 34. The dependence of the thermal conductivity of ammonia on the temperature with pressure  $p = 1$  bar according to the data of: 1 - Golubev, Kal'sina [117]; 2 - Keyes [105]; 3 - Strivastava, Gupta [93]; 4 - Ziebland, Needham [150]; 5 - Schäfer, Geier [25]; 6 - Eucken [83]; 7 - Frank [22].

The thermal conductivity of ammonia at elevated pressures was studied by Ziebland, Needham [150] and I. F. Golubev, N. V. Kal'sina [117] in a broad range of temperatures and pressures. These data at the coordinates of excess thermal conductivity-density are presented in Fig. 35. Points referring to the critical region, on the basis of the general assumptions mentioned in the introduction, were not put on the graph.

On the whole, the results of works [117, 150] are in completely satisfactory agreement with one another, which has allowed us to plot the averaging curve with sufficient reliability. On the basis of this curve and the data of Table 37 at atmospheric pressure Table 38 was compiled for the dependence of the thermal conductivity on temperature and pressure in the range  $T = 300-600^\circ\text{K}$  and  $p = 1-600$  bar. Table 38 does not include the data for the critical region,

i.e., for temperatures of 365-465°K in densities of 0.14-0.33 g/cm<sup>3</sup>. The error of the recommended values amounts to 3% with T up to 400°K and 4% - up to 600°K for the entire pressure interval.

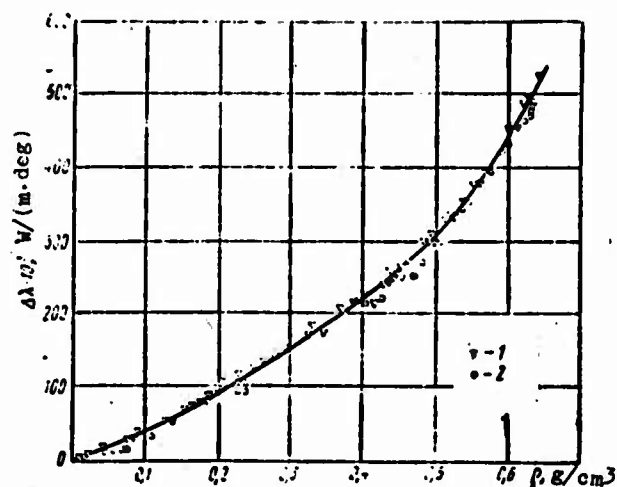


Fig. 35. Dependence of the excess thermal conductivity of ammonia on the density according to the data of: 1 - Ziebland, Needham [150]; 2 - Golubev, Kal'sina [117].

On the basis of the curve  $\Delta\lambda = f(\rho)$  and the data of Table 37 the thermal conductivity of liquid ammonia on the saturation line was obtained (Table 39).

Table 37. Recommended values of the thermal conductivity of gaseous ammonia at atmospheric pressure.

T, °K	$\lambda \cdot 10^3$ , вт/(м · град)	T, °K	$\lambda \cdot 10^3$ , вт/(м · град)	T, °K	$\lambda \cdot 10^3$ , вт/(м · град)
200	13,3	270	21,6	340	29,3
210	16,2	280	22,6	350	30,4
220	17,0	290	23,6	400	37,0
230	17,8	300	24,7	450	44,0
240	18,6	310	26,0	500	52,5
250	19,6	320	27,2	550	59,4
260	20,6	330	28,2	600	67,0

Designation: вт/(м · град) = W/(m · deg).

Table 38. Recommended values of the thermal conductivity of gaseous and liquid ammonia as a function of temperature and pressure.

T, °K	(1) $\lambda \cdot 10^3, \text{ст/}(m \cdot \text{град})$ , при p, бар										
	1	10	20	30	40	50	60	70	80	90	100
300	24,7	30,0	474	476	478	480	482	484	485	486	488
310	26,0	30,6	454	457	458	462	464	466	466	469	470
320	27,2	31,0	434	435	437	440	442	444	445	448	450
330	28,2	31,6	36,0	408	416	417	418	420	423	425	427
340	29,3	32,2	36,1	41,0	390	393	397	398	400	402	404
350	30,4	33,1	36,3	40,5	367	368	370	372	375	377	381
360	31,6	34,0	36,5	40,0	45,0	340	343	346	348	352	354
370	32,8	34,7	36,7	40,2	44,4	51,0	315	318	321	325	328
380	34,0	35,4	37,4	40,8	44,0	50,0	58,0	67,4	293	297	302
390	35,2	37,0	39,0	42,5	44,4	50,0	56,2	63,4	76,3	262	273
400	37,0	38,4	41,1	43,3	44,8	49,5	54,3	61,2	70,4	83,0	110
420	40,4	41,2	42,9	44,1	47,0	49,3	52,4	55,9	61,2	66,9	75,1
440	43,5	44,1	45,3	46,2	48,4	49,1	50,8	53,8	57,2	61,4	65,2
460	46,3	47,3	48,2	49,0	49,8	51,6	52,6	55,3	57,4	60,5	63,0
480	49,2	50,1	50,9	51,9	53,0	54,1	55,2	56,0	58,2	60,8	62,5
500	52,5	54,5	55,4	56,2	56,9	57,8	58,6	59,4	60,2	61,1	63,3
550	59,4	63,3	64,1	64,9	65,8	67,2	67,4	68,2	67,1	68,9	69,7
600	67,0	71,2	72,1	73,0	73,8	74,4	75,2	75,9	76,6	77,4	78,2

KEY: (1)  $\lambda \cdot 10^3$ , W/(m·deg), with p, bar.



Table 38 (Cont'd.).

T, K	(1) $\lambda \cdot 10^3$ , $\text{вт/(м} \cdot \text{град)}$ , при p, бар									
	130	200	250	300	350	400	450	500	550	600
300	493	500	506	513	520	527	534	540	546	553
310	477	484	490	496	502	509	515	521	527	533
320	456	463	470	477	484	491	498	505	509	514
330	436	444	452	459	466	473	479	484	493	498
340	416	423	430	438	447	454	461	468	474	480
350	391	402	411	419	427	435	442	449	455	461
360	367	379	388	398	408	418	424	431	438	445
370	345	357	370	380	388	398	406	414	422	427
380	320	335	348	359	370	380	388	395	403	410
390	296	314	327	340	352	362	370	377	384	391
400	269	292	307	321	334	344	352	360	368	374
420	—	244	265	282	295	308	319	328	338	345
440	—	183	219	240	258	273	286	298	310	320
460	84,5	133	173	199	220	238	256	273	286	296
480	76,4	97,3	127	162	182	204	228	252	263	273
500	73,2	94,5	123	156	179	203	222	240	202	263
550	71,6	85,4	105	128	149	166	186	204	216	228
600	79,0	79,8	82,1	91,2	110	134	151	168	178	187

KEY: (1)  $\lambda \cdot 10^3$ ,  $\text{W/(m} \cdot \text{deg)}$ , with p, bar.

Table 39. Recommended values of the thermal conductivity of liquid ammonia on the absorption line.

T, °K	$\lambda \cdot 10^3$ , $\text{вт/(м} \cdot \text{град)}$	T, °K	$\lambda \cdot 10^3$ , $\text{вт/(м} \cdot \text{град)}$	T, °K	$\lambda \cdot 10^3$ , $\text{вт/(м} \cdot \text{град)}$
300	470	330	403	360	335
305	457	335	391	365	325
310	445	340	379	370	315
315	435	345	369	375	305
320	424	350	356	380	289
325	413	355	345		

Designation:  $\text{вт/(м} \cdot \text{град)} = \text{W/(m} \cdot \text{deg)}$ .

## Vapors of Hydrocarbons of the Methane Series at Atmospheric Pressure

An examination of the thermal conductivity of the entire group of substances, referred to as n-alkanes, is explained by the possibilities of generalizing the experimental data in the use of the method of corresponding states. As can be seen from Table 40, the most detailed study at atmospheric pressure has been made for the lower members of the series — through the octanes, inclusively. There is especially a lot of data for methane, where experiments have been conducted in a wide temperature range from  $-180$  to  $700^{\circ}\text{C}$ . In the investigation of n-alkanes both stationary methods (heated filament, coaxial cylinders, and concentration spheres), as well as the stationary method of a regular regime (a variant of the method of coaxial cylinders) have been employed. In the majority of works the thermal conductivity was determined relatively, by means of a comparison with the thermal conductivity of sample gases, such as air, argon, nitrogen, carbon dioxide, etc.

Let us examine the basic works, where experimental data on the thermal conductivity of n-alkanes (several substances) in a wide temperature range were obtained.

Geier and Schäfer [25] using the heated filament method measured the thermal conductivity of ten gases, including methane and ethane, and three mixtures in a wide range of temperatures at pressures below atmospheric. One should note that according to the data of [25] the temperature pattern for the majority of gases (especially the light gases, as for example nitrogen) obtained was somewhat low. As was demonstrated in work [30], the understatement of results in [25] was caused by the incorrect consideration of the temperature jump. The absence of essential primary data for methane and ethane, unfortunately, does not allow us to introduce the corresponding corrections, as was done for nitrogen [30].

Table 40. Investigation of the thermal conductivity of the vapors of hydrocarbons of the methane series at atmospheric pressure.

Author	Year	Literature source	Method	Temperature, °C
<u>Investigation of methane CH<sub>4</sub></u>				
Eucken	1913	[83]	Heated filament	-182.6-9
Mann, Dickins	1931	[151]	" "	2-10
Johnston, Grilly	1946	[85]	" "	-176-110
Stolyarov, et al.	1950	[116]	" "	23-212
Lenoir, Commings	1951	[152]	Coaxial cylinder	41.1; 56.7
Schottky	1952	[24]	Heated filament	100-500
Lenoir et al.	1953	[153]	Coaxial cylinder	52.7
Vines	1953	[154]	Heated filament	109.4
Keyes	1954	[105]	Coaxial cylinder	50-300
	1955	[105]	" "	-152.7-300
Lambert, et al.	1955	[155]	Heated filament	66
Smith, et al.	1960	[156]	Coaxial cylinder	50-150
Geier, Schäfer	1961	[25]	Heated filament	0-700
Cheung, et al.	1962	[157]	Coaxial cylinder	98-537
Golubev	1963	[68]	Coaxial Cylinder (regular regime)	-77-235
Senftleben	1964	[158]	Heated filament variant	25-200
Carmichael, et al.	1966	[159]	Concentric spheres	4.5-171
Misic, Thodos	1966	[160]	Heated filament	1.9-43.6
Sokolova, Golubev	1967	[161]	Coaxial cylinders (regular regime)	-160-34.5
<u>Investigation of ethane C<sub>2</sub>H<sub>6</sub></u>				
Eucken	1913	[83]	Heated filament	-70.4-9
Mann, Dickins	1935	[151]	" "	2-10
Lenoir, et al.	1953	[153]	Coaxial cylinder	41.1-57.2
Keyes	1954	[105]	Coaxial cylinder	51.0-249
Vines, Bennett	1954	[162]	Heated filament	101-149
Lambert, et al.	1955	[155]	" "	66
Geier, Schäfer	1961	[25]	" "	0-600
Leng, Commings	1957	[163]	Coaxial cylinder	67.8

Table 40. (Cont'd.).

Author	Year	Literature source	Method	Temperature, °C
Carmichael, et al.	1963	[164]	Coaxial cylinder	4.4-171
Senftleben	1964	[158]	Heated filament variant	25-200
Gilmore, Comings	1956	[148]	Coaxial cylinder	75

Investigation of propane C<sub>3</sub>H<sub>8</sub>

Mann, Dickins	1931	[151]	Heated filament	2-10
Vines, Bennett	1954	[162]	" "	101-149
Lambert, et al.	1955	[155]	" "	66
Leng, Comings	1957	[163]	Coaxial cylinder	50-140
Smith, et al.	1960	[156]	" "	50-150
Cheung, et al.	1962	[157]	" "	100-537
Senftleben	1964	[158]	Heated filament variant	25-200

Investigation of n-butane C<sub>4</sub>H<sub>10</sub>

Mann, Dickins	1931	[151]	Heated filament	2-10
Smith, et al.	1960	[156]	Coaxial cylinder	50-150
Lambert, et al.	1955	[155]	Heated filament	66
Vilim	1960	[165]	" "	24
Krammer, Comings	1960	[166]	Coaxial cylinder	75.3-60
Senftleben	1964	[158]	Heated filament variant	25-200

Investigation of n-pentane C<sub>5</sub>H<sub>12</sub>

Moser	1913	[167]	Heated filament	0-20
Mann, Dickins	1931	[151]	" "	2-10
Lambert, et al.	1955	[155]	" "	66
Smith, et al.	1960	[156]	Coaxial cylinder	50-150

Table 40 (Cont'd.).

Author	Year	Liter- ature source	Method	Temper- ature, °C
<u>Investigation of n-hexane <math>C_6H_{14}</math></u>				
Moser	1913	[167]	Heated filament	0-20
Lambert, et al.	1950	[141]	" "	66.85
Vines	1953	[154]	" "	75-110
Vines, Bennett	1954	[162]	" "	126-149
Lambert, et al.	1955	[155]	" "	66
Golubev, Naziyev	1961	[69]	Coaxial cylinder (regular regime)	22-359.4
<u>Investigation of n-heptane <math>C_7H_{16}</math></u>				
Moser	1913	[167]	Heated filament	100
Lambert, et al.	1950	[141]	" "	82
Golubev, Naziyev	1961	[69]	Coaxial cylinder (regular regime)	23-361
Zaytseva	1961	[168]	Heated filament	117-249
Carmichael, Sage	1966	[169]	Concentric spheres	37.7; 71
Tarzhimov, Mashirov	1967	[170]	Heated filament	95-419
<u>Investigation of n-octane <math>C_8H_{18}</math></u>				
Lambert, et al.	1950	[141]	Heated filament	82
Golubev, Naziyev	1961	[69]	Coaxial cylinder (regular regime)	23-360
Carmichael, Sage	1966	[169]	Concentric spheres	37.7; 71
<u>Investigation of n-decane <math>C_{10}H_{22}</math></u>				
Carmichael, Sage	1967	[171]	Concentric spheres	104.5-171
<u>Investigation of n-undecane <math>C_{11}H_{24}</math></u>				
Tarzhimov, Mashirov	1967	[170]	Heated filament	224-420
<u>Investigation of n-tetradecane <math>C_{14}H_{30}</math></u>				
Tarzhimov, Mashirov	1967	[170]	Heated filament	276-481

Table 40 (Cont'd.).

Author	Year	Liter- ature source	Method	Temper- ature, °C
<u>Investigation of n-hexadecane <math>C_{16}H_{34}</math></u>				
Tarziminov, Mashirov	1967	[170]	Heated filament	311-425
<u>Investigation of n-octadecane <math>C_{18}H_{38}</math></u>				
Tarziminov, Mashirov	1967	[170]	Heated filament	334-394

I. F. Golubev and Ya. M. Naziyev [69], using the regular regime method, determined the thermal conductivity of n-hexane, n-heptane, and n-octane in a wide pressure range with temperatures up to 633°K. A comparison of the results on n-heptane [69] with the data of other authors [168, 170] with  $p = 1$  bar shows rather good correspondence at 100°C and a noticeable divergence in proportion to the increase in temperature (the data of I. F. Golubev and Ya. M. Naziyev are characterized by a weaker temperature dependence of the coefficient of thermal conductivity).

Senftleben [158], using the heated filament method, measured the thermal conductivity of around 30 substances, including methane, ethane, propane and n-butane, in the gaseous state with  $T = 25-200^\circ\text{C}$ . The apparatus was calibrated only for one substance - carbon dioxide. Here for  $\text{CO}_2$  the values of the coefficient of thermal conductivity, taken from work [172] which differ somewhat from the data of Table 33, were used. The divergence between them at  $t = 200^\circ\text{C}$  amounts to approximately 3%. Correspondingly, we also checked the results of the experiments of Senftleben. We considered it possible to use the data of Senftleben, since the thermal conductivity of the vapors of the n-alkanes differs relatively little from the thermal conductivity of  $\text{CO}_2$ .

Recently A. A. Tarziminov and V. Ye. Mashirov published data on thermal conductivity of vapors of the n-alkanes - from heptane to octadecane - at temperatures up to 450°C [170], obtained by the heated filament method. As can be seen from Table 40, for the above n-alkanes [170] there is only one research work. In generalizing we did not use these experimental data for the above alkane at high temperatures  $t > 370^\circ\text{C}$ , for which noticeable thermal decomposition was observed (in work [170] these points were noted).

In work [170] for the generalization of the experimental data on the thermal conductivity of the n-alkanes in a broad range of measurement of the molecular weights the method of corresponding states was employed. Its utilization enabled us to reciprocally connect the values of the thermal conductivity of various substances of one homologous series. This also facilitated the analysis of the temperature dependence of the thermal conductivity of substances, determined by different authors.

In connection with the fact that the generalization of [170] was made on the basis of a compilation of the tables of recommended data of the thermal conductivity of vapors of the n-alkanes at atmospheric pressure, let us introduce the fundamental aspects of this generalization.

The existing experimental data of various authors (see Table 40) were shown in the introduced coordinates  $\lambda/\lambda_{\tau=0.8} - \tau$ , where  $\tau = T/T_{17}$ ;  $\lambda_{\tau=0.8}$  - the thermal conductivity of the compounds of this series with  $\tau = 0.8$  (the value of  $\tau$  was selected in such a way that all the investigated substances were taken into consideration).

As can be seen from Fig. 36, where the results of processing are shown at the cited coordinates, the experimental points for the n-alkanes from ethane to n-octadecane (molecular weight  $M$  from 30 to 254) fall together rather well into a single curve, which can be described by the equation

$$\lambda/\lambda_{\tau=0.8} = -0.441 + 1.100\tau + 0.924\tau^2 - 0.0456\tau^3, \quad (61)$$

which is correct in the range  $\tau = 0.6-2.2$ .

A comparison of the experimental data  $\lambda_{\text{excn}}$  with the calculated data according to equation (61)  $\lambda_{\text{pacc}}$  shows (Fig. 37) that for the overwhelming majority of points the divergences  $\delta = \frac{\lambda_{\text{excn}} - \lambda_{\text{pacc}}}{\lambda_{\text{pacc}}}$  do not exceed 2-3%. The divergences here do not have a systematic character, i.e., the data on the thermal conductivity of the n-alkanes (with the exception of methane) are in completely satisfactory agreement with the law of corresponding states. Methane is an exception, since a molecule of it in contrast to molecules of other members of the series is rather symmetrical, compact, and possesses relatively low energy of rotation and vibration. The analogical behavior of methane was pointed out with generalizations in a number of works, for example, [173].

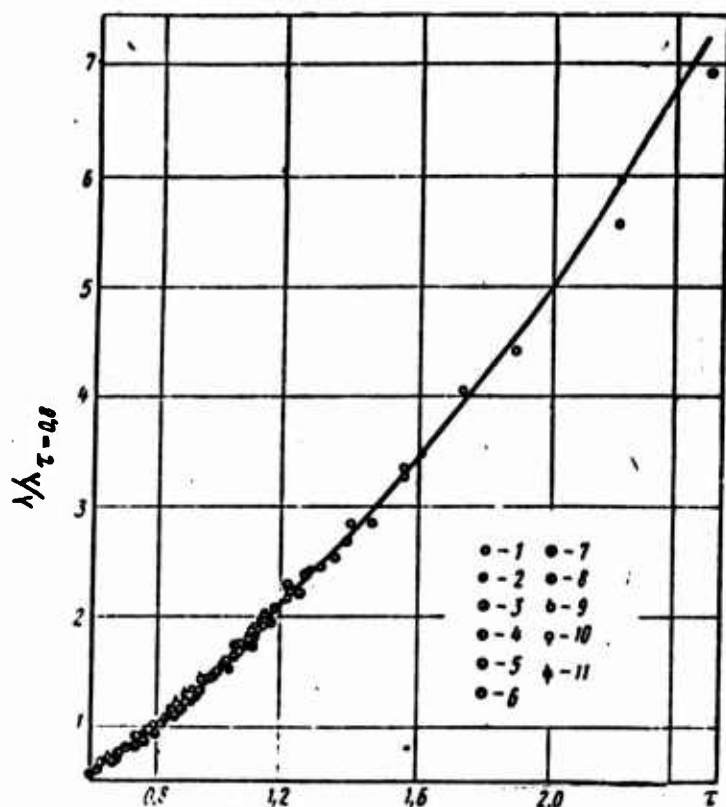


Fig. 36. Dependence of the thermal conductivity of vapors of the n-alkanes on temperature in the cited coordinates:

1 -  $C_2H_6$ ; 2 -  $C_3H_8$ ; 3 -  $C_4H_{10}$ ; 4 -  $C_5H_{12}$ ; 5 -  $C_6H_{14}$ ; 6 -  $C_7H_{16}$ ; 7 -  $C_8H_{18}$ ;  
8 -  $C_{11}H_{24}$ ; 9 -  $C_{14}H_{30}$ ; 10 -  $C_{16}H_{34}$ ; 11 -  $C_{18}H_{38}$



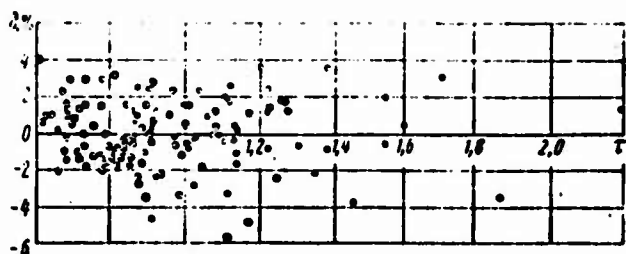


Fig. 37. Deviation of experimental data on the thermal conductivity of vapors of the n-alkanes from data calculated according to equation (61); designations are the same as in Fig. 36.

Figure 38 shows the dependence of  $\lambda_{\tau=0.8}$  on the molecular weight, from which it is clear that when  $\tau = \text{const}$  in proportion to the increase in the molecular weight the thermal conductivity of vapors of the n-alkanes increases and with  $M > 160$  tends toward a constant value equal to  $2.8 \times 10^{-2} \text{ W/(m}\cdot\text{deg)}$  when  $\tau = 0.8$ . We have used Fig. 36 to describe the interrelationships of the data within this series. In this case methane is an exception.

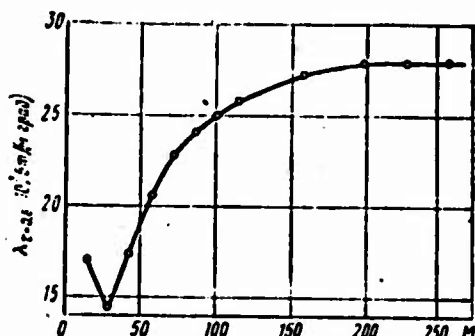


Fig. 38. The dependence of  $\lambda_{\tau=0.8}$  on the molecular weight. Designation:  $\lambda_{\tau}/(\text{m}\cdot\text{град}) = \text{W}/(\text{m}\cdot\text{deg})$ .

The results of the calculations of the thermal conductivity of n-alkane vapors from ethane to octane at various temperatures and at atmospheric pressure according to equation (61) are shown in Table 41.

Table 41. Recommended values of the thermal conductivity of vapors of normal alkanes at atmospheric pressure.

t, °C	$\lambda \cdot 10^3, \text{ вт/(м} \cdot \text{град)} \text{ (1)}$							
	(2) метана	(3) этана	(4) пропана	(5) бутана	(6) пентана	(7) гексана	(8) гептана	(9) октана
180	10,0	—	—	—	—	—	—	—
160	12,2	—	—	—	—	—	—	—
140	14,4	—	—	—	—	—	—	—
120	16,6	—	—	—	—	—	—	—
100	18,7	—	—	—	—	—	—	—
80	20,9	—	—	—	—	—	—	—
60	23,2	—	—	—	—	—	—	—
40	25,5	13,8	—	—	—	—	—	—
20	27,9	15,7	12,8	—	—	—	—	—
0	30,4	18,0	15,0	13,1	—	—	—	—
20	33,2	20,6	17,3	15,3	—	—	—	—
40	36,0	23,2	19,7	17,6	15,8	—	—	—
60	38,9	25,9	22,2	19,9	18,0	—	—	—
80	41,9	28,8	24,7	22,4	20,3	18,3	—	—
100	45,0	31,7	27,4	24,9	22,7	20,5	18,8	—
120	48,2	34,7	30,1	27,4	25,1	22,8	20,9	—
140	51,5	37,8	32,9	30,1	27,6	25,1	23,2	21,4
160	54,9	41,0	35,7	32,8	30,2	27,5	25,5	23,6
180	58,4	44,3	38,7	35,6	33,8	30,0	27,8	25,8
200	62,0	47,7	41,7	38,4	36,5	32,5	30,2	28,0
220	65,5	51,1	44,8	—	—	35,1	32,6	30,4
240	69,1	54,7	48,0	—	—	37,8	35,1	32,8
260	72,7	58,4	51,2	—	—	40,5	37,7	35,2
280	76,3	62,1	54,5	—	—	43,2	40,3	37,7
300	80,1	65,9	57,9	—	—	46,1	43,0	40,2
320	83,9	—	61,3	—	—	49,0	45,7	42,8
350	89,5	—	66,8	—	—	53,4	49,9	46,7
400	99,2	—	76,0	—	—	61,1	57,2	53,6
450	—	—	85,7	—	—	69,1	—	—
500	—	—	95,8	—	—	—	—	—
550	—	—	106,4	—	—	—	—	—

KEY: (1) W/(m·deg); (2) methane; (3) ethane; (4) propane; (5) butane; (6)pentane; (7) hexane; (8) heptane; (9) octane.

Fig. 39. Thermal conductivity of ethane vapors a) and the divergence of experimental values of various authors from the recommended ones b): 1 - Eucken [83], 2 - Mann, Dickins [151]; 3 - Lenoir, et al. [153]; 4 - Keyes [105]; 5 - Vines, Bennett [154]; 6 - Lambert, et al. [155]; 7 - Geier, Schäfer [25]; 8 - Leng, Commings [163]; 9 - Carmichael, et al. [164]; 10 - Senftleben [158].

Designation: вт/(м·град) = W/(m·deg).

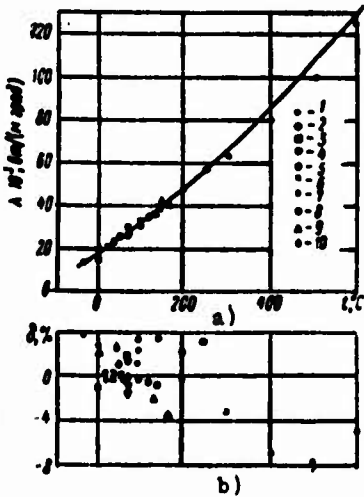
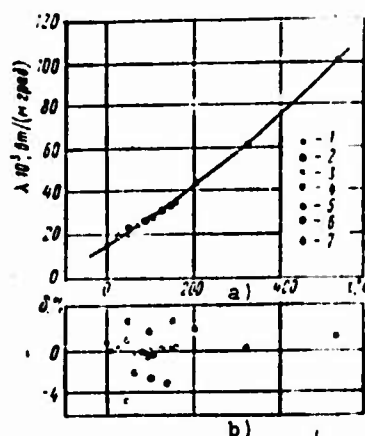


Fig. 40. Thermal conductivity of propane  
a) and the divergences of experimental  
values from the recommended ones b):  
1 - Mann, Dickins; 2 - Vines, Bennett [162];  
3 - Lambert, et al. [155]; 4 - Leng,  
Commins [163]; 5 - Smith, et al. [156];  
6 - Cheung, et al. [157]; 7 - Senftleben  
[158].

Designation:  $\lambda_T/(m \cdot \text{град}) = W/(m \cdot \text{deg})$ .



The limitation of the series by octane can be explained by the fact that the thermal conductivity of the n-alkanes has been most completely studied by different authors for members of the series up to  $n = 8$ , inclusively. Here the use of the value  $\lambda_{T=0.8} \cdot 10^3$  amounts to 144 - for  $C_2H_6$ ; 175 - for  $C_3H_8$ ; 206 - for  $C_4H_{10}$ ; 228 - for  $C_5H_{12}$ ; 241 - for  $C_6H_{14}$ ; 251 - for  $C_7H_{16}$ ; 258 - for  $C_8H_{18}$ ; they are also shown in Fig. 38.

Figures 39-45 show a comparison of the experimental values of the thermal conductivity, obtained by various authors on each substance individually, with values calculated according to equation (61) and, similarly, with values cited in Table 41. The possible error of the tabulated values of the thermal conductivity amounts to 2% with  $t \leq 200^\circ C$  and 3% with  $t > 200^\circ C$ . As can be seen from the graphs, the overwhelming majority of points fall within the tolerance limits. Only the data of Geier and Schäfer [25] diverge significantly for ethane at high temperatures. The above is mentioned concerning the possible reasons for the errors in [25]. Because of this, the table of values of the thermal conductivity of ethane compiled only up to  $t = 300^\circ C$ . At higher temperatures additional investigations for ethane would be desirable.

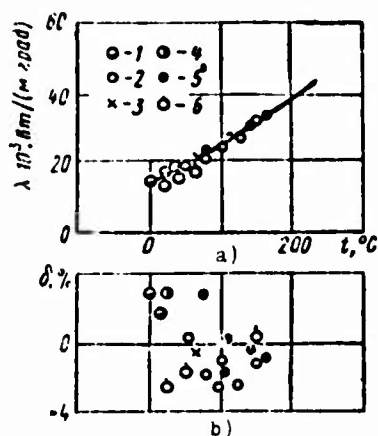
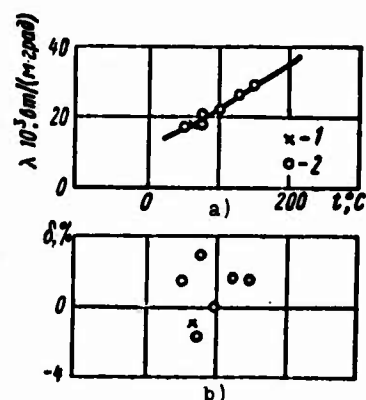


Fig. 41. The thermal conductivity of n-butane a) and divergences of the experimental values of various authors from the recommended ones b): 1 - Mann, Dickins [151]; 2 - Smith, et al. [156]; 3 - Lambert, et al. [155]; 4 - Vilim [165]; 5 - Krammer, Commings [166]; 6 - Senftleben [158].

Designation:  $\text{Вт}/(\text{м}\cdot\text{град}) = \text{W}/(\text{m}\cdot\text{deg})$ .

Fig. 42. Thermal conductivity of n-pentane a) and deviations of the experimental values of various authors from the recommended ones b): 1 - Lambert, et al. [155]; 2 - Smith, et al. [156].

Designation:  $\text{Вт}/(\text{м}\cdot\text{град}) = \text{W}/(\text{m}\cdot\text{deg})$ .



As was already noted above, with the generalization of the results of the experiments with respect to the determination of the thermal conductivity of the n-alkanes at the cited coordinates the data for methane sharply diverge. The experimental data of various authors of the thermal conductivity of methane at  $p = 1$  bar were transferred to the graph at the usual coordinates  $\lambda - T$  and an averaging curve was plotted. A comparison showed that the curve corresponds well with the values recommended by V. P. Sokolova and I. F. Golubev [161]. These values were also adopted in the present article (see Table 41). The results of the investigations of Schottky [24] were not taken into account, since the significant correction for the temperature jump [30] was not introduced in them.

At high temperatures ( $t > 400^\circ\text{C}$ ) for the thermal conductivity of methane there are only the data of Geier and Schäfer [25], which are not reliable enough, and also the singular experimental point at  $t = 537^\circ\text{C}$ , obtained by Chenung, et al. [157], which has turned out to be clearly erroneous. Because of this, in Table 40 the data for methane are included only up to  $t = 400^\circ\text{C}$ . The values of thermal conductivity, recommended in [161] at higher temperatures, should be viewed as tentative, requiring further experimental confirmation.

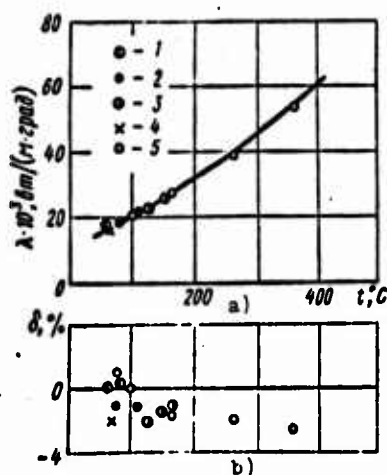


Fig. 43. Thermal conductivity of n-hexane a) and divergences of experimental values of various authors from the recommended ones b): 1 - Lambert, et al. [141]; 2 - Vines [154]; 3 - Vines and Benne [162]; 4 - Lambert, et al. [155]; 5 - Golubev, Naziyev [69].

Designation:  $\text{Вт}/(\text{м} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ .

Fig. 44. Thermal conductivity of n-heptane a) and deviations of the experimental values of various authors from the recommended ones b): 1 - Moser [167]; 2 - Lambert, et al. [155]; 3 - Golubev, Naziyev [69]; 4 - Zaytseva [168]; 5 - Carmichael, Sage [169]; 6 - Tarziminov, Mashirov [170].

Designation:  $\text{Вт}/(\text{м} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ .

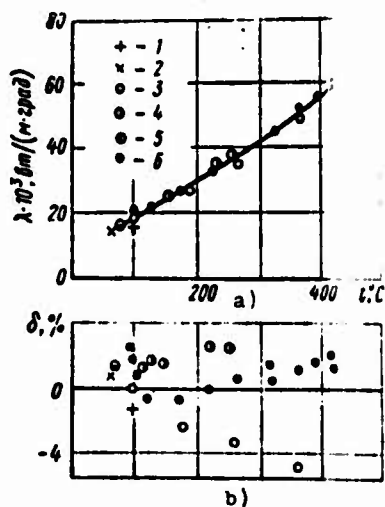


Fig. 45. Thermal conductivity of n-octane a) and divergences of the experimental values of various authors from the recommended ones b): 1 - Lambert, et al. [141]; 2 - Golubev, Naziyev [69]; 3 - Carmichael, Sage [169].

Designation:  $\text{вт}/(\text{м} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ .

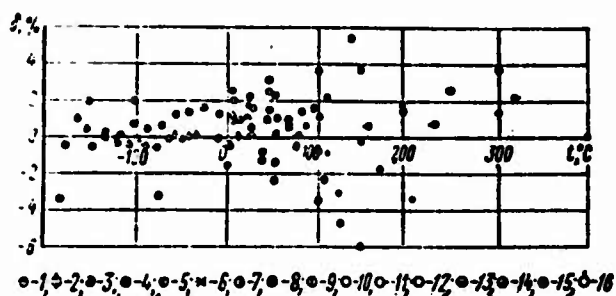
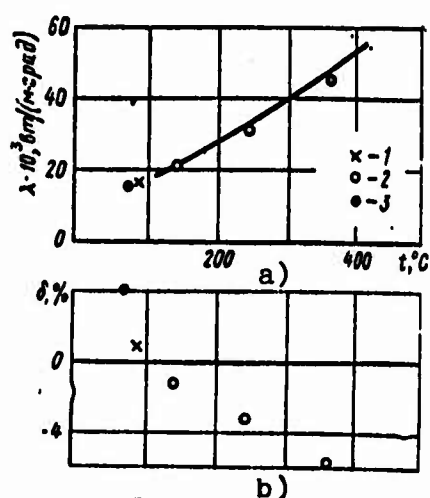


Fig. 46. Divergences of the experimental values of the thermal conductivity of gaseous methane from the recommended ones according to the data of: 1 - Eucken [83]; 2 - Mann, Dickins [151]; 3 - Johnston, Grilly [85]; 4 - Stolyarov, et al. [116]; 5 - Lenoir, et al. [153]; 6 - Vines [60]; 7 - Keyes [105]; 8 - Lambert, et al. [155]; 9 - Smith, et al. [156]; 10 - Geier, Schäfer [25]; 11 - Cheung, et al. [157]; 12 - Golubev [68]; 13 - Senftleben [158]; 14 - Carmichael, et al. [159]; 15 - Misic, Thodos [160]; 16 - Sokolova, Golubev [161].

A comparison of the experimental data of various authors for methane at  $p = 1$  bar with the tabulated values was made in Fig. 46. The possible error of the recommended value amounts to 1.5% at  $t \leq 200^\circ\text{C}$  and 3% at  $t > 200^\circ\text{C}$ .

### Methane

The thermal conductivity of liquid methane has been investigated in three works. Ye. Borovik, A. Matveyev and Ye. Panin [174] in 1940, using the heated filament method, carried out measurements in the

range of  $t = -(100-170)^{\circ}\text{C}$ . In 1963 Ikenberry and Rice [108] and later V. P. Sokolova and I. F. Golubev [161] determined the thermal conductivity of methane in a wide pressure and temperature range [Table 42), including also for the liquid phase. The results close to the saturation line are shown in Fig. 47. For certain points the divergences go as high as  $\approx 10\%$ . Here the results of works [108] and [174] correspond satisfactorily with one another. The values of thermal conductivity of methane according to [161], and also in the investigation of other n-alkanes in the liquid phase by the method of regular regime (cylindrical bicalorimeter) [69], fall somewhat higher than the averaging curve. Divergences of the examined experimental data from it amount to 3.4% on the average.

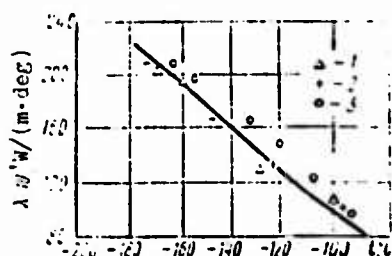


Fig. 47. The thermal conductivity of liquid methane close to the saturation line according to the data of: 1 - Borovik, et al. [174]; 2 - Ikenberry, Rice [108]; 3 - Sokolova, Golubev [161].

From the viewpoint of the dependence of the thermal conductivity of methane on the pressure methane has been examined in most detail among the examined n-alkanes. This can apparently be explained not only by the fact that methane, as the basic part of natural gases, is of the most practical interest, but also by the fact that methane is close in its properties in connection with the compactness and symmetry of its molecules to monoatomic gases and, consequently, is suitable for theoretical examination.

As can be seen from Table 42, the experiments embrace the pressure region from 1 to 600 bar and the temperature region from  $-174$  to  $300^{\circ}\text{C}$ . The greatest number of experimental points was obtained in the works of I. F. Golubev [68], V. P. Sokolova and I. F. Golubev [161].

Table 42. Investigation of the thermal conductivity of methane at elevated pressures.

Author	Year	Literature source	Method	Temperature, °C	Pressure, bar
Stolyarov, Ipat'yev, Teodorovich	1950	[116]	Heated filament	11-212	1-500
Lenoir, Commings	1951	[152]	Coaxial cylinders	41	1-200
Lenoir, Junk, Commings	1953	[153]	The same	53	1-200
Keyes	1954	[105]	The same	50-300 -153-0	1-61 1-3
Pavlovich	1960	[175]	Heated filament	149-73	1-600
Golubev	1963	[68]	Coaxial cylinder (regular regime)	77-235	1-500
Ikenberry, Rice	1963	[108]	Coaxial cylinders	-(38-174)	1-500
Misic, Thodos	1966	[160]	The same	2-75	1-600
Carmichael, Reamer, Sage	1966	[159]	Spherical layers	4-171	1-350
Sokolova, Golubev	1967	[176](sic)	Coaxial cylinder (regular regime)	-(34-164)	1-500



The results of measurements obtained by various authors were processed at coordinates  $\Delta\lambda - f(\rho)$  and are shown in Fig. 48. Data on the density of methane were taken from work [177]. The figure does not contain points referring to the circumcritical region, embracing the temperature interval  $t = -(50-100)^\circ\text{C}$  and the density interval  $\rho = 0.10-0.22 \text{ g/cm}^3$ , in conformance with the criteria set down in the forward.

As can be seen from Fig. 48, the experimental data of various authors are situated around an averaging curve with a scatter, which basically does not exceed 5-6%. Closest of all to the curve are the points of Misic and Thodos [160]. The points of I. F. Golubev [68] generally lie somewhat higher, while those of Ye. A. Stolyarov, et al. [116], and also those of Carmichael [159] are somewhat below the curve.

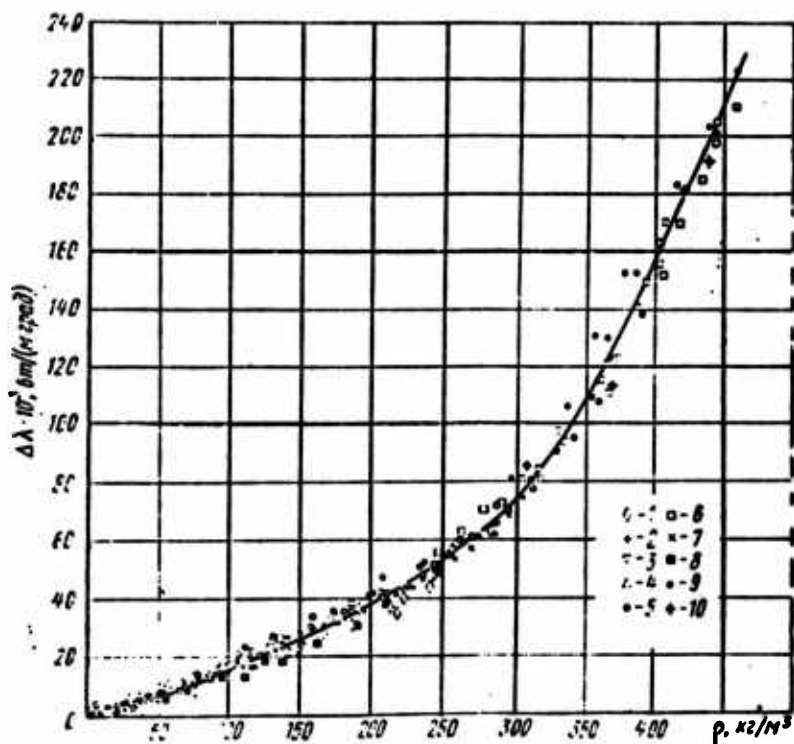


Fig. 48. Dependence of the excess thermal conductivity of methane on the density according to the data of: 1 - Stolyarov, et al. [116]; 2 - Lenoir, Commings [152]; 3 - Lenoir, et al. [153]; 4 - Keyes [105]; 5 - Golubev [68]; 6 - Ikenberry, Rice [108]; 7 - Misic, Thodos [160]; 8 - Carmichael, et al. [159]; 9 - Sokolova, Golubev [161]; 10 - Borovik, et al. [174].

Designations:  $\text{Вт}/(\text{м} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ ;  $\text{кг}/\text{м}^3 = \text{kg}/\text{m}^3$ .

We do not detect any kind of system of stratification at the coordinates  $\Delta\lambda - \rho$ . However, according to the results of [159] one may note that the isotherms of excess thermal conductivity as a function of the density do not fall on a single curve. The higher the temperature, the lower is the isotherm. Stratification in the measured temperature range of 4-171°C (or  $\tau = 1.45-2.32$ ) reaches 4-6% of the value of  $\lambda$ . For other substances with  $\tau > 1.20$  stratification of isotherms is not observed. Therefore, it is difficult to expect the occurrence of this effect with methane at such comparatively high temperatures. Most likely, here one should find some kind of systematic errors in the results of the experiments [159]; so much the more, since stratification is close to the limits of the degree of precision of the experiments.

The averaging curve (see Fig. 48) was used for determining the tabulated values of the thermal conductivity of methane at elevated pressures (Table 43). The error of the recommended values for the thermal conductivity of gaseous methane at relatively low pressures amounts to 2% with  $t$  up to 200°C and 3% - with  $t > 200^\circ\text{C}$ . At high pressures and for liquid methane this error is equal to 3-4%.

### Ethane

The experimental study of the coefficient of thermal conductivity of ethane at elevated pressures is taken up in a number of works (Table 44). Measurements are made using the coaxial cylinders and spherical layer methods.

Practically speaking, there are no experimental data on the thermal conductivity in the liquid phase. With the exception of one work [164], the studies referred to a comparatively narrow temperature range. However, the range of pressures is broad - up to 200-300 bar, and on one isotherm (75°C) - up to 3000 bar.

Table 43. Recommended values of the thermal conductivity of gaseous and liquid methane as a function of temperature and pressure.

t, °C	$\lambda \cdot 10^3$ , W/(m-deg) with p, bar																		
	1	10	20	30	40	50	60	80	100	150	200	250	300	350	400	450	500	550	600
-170	208	209	210	211	212	213	214	216	218	222	225	229	233	236	240	243	246	249	252
-160	12.2	193	194	195	196	197	198	200	202	206	209	213	217	220	224	228	232	236	240
-150	13.3	178	180	181	183	184	185	187	189	193	197	201	205	209	213	217	221	225	229
-140	14.4	162	164	166	167	169	170	173	175	180	184	189	193	198	203	207	212	216	220
-130	15.5	146	147	149	150	152	154	157	160	166	171	176	181	186	191	196	201	206	211
-120	16.6	18.5	130	132	134	136	138	141	144	151	158	164	169	175	180	185	190	195	200
-110	17.6	19.4	114	116	119	122	124	128	131	138	145	152	159	165	171	176	181	186	191
-100	18.7	20.2	22.2	99	102	105	108	113	117	125	134	141	148	154	160	166	171	176	181
-90	19.8	21.2	22.9	25.0	—	—	89	97	103	113	123	130	137	143	149	155	161	166	171
-80	20.9	22.0	23.6	25.5	28.7	34.1	—	—	88	101	112	120	128	134	140	146	151	157	162
-60	23.2	21.3	25.6	27.1	29.3	32.2	35.0	—	—	80	93	103	111	117	123	129	134	140	146
-40	25.5	26.5	27.6	28.9	30.5	32.4	34.7	40.9	50.7	65.2	78.0	87.8	96.6	104	111	117	122	127	132
0	27.9	28.9	29.9	30.9	32.2	33.7	36.0	39.4	44.6	57.6	68.6	77.5	86.3	93.8	101	107	112	117	121
20	30.4	31.3	32.3	33.2	34.2	35.4	36.7	39.8	43.8	54.3	63.8	72.2	80.0	86.7	93.0	98.5	104	109	113
40	33.2	34.0	34.8	35.7	36.6	37.6	38.7	41.3	44.4	52.6	61.0	68.5	75.0	81.2	87.1	92.4	97.6	103	107
60	36.0	36.7	37.5	38.3	39.1	40.0	41.0	43.2	45.5	52.3	59.3	66.2	72.8	78.8	84.3	89.1	93.9	98.5	103
80	38.9	39.6	40.3	41.1	41.8	42.5	43.4	45.4	47.5	53.2	59.0	64.8	70.9	76.5	81.9	87.0	91.6	95.9	100
100	41.9	42.5	43.2	43.9	44.6	45.3	46.1	48.0	50.0	55.0	60.1	65.4	71.0	76.0	81.0	85.5	89.9	94.1	98.1
150	45.0	45.6	46.2	46.9	47.6	48.2	48.9	50.4	52.0	56.7	61.4	66.2	71.0	75.6	80.1	83.7	88.3	92.4	96.3
200	53.2	53.7	54.2	54.8	55.4	56.0	56.6	57.9	59.2	62.8	66.4	70.2	74.0	77.8	81.6	85.2	88.8	92.3	95.7
250	62.0	62.5	63.0	63.5	64.0	64.5	65.0	66.0	67.1	70.0	73.0	76.1	79.3	82.6	86.0	89.3	92.6	95.4	98.2
300	70.9	71.4	71.8	72.2	72.6	73.0	73.4	74.4	75.4	78.0	80.7	83.5	86.3	89.1	91.9	94.6	97.2	99.8	102
350	80.1	80.5	80.9	81.3	81.7	82.1	82.5	83.2	84.0	86.3	88.5	90.8	93.2	95.5	97.7	101	103	105	107

Table 44. Studies of the thermal conductivity of ethane at elevated pressures.

Author	Year	Liter- ature source	Method	Temperature, °C	Pressure, bar
Lenoir, Junk, Commings	1953	[153]	Coaxial cylinders	42.0-57.3	1-198
Keyes	1954	[105]	The same	51.9	1-40
Leng, Commings	1957	[163]	The same	68	1-264
Carmichael, Berry, Sage	1963	[164]	Spherical layer	4-171	1-366
Gilmore, Commings	1966	[148]	Coaxial cylinder	75	1-3000

Figure 49 shows the experimental values obtained by various authors at coordinates  $\Delta\lambda - \rho$ . The density of ethane was adopted from the data of [178, 179]. In the graph the experimental points of [148] are shown only up to  $p = 500$  bar, since at higher pressures data on the density are lacking. Data on the thermal conductivity close to the critical region are found in work [153]; here they are not taken into consideration.

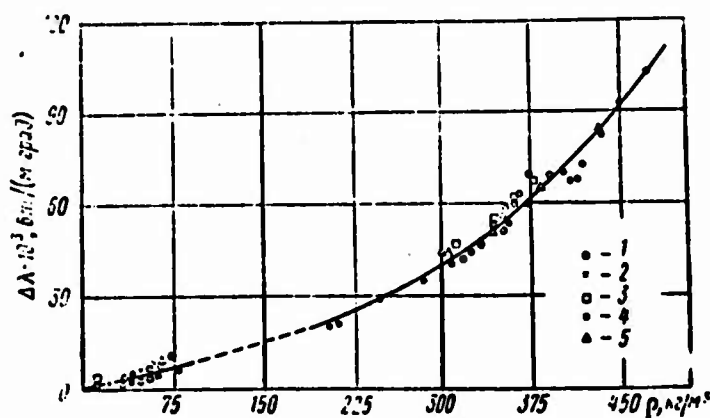


Fig. 49. Dependence of the excess thermal conductivity of ethane on the density according to the data of: 1 - Lenoir, et al. [153]; 2 - Keyes [105]; 3 - Leng, Commings [163]; 4 - Carmichael, et al. [164] 5 - Gilmore, Commings [148].

Designations:  $\text{Вт}/(\text{м} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ ;  $\text{кг}/\text{м}^3 = \text{kg}/\text{m}^3$ .

The scattering of points with respect to the generalizing curve reaches 3-7%. Any definite system cannot be detected, i.e., the scattering of points is the result of the divergence of results of the experiments of various investigations. Thus, at a temperature of  $\sim 70^\circ\text{C}$  there are data in four works [148, 153, 163, 164]. The points on the isotherm  $67.3^\circ\text{C}$  [153] are situated 5-6% lower than in isotherms  $42.0$  and  $56.7^\circ\text{C}$  of this same work, but they correspond well with the data of [164] on the isotherm  $71.0^\circ\text{C}$  (see Fig. 49). On the other hand, the later investigations of Gilmore and Commings [148] at  $t = 75^\circ\text{C}$  are in complete correspondence with the data of [153] on the isotherms of  $42.0$  and  $56.7^\circ\text{C}$  and with the results of [163] with  $t = 68.0^\circ\text{C}$ .

Consideration of the conditions of conducting the experiments in these works do not permit us to give any preference for any one of them. Therefore, the averaging curve was plotted by us according to the data of all the authors. It was used to determine the coefficient of the thermal conductivity of ethane with p up to 350 bar and t up to 200°C (Table 45). The possible error of the tabulated values of the thermal conductivity under pressure may be estimated at 4%.

Table 45. Recommended values of the thermal conductivity of ethane as a function of temperature and pressure.

(2) p, bar	(1) $\lambda \cdot 10^3$ , $\text{BT}/(\text{m} \cdot \text{град})$ , при t, °C								
	-20	-10	00	10	100	125	150	175	200
1	20,6	23,2	25,9	28,8	31,7	35,5	39,4	43,5	47,7
25	24,1	26,2	28,6	31,4	34,2	37,7	41,4	45,3	49,4
50	—	33,2	33,0	34,7	36,9	40,1	43,6	47,3	51,3
75	—	—	44,4	40,6	41,1	43,4	46,2	49,4	53,2
100	89	79	61,6	50,0	47,0	47,3	49,3	52,2	55,5
125	93	84	70,9	58,6	52,8	51,7	52,3	55,1	57,9
150	97	87	78,5	68,6	61,3	57,2	56,9	58,2	60,5
200	103	95	87,6	79,8	72,4	66,8	64,8	64,8	66,1
250	108	101	94,0	87,0	81,2	75,1	72,0	71,0	71,4
300	112	106	100	94,0	88,0	81,8	77,5	76,5	76,6
350	116	111	105	99,0	93,5	87,4	82,8	81,6	81,1

KEY: (1)  $\lambda \cdot 10^3$ ,  $\text{BT}/(\text{m} \cdot \text{deg})$ , with t, °C; (2) p, bar.

The thermal conductivity of ethane at t = 75°C according to the results of experiments of [148] amounts to

p, bar	$\lambda \cdot 10^3$ , $\text{BT}/(\text{m} \cdot \text{град})$	p, bar	$\lambda \cdot 10^3$ , $\text{BT}/(\text{m} \cdot \text{град})$
1	27,6	750	130,6
200	80,6	1000	145,6
300	93,7	2000	182,8
500	112,7	3000	228,6

Designations: p, bar = p, bar;  
 $\text{BT}/(\text{m} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ .

In conclusion we should note that the study of the thermal conductivity of ethane at low temperatures, especially for the liquid state, is of interest.

## Propane

The thermal conductivity of propane under pressure was studied in a single work [163],<sup>1</sup> in which the thermal conductivity was determined in the gaseous and liquid states of propane on five isotherms in the temperature interval of 50-140°C and the pressure interval 1-286 bar. The experiments embrace the precritical and supercritical regions. Just as in the experiments with ethane, the relative method of two-layered coaxial cylinders was employed.

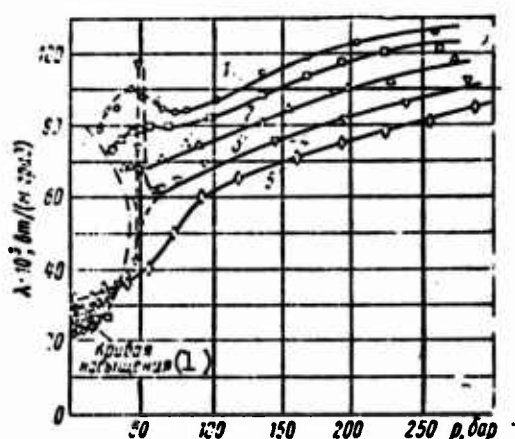


Fig. 50. Dependence of the thermal conductivity of propane on the pressure at various temperatures according to the data of [163]:

1 - 50°C; 2 - 67.8°C; 3 - 87.2°C; 4 - 105.5°C; 5 - 140°C.

KEY: (1) Saturation curve.

Designations:  $\lambda / (\text{м} \cdot \text{град}) = \text{W} / (\text{м} \cdot \text{deg})$ ;  $p, \text{бар} = p, \text{bar}$ .

The continuous lines in Fig. 50 show the isotherms, and the dashed-dotted line shows the line of saturation obtained by extrapolation. As can be seen from Fig. 50, on the isotherms of 50, 67.8, and 87.2°C in the liquid phase a little above the saturation line there are "humps," which decrease in proportion to the increase in

<sup>1</sup>After preparation of the book for printing there occurred one more work dedicated to the thermal conductivity of propane [180]. Its results coincide in the main with the data of [163].

temperature. In work [163] there is a discussion of the possible reasons for the occurrence of the "humps." In particular, it is noted that this phenomenon is not connected with the occurrence of convection in the measured layer: the product of the criteria  $Gr \cdot Pr$ , characterizing the conditions of development for natural convection, was less than 600 in the experiments. Moreover, if convection were the reason, then the size of the "humps" with the approach to the critical temperature would have to increase, rather than decrease.

The following circumstance deserves attention. In processing at coordinates  $\Delta\lambda - \rho$  the points referring to the region of "humps" are situated both higher and lower than the averaging line; moreover, in the narrow range of densities there is observed a reduction in the coefficient of thermal conductivity (up to 6%) with the increase in  $\rho$ . Usually just the opposite occurs.

Bearing in mind that the reason for the occurrence of "humps" is not certain, and in other substances in this region of  $p$  and  $t$  a similar anomaly was not observed, in generalizing as the function of the density we did not take into account the experimental points referring to the given region. This problem requires further investigation. In our opinion, the distortion of the results close to the saturation curve may be due to the insufficiently high purity of the investigated propane (99%).

The isotherm  $105.5^\circ\text{C}$  (or  $\tau = 1.026$ ) at a pressure of  $\sim 50$  bar (or  $\pi \approx 1.15$ ) has a sharp peak (see Fig. 50). As the authors themselves point out [163] the peak occurred as a result of the emergence of convection, since in the experiments  $Gr \cdot Pr \gg 600$ . In order to be convinced of the correctness of this explanation, the authors made measurements at two different drops of  $\Delta t_m$  - at 4.6 and 2.3 deg. In the latter case, as was to be expected, the thermal conductivity turned out to be less.

On the basis of the considerations outlined in the forward, in generalizing the data on thermal conductivity the critical region was excluded from examination.



Figure 51 shows the dependence of the excess thermal conductivity of propane on the density according to the data of Leng and Comings. For a better account of the effect of the pressure the values of  $\lambda$  at  $p = 1$  bar were also taken from [163]. The density of propane was taken from the data of [178]. As can be seen from Fig. 51, the scattering of points around the averaging curve generally amounts to 2-4%, and for one point close to the saturation curve ( $t = 87.2^\circ\text{C}$  and  $p = 30.4$  bar) - it reaches 9%. This graph was used to determine the coefficient of thermal conductivity. The recommended values are shown in Table 46. With consideration of the observations made the possible error of the tabulated data on the thermal conductivity of propane under pressure is estimated by us at 4-5%.

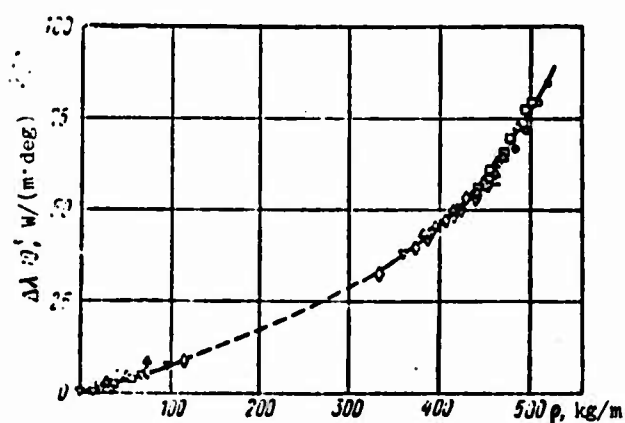


Fig. 51. Dependence of the excess thermal conductivity of propane on the density according to the data of [163]. The designations are the same as in Fig. 50.

Table 46. Thermal conductivity of liquid and gaseous propane as a function of temperature and pressure.

p, bar	$\lambda \cdot 10^3$ , W/(m·deg), with $t$ , $^\circ\text{C}$					
	50	60	80	100	120	140
1	21,0	22,2	24,7	27,4	30,1	32,9
10	22,2	23,3	25,7	28,3	31,0	33,7
20	80	25,4	27,5	29,9	32,2	34,9
30	82	77	30,5	31,7	33,8	36,3
40	84	79	68	37,2	36,4	38,0
50	86	80	71	—	40,5	41,3
60	88	82	73	63	—	45,3
70	89	83	75	66	—	—
80	90	85	76	69	61	—
100	92	88	79	73	67	—
150	97	93	86	80	75	71
200	102	98	92	86	82	78
250	106	102	96	92	87	83
300	109	106	100	96	91	87

## Butane

Studying the thermal conductivity of butane under pressure in the gaseous and liquid states, Krammer and Commings [166] made measurements on four isotherms:  $t = 75.3$  and  $105.5^\circ\text{C}$  with pressures from 1 to 1000 bar,  $t = 140.3^\circ\text{C}$  - up to 850 bar and  $t = 164^\circ\text{C}$  - up to 500 bar. The experimental data were obtained both in direct proximity to the saturation curve, and in the supercritical region (isotherm of  $164^\circ\text{C}$  or  $\tau = 1.03$ ) by the relative method of coaxial cylinders. The apparatus was calibrated at atmospheric pressure and various temperatures with four gases of known thermal conductivity: helium, methane, nitrogen and carbon dioxide. The purity of the investigated butane was 99.5%. The error of the results of the experiments according to the authors is 2%. As a result of the fact that  $\Delta t_m$  was measured with an error of 1.0-1.5%, and the apparatus was calibrated with four substances, the actual error must be somewhat greater.

The authors of work [166] note that in the liquid phase close to the saturation curve on isotherms of  $75.3$  and  $105.5^\circ\text{C}$  there are small "humps," similar to those observed for propane [163]. However, in this case the divergences from the normal pattern were relatively small (1-2%), within the limits of accuracy for the experiment and, in our opinion, their importance should not be exaggerated. More important is the rise in thermal conductivity in porportion to the decrease in pressure on the isotherm of  $140.3^\circ\text{C}$ . As is known, with liquids the opposite is usually observed, i.e., the thermal conductivity increases with the increase in pressure. Moreover this effect, as a rule, is small - it amounts to approximately 1-3% at 100 bar.

With careful consideration of the experimental data of [163] one may note that a significant reduction in the thermal conductivity with  $t = 140.3^\circ\text{C}$  occurs in a relatively narrow pressure range for the experimental points, occurring in direct proximity to the saturation curve. Thus, with a change in pressure from 38 to 32 bar the

coefficient of thermal conductivity increases by 5.4%. Here it is necessary to point out the following. The average temperature in the experiment was  $140.3^{\circ}\text{C}$ . With  $\Delta t_{\text{m}} \approx 1$  deg the temperature of the "hot" (inner) cylinder amounted to  $140.8^{\circ}\text{C}$ . The saturation pressure  $p_s$ , corresponding to this temperature, was approximately equal to 31 bar. The minimum pressure at this isotherm in the experiments was 31.9 bar. To determine the pressure spring-loaded manometers of class 0.5, designed for measuring pressures of 250-350 bar, were employed, i.e., the measuring error might have been  $\pm(1.2-1.8)$  bar. Consequently, the pressure during the experiment might have been lower than the saturation pressure, corresponding to the temperature of the hot cylinder, and this experiment refers not to the liquid, but to the two-phase region. For sufficient reliability of the experimental data it would be necessary to measure the pressure more accurately and to conduct experiments at a greater distance from the saturation curve.

In connection with the aforesaid the experimental points on the isotherm of  $t = 140.3^{\circ}\text{C}$ , situated close to the saturation curve, for which a negative pressure effect is observed, were not taken into account in generalizing. Also not taken into consideration as clearly erroneous were the two points on the isotherm of  $t = 75.3^{\circ}\text{C}$  at pressure 8.8 bar. Also excluded were the data on the isotherm of  $t = 164^{\circ}\text{C}$ , referring to the region approaching critical.

Fig. 52. Dependence of the excess thermal conductivity of n-butane on the density according to the data of [166] on the isotherm: 1 -  $75.3^{\circ}\text{C}$ ; 2 -  $103.5^{\circ}\text{C}$ ; 3 -  $140.3^{\circ}\text{C}$ ; 4 -  $164^{\circ}\text{C}$ .

Designations:  $\text{Вт}/(\text{м} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ ;  $\text{кг}/\text{м}^3 = \text{kg}/\text{m}^3$ .

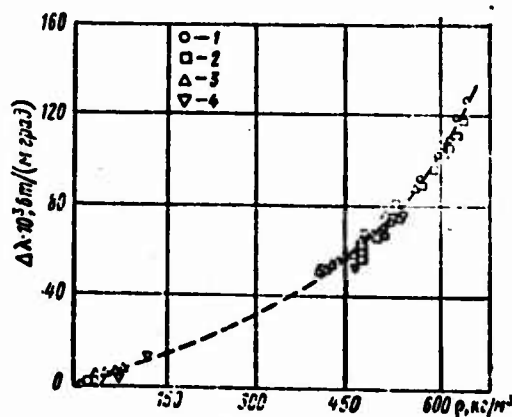


Figure 52 shows the dependence of  $\Delta\lambda = f(p)$ . Data on the density of butane was taken from [178, 179]. The scattering of points around the averaging curve generally amounts to 2-4%. This graph was used for the compilation of Table 47 for the values of the thermal conductivity of butane at uniform pressures and temperatures. The error of the data of Table 47 at elevated pressure amounts to 4%.

Table 47. Thermal conductivity of butane in the liquid and gas states.

(1) p, bar	(2) $\lambda \cdot 10^3$ , wt. (m · grad), при t, °C						
	60	80	100	120	140	160	180
1	19,9	22,4	24,9	27,4	30,1	32,8	35,6
10	94	24,0	26,4	28,7	31,3	34,0	36,7
20	94	89	84	31,7	33,5	35,8	38,3
40	95	90	85	79	68	—	44,6
60	96	92	87	82	77	71	—
80	98	94	89	85	81	76	73
100	99	95	91	87	84	80	77
150	102	98	94	90	86	86	84
200	105	101	98	94	92	89	88
250	108	104	101	97	95	93	92
300	111	107	103	100	98	96	95
400	115	112	108	105	103	101	100
500	118	115	112	110	108	106	105
600	122	119	116	114	112	110	109

KEY: (1) p, bar; (2)  $\lambda \cdot 10^3$ , W/(m · deg), with t°C.

### Pentane

N-pentane refers to a number of less well studied n-alkanes. There are no works dedicated to the study of thermal conductivity of the vapors of n-pentane under pressure. The thermal conductivity of liquid n-pentane has been very poorly studied.

The first experiments were conducted by the heated filament method in 1911 by Goldschmidt [181]; his measurements were relative ones. The results of Goldschmidt's experiments were corrected by us to -4.5% in conformance with the more reliable data for toluene (see below). In 1955 Sakiadis and Coates [182], and in 1960 Vilim [165], determined the thermal conductivity for liquid n-pentane at room temperature.

Bridgman [183] investigated the dependence of the thermal conductivity of n-pentane on the pressure in the interval  $t = 30-75^{\circ}\text{C}$  by the absolute cylindrical layer method. However, the influence of boundary effects was not taken into account with sufficient accuracy by this method. On the basis of a compilation of data for water and toluene L. P. Filippov [4] corrected the data of Bridgman.

A comparison of the corrected data of Bridgman and Goldschmidt with the results of works [165, 182] at room temperature shows satisfactory correspondence. With  $t = 30^{\circ}\text{C}$  for liquid pentane, the average value  $\lambda = 0.112 \text{ W/(m}\cdot\text{deg)}$  is recommended with a probable error of 3%. For a tentative judgment on the temperature pattern of the thermal conductivity of liquid n-pentane one may use the corrected value from Bridgman:  $\lambda = 0.100 \text{ W/(m}\cdot\text{deg)}$  with  $t = 75^{\circ}\text{C}$ . The dependence of the thermal conductivity on the pressure may be found in work [183].

One should note the obviousness for further studies on the thermal conductivity of n-pentane within broad measurement limits of  $p$  and  $t$ .

#### Hexane

The thermal conductivity of liquid n-hexane at atmospheric pressure was studied in a number of works (Table 48) both by stationary methods (coaxial cylinders, and by an optical variant of the flat method), and also by a nonstationary method — that of the regular regime.

From Fig. 53 and the value of the thermal conductivity at  $30^{\circ}\text{C}$  in Table 48 (the figures in brackets were obtained by extrapolation) it is clear that between the results of the various authors there is a good correspondence. The greatest value of  $\lambda_{30}$  was obtained from the data of Vilim [165]. The probable reason for this may be the absence of guard rings for the heaters in the apparatus and the lack of consideration of boundary effects.

Table 48. Studies on the thermal conductivity of liquid n-hexane.

Author	Year	Liter- ature source	Method	Temperature, °C	$\lambda_{30} \cdot 10^3$ W/(m·deg)
Smith	1930	[184]	Coaxial cylinders	30-60	122
Filippov	1954	[185]	The same	16-60	123
Sakiadis, Coates	1955	[182]	Flat layer	38-68	(125)
Frontas'ev, Gusakov	1959	[186]	Optical	20	(122)
Vilim	1960	[165]	Coaxial cylinders	20	(131)
Golubev, Maznev	1961	[69]	Cylindrical bicalorimeter	20-360*	126
Mukhnamedzyanov, Muzmanov, Tarznmanov	1963	[187]	Heated filament	30-47	122

\*Experiments conducted at pressures from 1 to 500 bar.

Attention is called to the stronger temperature dependence of the thermal conductivity in work [182] in comparison with the works of other authors. In extrapolating the data of [182] with  $t = 38^\circ\text{C}$  to  $t = 20^\circ\text{C}$  one obtains an apparently good correspondence between the measurements of Sakiadis, Coates, and Vilim, to which Vilim [165] points for confirmation of his data with insufficient foundation.

In generalizing, we introduced a correction into Smith's data [184] in conformance with the recommendations of L. P. Filippov [118]. Smith investigated Bridgman's apparatus [183], however, just like Bridgman, he did not take into account with sufficient accuracy the influence of boundary effects.

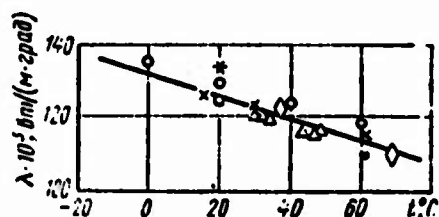


Fig. 53. Thermal conductivity of liquid n-hexane at atmospheric pressure. (The designations are the same as in Fig. 50.)

Designation:  $\text{BT}/(\text{m}\cdot\text{град}) = \text{W}/(\text{m}\cdot\text{deg})$ .

The averaging curve of Fig. 53 was taken as basic for the compilation of the table of values of thermal conductivity of liquid n-hexane at atmospheric pressure (see Table 49). The probable error in the temperature interval of  $0-70^\circ\text{C}$  amounts to 2%.

The thermal conductivity of n-hexane under pressure has until this time been investigated only in the work of I. F. Golubev and Ya. M. Naziyev [69] by the regular regime method (cylindrical bicalorimeter). The experiments embrace the pressure interval of  $p = 1-500$  bar at temperatures from  $20-360^\circ\text{C}$ .

Work [189] the experimental data are generalized using the expression for excess thermal conductivity as the function of the density. The table for the values of the thermal conductivity of n-hexane at uniform values of pressure and temperature is given. We made use of the results of this generalization, however we slightly

adjusted the values of thermal conductivity of liquid n-hexane, in order to obtain agreement with the averaging curve in Fig. 53. These corrections do not exceed 2-3%. The effect of pressure on the thermal conductivity was taken as in work [189].

Table 49. Thermal conductivity of liquid and gaseous n-hexane as a function of temperature and pressure.

t, °C	(1) $\lambda \cdot 10^3$ , вт/(м · град), при p, бар								
	1	20	40	100	150	200	300	500	
0	132	133	135	137	139	141	145	154	
20	126	127	129	132	134	136	140	149	
40	120	121	124	126	128	130	135	143	
60	114	116	118	121	123	125	130	138	
80	108,3	110	113	115	118	120	125	134	
100	102,5	106	109	111	114	116	121	130	
120	22,8	101	103	106	109	111	117	122	
140	25,1	97	99	102	105	108	111	119	
160	27,5	92	95	98	101	105	112	117	
180	30,0	87	92	95	99	103	109	115	
200	32,5	81	87	92	96	99	106	112	
220	35,1	39,3	83	89	93	97	104	110	
240	37,8	41,0	77	86	91	95	102	108	
260	40,5	43,4	69	83	89	94	101	107	
280	43,2	45,5	62,0	80	87	92	99	105	
300	46,1	48,3	58,8	78	86	91	98	104	
320	49,0	51,2	56,3	77	85	90	—	—	
340	51,9	54,0	60,6	76	84	89	—	—	
360	54,9	56,9	62,6	76	83	88	—	—	

KEY: (1)  $\lambda \cdot 10^3$ , W/(m · deg), with p, bar.

Table 49 shows the recommended values for the thermal conductivity at p = 1-500 bar and t = 0-360°C. The probable error of the data at elevated pressures amounts to 5%.

#### Heptane

Up to the present time the thermal conductivity of liquid n-heptane has been studied only in the region of positive temperatures (Table 50). The values for the coefficient of thermal conductivity at t = 30°C according to the data of various authors agree in full (figures in parentheses were obtained by extrapolation).



In 1968 V. P. Bryakov, et al. [190], using the heated filament method, rather carefully measured this value at negative temperatures.

From Fig. 54 it is clear that all the existing experimental data on the thermal conductivity of liquid n-heptane in the range  $t = -80$  to  $100^\circ\text{C}$  may be generalized by the straight line. In Vilim's apparatus [165] slightly exaggerated data could have been obtained, than was noted even for n-hexane.

The smoothed out values for the coefficient for the thermal conductivity of liquid n-heptane at  $p = 1$  bar, determined according to the averaging curve of Fig. 54, amount to

$t, ^\circ\text{C}$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$	$t, ^\circ\text{C}$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$
-80	156	0	134
-60	151	20	129
-40	145	40	123
-20	140	60	118
		80	113

Designation:  $\text{вт/(м} \cdot \text{град)} =$   
 $= \text{W/(m} \cdot \text{deg)}.$

(probable error is 2%).

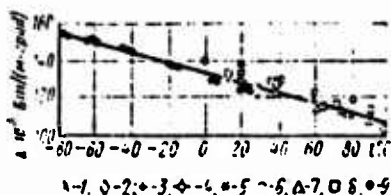


Fig. 54. Thermal conductivity of liquid n-heptane at atmospheric pressure according to the data of: 1 - Filippov [185]; 2 - Sakiadis, Coates [182]; 3 - Briggs [191]; 4 - Frontas'yev, Gusakov [186]; 5 - Vilim [165]; 6 - Golubev, Naziyev [69]; 7 - Mukhamedzyanov, et al. [187]; 8 - Abas-Zade, Guseynov [192]; 9 - Brykov, et al. [190].

Designation:  $\text{вт/(м} \cdot \text{град)} = \text{W/(m} \cdot \text{deg)}.$

Table 50. Investigation of the thermal conductivity of liquid n-heptane.

Author	Year	Liter- ature source	Method	Temperature, °C	$\lambda_{30} \cdot 10^3$ , W/(m·deg)
Filippov	1954	[185]	Coaxial cylinders	13-90	126
Sakiadis, Coates,	1955	[182]	Flat layer	38-98	(130)
Briggs	1957	[191]	Coaxial cylinders	30-60	122
Frontas'jev, Gusakov	1959	[186]	Optical	20	(127)
Vilim	1960	[165]	Coaxial cylinders	20	(133)
Golubev, Naziyev	1961	[69]	Coaxial cylinders (regular regime)	20-360*	131
Mukhamedzyanov, Usmanov, Tarznmanov	1963	[187]	Heated filament	36-90	(125)
Abas-Zade, Guseynov	1966	[192]	Coaxial cylinders (regular regime)	13-90*	130
Bryakov, Mukhamedzyanov, Usmanov	1968	[190]	Heated filament	-80 to +24	(123)

\*Experiments were also conducted at high pressures.

The thermal conductivity of n-heptane at elevated pressures was investigated in two works by the regular regime method. In 1961 I. F. Golubev and Ya. M. Naziyev [69] measured the thermal conductivity of n-heptane in the gas and liquid state in the interval of  $t = 20$  to  $360^{\circ}\text{C}$  at pressures of up to 500 bar.

In 1966 A. K. Abas-Zade and K. D. Guseynov [192], using an apparatus similar to that employed by Ya. M. Naziyev, investigated the influence of pressure on the thermal conductivity of liquid n-heptane in the ranges of  $t = 13$ - $90^{\circ}\text{C}$  and  $p = 1$ -400 bar. The results of these two works are close to one another, the data of [192] are lower than results of [69] by 1-2%.

In compiling the table of values (Table 51) for the thermal conductivity of n-heptane we employed the results of the generalization of coordinates  $\Delta\lambda - p$ , done in work [189], and the values of the thermal conductivity in the gas state at  $p = 1$  bar. The thermal conductivity of liquid n-heptane was adjusted by 4-5% in conformance with the averaging curve of Fig. 54. The effect of pressure was taken into account from the data of work [189]. The probable error of the data in the region of elevated pressures amounts to 5%.

Table 51. Thermal conductivity of liquid and gaseous n-heptane as a function of temperature and pressure.

$t, ^{\circ}\text{C}$	$\lambda \cdot 10^3, \text{W}/(\text{m} \cdot \text{deg}), \text{ with } p, \text{ bar}$								
	1	20	50	100	150	200	300	400	500
0	134	135	136	139	141	142	146	150	154
20	129	130	132	134	136	138	142	146	150
40	123	125	127	129	131	134	138	142	146
60	118	120	122	124	126	129	134	138	142
80	113	115	117	119	122	124	129	133	138
100	108	110	112	115	117	120	125	129	134
120	20,9	106	108	111	114	117	122	127	131
140	23,2	101	104	107	110	113	119	124	128
160	25,5	97	100	104	107	110	116	121	126
180	27,8	94	97	101	105	108	114	119	124
200	30,2	90	94	98	102	106	112	117	123
220	32,6	85	91	96	100	104	110	116	121
240	35,1	79	87	93	98	102	109	115	120
260	37,7	42,4	83	90	96	100	107	113	119
280	40,3	43,9	77	87	94	98	106	112	117
300	43,0	46,1	71	85	92	97	104	110	116
320	45,7	48,5	65,6	83	91	96	—	—	—
340	48,5	50,9	63,2	82	90	95	—	—	—
360	51,4	53,3	63,2	81	89	94	—	—	—

## Octane

The thermal conductivity of liquid n-octane at atmospheric pressure was measured by the investigators who conducted the measurements with n-hexane and n-heptane (Table 52). Practically speaking, the entire temperature range of the liquid state is encompassed.

Figure 55 shows the existing experimental material for liquid n-octane with  $p = 1$  bar, in which the data of Smith [184] were corrected for end effects, just as for n-hexane. From Fig. 55 and Table 52 (where the values in parentheses were obtained by extrapolation), it is clear that the divergences in the results of the experiments of various authors reach 8%. Higher than others are the data of I. F. Golubev and Ya. M. Naziyev [69].

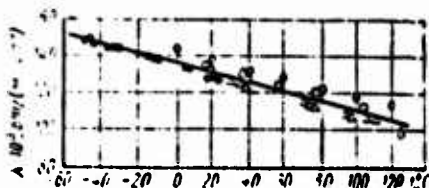


Fig. 55. Thermal conductivity of liquid n-octane at atmospheric pressure. (The designations are the same as in Fig. 50).

Designation:  $\lambda / (\text{m.град}) = W / (\text{m. deg})$ .

The experimental points of Sakiadis and Coates [182] show a stronger temperature dependence for the thermal conductivity of n-octane, as well as for n-hexane, and n-heptane according to the same data.

The averaging curve of Fig. 55 was used to determine the smoothed out values of the thermal conductivity of liquid n-octane at atmospheric pressure:

$t, ^\circ\text{C}$	$\lambda \cdot 10^3$ $W / (\text{m. deg})$	$t, ^\circ\text{C}$	$\lambda \cdot 10^3$ $W / (\text{m. deg})$
-40	148	60	121
-20	142	80	116
0	137	100	111
20	132	120	106
40	126		

(probable error is 2%).

Table 52. Investigation of the thermal conductivity of liquid n-octane.

Author	Year	Liter- ature source	Method	Temperature, °C	$\lambda_{30} \cdot 10^3$ W/(m·deg)
Smith	1930	[184]	Coaxial cylinders	30-170	127
Filippov	1954	[185]	The same	28-37	127
Sakiadis, Coates	1955	[182]	Flat layer	38-126	(134)
Frontas'yev, Gusakov	1959	[186]	Optical	20	(131)
Golubev, Naziyev	1961	[69]	Coaxial cylinders (regular regime)	20-360	136
Mukhamedzyanov, Usmanov, Tarznmanov	1963	[187]	Heated filament	31-110	127
Abas-Zade, Guseynov	1966	[192]	Coaxial cylinders (regular regime)	17-105*	131
Brykov, Mukhamedzyanov, Usmanov	1968	[190]	Heated filament	-48 to +21	(126)

\*Experiments were also conducted at high pressures.

The effective pressure on the thermal conductivity of n-octane was investigated by I. F. Golubev, Ya. M. Naziyev [69] in the pressure interval from 1 to 500 bar at temperatures from 20 to 360°C, by A. K. Abas-Zade, K. D. Guseynov [192] only for the liquid phase in the interval  $t = 17-105^{\circ}\text{C}$  and  $p = 1-400$  bar. As was already noted for n-heptane, in these works identical measurement methods and similarly constructed apparatus were employed. Divergences in the results of the cited investigations amount to 3-4%, but the effect of pressure is identical. Proceeding from this, when compiling the table of recommended values (Table 53) for the thermal conductivity, we considered it possible to use the results of processing of coordinates  $\Delta\lambda - p$ , made earlier in [189]. The data for gaseous n-octane at atmospheric pressure were taken as the basis for the generalization, made for a number of n-alkanes, and for the liquid with  $p = 1$  bar - in conformance with the averaging curve - Fig. 55. The effect of pressure on the thermal conductivity was taken from the data of [189].

Table 53 shows the recommended values of the thermal conductivity of n-octane. The probable error of the recommended values at elevated pressures is 5%.

Table 53. Thermal conductivity of liquid and gaseous n-octane as a function of temperature and pressure.

$t, ^{\circ}\text{C}$	$\lambda \cdot 10^3, \text{W}/(\text{m} \cdot \text{deg})$ with $p$ , bar								
	1	20	50	100	150	200	300	400	500
0	137	138	139	141	143	145	148	151	155
20	132	133	134	136	138	140	144	147	150
40	126	128	129	131	133	135	139	142	146
60	121	123	124	126	128	130	134	138	142
80	116	118	119	121	124	126	130	134	138
100	111	112	114	116	119	121	126	130	134
120	106	107	110	112	115	118	123	127	131
140	21.4	104	107	109	113	116	121	125	129
160	23.6	101	104	107	111	114	119	124	129
180	25.8	98	101	105	109	112	118	123	127
200	28.0	95	98	103	106	110	116	121	126
220	30.4	91	95	100	105	109	115	120	125
240	32.8	87	92	98	103	107	113	119	124
260	35.2	82	89	96	101	105	112	117	123
280	37.7	73	84	93	98	103	109	115	121
300	40.2	44.7	79	90	96	101	107	113	119
320	42.8	45.9	73	88	95	100	—	—	—
340	45.4	48.2	68	85	93	98	—	—	—
360	48.0	50.4	65	83	91	96	—	—	—

## Toluene

Toluene is one of three substances recommended by us as a sample substances for the liquid phase. The following reasons are the basis for this recommendation.

The values of the thermal conductivity of toluene are typical for the majority of organic liquids. Toluene is suitable for investigation in a comparatively wide temperature range (from  $-95$  to  $+110^{\circ}\text{C}$ ) without elevated pressure. Toluene may be comparatively easily purified of impurities. Working with toluene is suitable, since it is nontoxic, nonaggressive, and the pressure of its saturated vapors at room temperatures is small. Last but not least, the thermal conductivity of toluene has been well investigated by very many methods (three varieties of the flat layer method, stationary and nonstationary methods of coaxial cylinders, the heated filament method, its nonstationary variant, and stationary and nonstationary methods of a spherical layer). It was not by accident that toluene long ago came into use as a substance employed in calibrating instruments in relative measurements, particularly, in the works of L. P. Filippov [193], and F. G. El'darov [194]. Recommendations for the use of toluene as a sample substance are found in the works of Riedel [195], V. P. Frontas'yev and M. Ya. Gusakov [186], and V. Z. Geller [196, 197].

The authors of this handbook compared the results of 24 works selected in conformance with the criteria set down in the forward (a detailed summary of the results of measurements of the thermal conductivity of toluene may be found in the works of V. Z. Geller [196, 197]). Processing of these data was conducted by two means -- without consideration of corrections for heat transfer by radiation and with the introduction of calculated corrections. The advisability of examination of the two variants is determined by the considerations set down in Chapter I, where attention was given to the significant indeterminacy of the value of the radiation thermal conductivity.

Table 54. Investigation of the thermal conductivity of liquid toluene.

Author	Year	Literature source	Method	Temperature, °C	$\lambda_{20} \cdot 10^3$ W/(m·deg)
Goldschmidt	1911	[181]	Heated filament (relative variant)	-80 to +15	(134.5)
Vargaftik	1949	[36, 198]	Heated filament	-30-85	(137.2)
Riedel	1940	[199]	Flat layer	-80 to +80	135
	1951	[195]	Coaxial cylinders	-80 to +80	136
	1951	[195]	Spherical layer	20	134
Filippov	1953	[123]	Flat layer (relative variant)	-30-240	(135)
Schmidt, Leidenfrost	1954	[200]	Coaxial cylinders	20-80	135
Challoner, Powell	1956	[55]	Flat layer	0-80	138
Challoner, et al.	1958	[201]	Coaxial cylinders	30-80	(140)
Z. Geller, Rastorguyev	1958	[202]	Spherical bicalorimeter	30-80	(137)
Frontas'yev, Gusakov	1959	[186]	Optical (variant of the flat layer method)	20	136
Mustafayev	1959	[203]	Regular regime (non-stationary variant of the coaxial cylinder method)	0-30	134
Ziebland	1961	[51]	Coaxial cylinders	-15 to +110	134
Horrocks, McLoughlin	1963	[74, 204]	Heated filament (nonstationary variant)	25-60	(134)
Mukhamedzyanov	1964	[205-207]	Heated filament	30-100	(133)



Table 54 (Cont'd.).

Author	Year	Liter- ature source	Method	Temperature, °K	Pressure, bar
Venart	1965	[208]	Coaxial cylinders	20-80	135
Z. Geller, Rastorguyev, Ganiyev	1965	[209]	The same	25-80	(133)
Tsvetkov	1965	[210]	Cylindrical bicalorimeter	-80 to +90	136.5
Tufeu, Le Neindre, Johannin	1966	[211]	Coaxial cylinders	0-100	142
Rastorguyev, V. Geller	1967	[15]	Heated filament	30-200	135
Poltz	1967	[46, 48]	Flat layer	20-50	134*
Grigor'yev	1967	[212]	Heated filament	25-170	(136)
V. Geller, Rastorguyev	1968	[196]	Coaxial cylinders	20-200	135.5
Brykov, Mukhamedzyanov, Usmanov	1968	[190]	Heated filament	-80 to +20	134.5

\*For  $\lambda = 1$  mm.

No other corrections were introduced into the results of the selected works, except for the work of Goldschmidt [181], the data of which were reduced by 4.5% by recalculating for a more reliable value of the thermal conductivity of the graduated substance - ethyl alcohol [188].

On the degree of conformity of the data obtained by various authors one can judge from Table 54, which contains the results of the smoothed out values of the thermal conductivity at  $t = 20^{\circ}\text{C}$ . Included in parentheses are data obtained by extrapolation (within the limit of several degrees). The agreement may be considered as completely satisfactory. The maximum divergences from the average value - 135 mW/(m·deg) amount to +3.5 and -1.5% (work [211] is an exception).

With the appearance of more reliable values for the thermal conductivity all the experimental data were broken into two groups. Into the first of these were put the results, the error of which lies within the limits of 1 to 2%, and into the second - those from 2 to 3%. Into the second group go the results of Goldschmidt [181] due to the introduced correction, the data of L. P. Filippov [123], Venarta [208], O. B. Tsvetkov [210], Z. I. Geller and Yu. L. Rostorguev [202], Challoner, et al. [201] in conformance with the authors' estimate of the error, the data of Tyufo, et al. [211], the author's estimate of the degree of error of which (-1%), in our opinion, is somewhat low, which is confirmed by the significantly greater divergences of the results of these same authors for other substances for more reliable ones [4].

In averaging the data the results of the first group of works were selected with a weight of 1, the results of the second group - with a weight of 0.5. The probable error of the data of the first group was taken as equal to 1.5%, the second - 2.5%. The estimated error of the result was found from the formula

$$\Delta = \frac{1}{\sqrt{\sum 1/\Delta_i^2}}, \quad (62)$$

where  $\Delta_1$  – the probability errors of the employed values; formula (62) is an expression for the probable divergence of the general average of [6].

Averaging without corrections for radiation was conducted at each 10 deg in the temperature interval from 20 to 80°C and at each 20 deg in the intervals from -80 to 20° and from 80 to 240°C. The obtained results are shown in Table 55. Here, however, the values of the estimated error  $\Delta$  are given. For the temperature range where there is a sufficiently large quantity of data from various authors, along with the value of  $\Delta$  the probability error  $\Delta'$  of the result is also determined on the basis of consideration of the unestimated degree of error of the data, and of the actual divergences of the values of thermal conductivity  $\lambda_1$  from the weighted average [6]:

$$\Delta' = 0,67 \sqrt{\frac{\sum w_i \left(\frac{\Delta \lambda_i}{\lambda}\right)^2}{N \sum w_i}}, \tag{63}$$

where  $w_1$  – measurement weight;  $N$  – number of measurement. The values of the probability  $2\Delta'$ , as a rule, are close to  $\Delta$ .

Table 55. Thermal conductivity of liquid toluene on the saturation line.

t, °C	$\lambda \cdot 10^3$ вт/(м·град)	$\Delta$ , %	$\Delta'$ , %	$\lambda \cdot 10^3$ вт/(м·град)	$\delta$ , %	$\lambda_0 \cdot 10^3$ вт/(м·град)	$\lambda_0 \cdot 10^3$ вт/(м·град)
-80	169,8	0,7 <sub>8</sub>	—	158,8	0,4	—	—
-60	155	0,7 <sub>5</sub>	—	153,7	0,5	—	—
-40	150	0,7 <sub>5</sub>	—	140,0	0,7	—	—
-20	145	0,7	—	144,3	0,9	—	—
0	140	0,5 <sub>5</sub>	0,4 <sub>3</sub>	139,5	1,1	—	—
20	135,8	0,3 <sub>5</sub>	0,1 <sub>5</sub>	134,7	1,4	132,5	132
30	132,6	0,3 <sub>5</sub>	0,1 <sub>5</sub>	132,8	1,7	129,5	129,5
40	130,1	0,3 <sub>7</sub>	0,2 <sub>5</sub>	129,9	1,9	126,9	127
50	127,8	0,3 <sub>7</sub>	0,2 <sub>5</sub>	127,5	2,1	123,5	124,5
60	124,8	0,3 <sub>8</sub>	0,2 <sub>5</sub>	125,1	2,4	120,8	122
70	122,1	0,4 <sub>1</sub>	0,2 <sub>9</sub>	122,7	2,6	117,7	119,5
80	120	0,4 <sub>7</sub>	0,2 <sub>7</sub>	120,4	2,9	114,7	117
100	115,5	0,6	0,3 <sub>7</sub>	115,7	3,5	113	112
120	111,4	0,6 <sub>7</sub>	—	111,0	4,4	106	107
140	106	0,7 <sub>4</sub>	—	106,8	5,3	101,5	102
160	101,5	0,7 <sub>4</sub>	—	101,3	6,4	97	97
180	97,8	1,0	—	96,8	7,6	92,5	92
200	92,7	1	—	92,1	9,0	86,4	87
220	90	3	—	87,4	11	84,5	82
240	83	3	—	82,7	13	79	77

Designation: вт/(м·град) = W/(m·deg).

The results of averaging together with the region of probability error as a function of temperature are depicted as shown in Fig. 56. In the entire investigated region the results within the limits of  $\Delta$  may be interpolated by a straight line, the equation of which is as follows:

$$\lambda \cdot 10^3 = 139,5 - 0,237t \text{ [W/(m.deg)]}. \quad (64)$$

Values of the thermal conductivity  $\lambda$ , smoothed according to formula (64), are also shown in Table 55.

For a judgment about the probable boundary of the effect of heat transfer by radiation an estimate is given in the table according to the formula

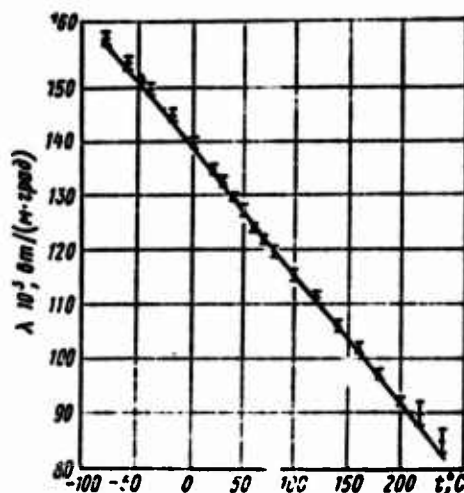
$$\epsilon' = \frac{\alpha}{\lambda} = \frac{1}{2} Bl = \frac{2\pi T^4}{\lambda}. \quad (65)$$

In the calculations the thickness of the layer of liquid was taken as equal to 0.7 mm, which corresponds approximately to the average width in the works of the various authors.

For the second variant for the processing of the literature data the correction for radiation was introduced into the results of each individual work. Here the results obtained by the heated filament method were not used in view of the lack of study of the problem of radiation transfer in systems of such configuration with relatively strong absorption.

Fig. 56. Temperature dependence of the thermal conductivity of liquid toluene on the saturation line (smoothed values).

Designations:  $\text{BT}/(\text{m} \cdot \text{град}) =$   
 $= \text{W}/(\text{m} \cdot \text{deg}).$



Corrections in the estimated approximation were calculated by the Poltz method [47]; for the average coefficient of absorption the value of  $3.5 \text{ mm}^{-1}$  introduced into [47] was used. Each experiment had its own values of layer thickness and degree of blackness of the surface (the latter, naturally, could have been determined only tentatively). As weights in averaging those same values were taken, as in the averaging without correction.

Table 55 gives the average values for the thermal conductivity with correction for radiation, i.e., values of thermal conductivity, reduced to the zero thickness of the layer of substance ( $\lambda_0$ ), and also the values of  $\bar{\lambda}_0$ , smoothed with respect to temperature. The difference between the values  $\bar{\lambda}$  and  $\lambda_0$  at temperature 100-140°C corresponds to the estimates of  $\delta'$ , and at higher temperatures the relative difference of  $\bar{\lambda}$  and  $\lambda_0$  is less than  $\delta'$ , which can be explained by the weight of the results with a clearance width of  $<0.7 \text{ mm}$ . One should note that the introduction of individual corrections for radiation not only does not reduce the scattering of the data obtained by various authors, but, on the contrary, increases the root mean square divergence from the average values by approximately 1.5-2 times. This may serve as an additional argument in the criticism of the calculations of Poltz (see Chapter I).

Let us formulate final recommendations:

toluene can be most suitably employed as a graduation liquid in temperature ranges from  $-80$  to  $+30^\circ$ . The maximum degree of error of the recommended values of  $\bar{\lambda}$  in this range with consideration of the indeterminacy of the values of heat transfer by radiation lies within the limits of 1-2% (total of  $\Delta$  and  $\delta$ ); the probability error amounts to approximately one half of this value;

at higher temperatures toluene may apparently not be used as a calibrating substance. In this range of temperatures the degree of error may be greater than in calibrating with water or gases;

Table 56. Investigation of the thermal conductivity of liquid benzene.

Author	Year	Liter- ature source	Method	Temperature, °C	$\lambda_{20} \cdot 10^3$ W/(m-deg)
Riedel	1940- 1951	[195, 199]	Flat layer	20	148
Vargaftik	1949	[198]	Heated filament	30-70	(145.5)
Riedel	1951	[195]	Coaxial cylinders	20-50	147.5
Kerzheatsev	1951	[213]	Spherical instruments	20	145
Schmidt, Leidenfrost	1954	[200]	Heated filament	25-75	(145)
Filippov	1954	[185]	Coaxial cylinders	20-70	145.5
Frontas'yev, Gusakov	1959	[186]	The same	15-70	145.5
El'darov	1958	[194]	Flat layer (optical)	20	145
Horrocks, McLaughlin	1963	[74-204]	Coaxial cylinders	25-80	(147)
Mukhamedzyanov	1964	[205-207]	Heated filament (non- stationary variant)	23-75	(143)
Venart	1965	[208]	Heated filament	25-75	145
Poltz	1965, 1967	[46, 48]	Coaxial cylinders	10-80	147
Z. Geller, et al.	1965	[209]	Flat layer	10-40	144
Tufeu, et al.	1966	[211]	Coaxial cylinders	25-60	(144)
V. Geller	1968	[196]	The same	20-80	152
			Heated filament	20-160	146.5

as tentative values for the thermal conductivity at temperatures above 30°C one may take the values of  $\bar{\lambda}$  from Table 55, which should be considered as effective with a layer width of  $\sim 0.7$  mm. A possible change in these values for limitedly small widths is characterized by the difference  $\bar{\lambda} - \bar{\lambda}_0$ . The maximum limit of indeterminacy of the values of thermal conductivity due to radiation (from maximally small to maximally large thicknesses of the layer) amounts to approximately double the value of  $\bar{\lambda} - \bar{\lambda}_0$ , as follows from work [48], i.e., the effective values of the thermal conductivity may lie within the limits of  $\lambda_0$  to  $\lambda_{\infty} \approx \bar{\lambda} + (\bar{\lambda} - \lambda_0)$ .

### Benzene

Benzene belongs to that class of organic substances, the thermal conductivity of which has been studied rather well. The innumeration of 16 works, selected in accordance with the criteria formulated in the preface, is shown in Table 56. The values of the thermal conductivity at  $t = 20^\circ\text{C}$  in all the works correspond well. In averaging, the majority of data were assigned the weight of 1: the weight of 0.5 was ascribed to only four works: Venart [208], V. V. Kerzhentsev [213] (in conformance with the authors' estimate of the degree of error) and Tufeu, et al. [211] (according to the considerations laid down for toluene).

The smoothed values of thermal conductivity together with the values of  $\Delta$ , calculated from (62) are shown in Table 57.

The problem of corrections for radiation was not examined specially.

Processing of the data was limited to the 80°C temperature region, where there is a sufficient quantity of reliable data. At higher temperatures there is a substantial divergence between the data of V. Geller [196] and Reiter [214], reaching as high as 13% when  $t = 160^\circ\text{C}$  at room temperatures the difference is small. An analysis of the work of Reiter forces us to refer to it with caution. Thus, for the product of the Grashof and Prandtl numbers, corresponding to

the start of convection, the author obtained the number 600, which is significantly less than that obtained in the majority of experiments carried out by the heated filament method. In this work there are no data on the employed temperature drops, and it is unknown whether calibration of the resistance thermometers on the assembled apparatus was carried out, nor is it clear how the author took into account the "partial absorption" of radiation in the liquid. All this taken together forced us to refrain from considering the data of Reiter.

Table 57. Recommended values of thermal conductivity of liquid benzene on the saturation line.

$t, ^\circ\text{C}$	$\lambda \cdot 10^3$ $\text{W}/(\text{m} \cdot \text{deg})$	$\Delta, \%$	$t, ^\circ\text{C}$	$\lambda \cdot 10^3$ $\text{W}/(\text{m} \cdot \text{deg})$
10	149	1	90	(125)
20	146.5	0.4	100	(122)
30	143.5	0.5	110	(119)
40	140.5	0.5	120	(116)
50	137.5	0.5	130	(113)
60	134.5	0.5	140	(110)
70	131.5	0.7	150	(106.5)
80	128.5	1	160	(103)

For the sake of orientation in the temperature region above 80°C in Table 57 introduced in parentheses are the results of measurements of V. Geller, which, in our opinion, are the most reliable. The error of the data may be taken as equal to ~3% (without consideration of the role of radiation). Close to these values of  $\lambda$  are those obtained by means of extrapolation of the data of Table 57 at temperatures below 80°C according to the formula

$$\lambda \cdot 10^3 = 152 - 0.29t \text{ [W}/(\text{m} \cdot \text{deg})]. \quad (66)$$

The thermal conductivity of vapors of benzene was measured in 1913 by Moser [167] in the temperature range from 0 to 212°C. In 1954 new data were published by Vines and Bennett [162] for the region from 0 to 160°C (the first results of this work were given by Vines in 1953 - [154]). These values show good correspondence with the results of measurements of Lambert, Staines, and Woods [141], carried out at temperatures of 66 and 85°C. Between



the data of Mosier<sup>1</sup> and Vines there are rather large differences: at  $t = 80^{\circ}\text{C}$  they comprise 6.5%, and at  $160^{\circ}\text{C}$  - they fall to 2.5%.

The data of Reiter [214] for saturated vapors of benzene lie between the results of Mosier and Vines. However, considering the aforesaid relative to the experiment of Reiter, we refrained from using these data.

As the most reliable values let us set forth the averages from the results of Vines and Mosier:

$T, ^{\circ}\text{K}$	$\lambda \cdot 10^3,$ $\text{вт}/(\text{м} \cdot \text{град})$	$T, ^{\circ}\text{K}$	$\lambda \cdot 10^3,$ $\text{вт}/(\text{м} \cdot \text{град})$
325	12.5	400	20.2
350	15.0	425	22.8
375	17.6	450	25.4

Designation:  $\text{вт}/(\text{м} \cdot \text{град}) =$   
 $= \text{W}/(\text{m} \cdot \text{deg}).$

(their error may be taken as  $\sim 2-3\%$ ).

The dependence of the thermal conductivity of benzene vapors on pressure was studied in works [141, 154, 162] in the interval  $p = 50-700 \text{ mm Hg}$  [141] and  $150-500 \text{ mm Hg}$  [154]. The change in thermal conductivity with the change in  $p$  by 1 atm amounts to 1.7-1% according to [141] and 0.3-0.6% according to [154, 162]. However, one must refer to these data with care in view of the very limited range of investigated pressures.

### Carbon Tetrachloride

Liquid carbon tetrachloride is the second of the organic substances recommended by us as a sample substance. It belongs to the class of liquids with the smallest values of thermal conductivity

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<sup>1</sup>Mosier's results were obtained by a relative method: the sample substance was air. Taking into account that the value of thermal conductivity of air, as used by Mosier, is less than that assumed at the present time by 3%, Mosier's data are exaggerated by 3%.

and from this viewpoint is suitable for calibrating equipment in cases, where it is desirable to carry out calibration for the widest possible range of measurements of thermal conductivity. The use of carbon tetrachloride as a calibrating substance can also be preferable in the case where the investigation objects are Freons - substances close to it in thermal conductivity.

One can work with carbon tetrachloride in a temperature range from  $-20$  to  $77^{\circ}\text{C}$  without increased pressure. The existing data encompass a temperature range up to  $200^{\circ}\text{C}$ . Similar to toluene, carbon tetrachloride also possesses other advantages: it is nontoxic, nonaggressive, and it can be purified relatively easily.

The thermal conductivity of carbon tetrachloride has been studied sufficiently well, even if somewhat worse than toluene. Data have been obtained by the following methods: flat layer, coaxial layer, spherical layer, and heated filament (in two variants).

On the degree of coincidence of the data of various authors one can judge from Table 58, in which are shown the values of  $\lambda$  at  $t = 2$  (the numbers in the brackets were obtained by extrapolation).

The selection of the works included in the table was based on general considerations formulated in the preface (a summary of the literature data can be found in works [196, 197]).

The results given in Table 58 were used in processing without the introduction of any kind of corrections. An exception was made for the data of Goldschmidt [181], which were adjusted by  $-4.5\%$  in conformance with the considerations set down for toluene (in Table 58 the value of the thermal conductivity is given with the correction).

Table 58. Investigation of thermal conductivity of  $\alpha$ - $\beta$  carbon tetrachloride.

Author	Year	Liter- ature source	Method	Temperature, °C	$\lambda_{20} \cdot 10^3$ , W/(m·deg)
Goldschmidt	1911	[181]	Heated filament (relative variant)	0	(100)
Riedel	1940- 1951	[195, 199]	Flat layer	20	103
	1951	[195]	Coaxial cylinders	-20 to +50	103
Schmidt, Leidenfrost			Spherical instruments	20	102
Mason	1954	[200]	Coaxial cylinders	20-50	102.5
Filippov	1954	[215]	The same	20-65	103
	1954	[185]	The same	20-95	104
Challoner, Powell	1956	[55]	Flat layer	0-60	107
Geru, Filippov	1956	[216]	Heated filament (differential variant)	20-60	104
Filippov	1957	[217]	Heated filament (relative variant)	30	(103)
Challoner, et al.	1958	[201]	Coaxial cylinders	25-55	(107)
Frontas'yev, Gusakov	1959	[186]	Flat layer (optical)	20	106
Venart	1964	[218]	Coaxial cylinders	20-30	103.5
Tufeu, Le Neindre, Johannin	1966	[211]	The same	20-80	106
Z. Geller, Rastorguyev Gannev	1966	[219]	The same	20-155	(106)
Rastorguyev, V. Geller	1967	[15, 196]	Heated filament	20-200	103
Poltz	1967	[46, 48]	Flat layer	10-40	100*

\*For  $l = 1$  mm.

The most reliable values for the thermal conductivity were found by a method analogous to that used for toluene. The selected data were divided into two groups. The first includes the results, the error of which lay within the limit of 1-2%, and for these data an error value of 1.5% was adopted; the gravimetric factor was taken as equal to unity. The second group includes results, obtained with an error of 2-3%; their error was taken as 2.5% and the gravimetric factor as 0.5. The second group includes the data of Goldschmidt [181], Tufeu and coauthors [211], Venart [218], Challoner, et al. [201], on the same reasons set down for toluene. Besides these works, the second group also contains the data of Mason [215] in conformance with the estimate of error of these data, made in work [4].

Averaging of the data was accomplished each 10° in the temperature interval from -20 to 80°C and each 20° in the region from 80 to 200°C. The results of averaging together with the area of error, determined from formula (62), are given in Fig. 57. In the entire investigated temperature region these data may be interpolated by the straight line, the equation for which assumes the form

$$\lambda \cdot 10^3 = 108,6 - 0,22t \text{ [W/(m} \cdot \text{deg)]}. \quad (67)$$

The smoothed values of thermal conductivity, an estimate of the degree of error  $\Delta$  and the probability limit of correction for radiation  $\delta'$ , calculated from formula (65), with an average width of the layer  $d \approx 0.7$  mm are given in Table 59. For carbon tetrachloride, in contrast to toluene, no alternative processing of the data was accomplished by introducing individual corrections for radiation, since there are also no tentative values of the effective coefficient of absorption.

Let us formulate the final recommendations:

Carbon tetrachloride may be used as a sample liquid in the temperature range from -20 to +30°C. The maximum error ( $\Delta + \delta'$ ) in this temperature region amounts to  $\sim 2.5\%$ . The use of carbon

tetrachloride as a sample substance at higher temperatures can at this time not be recommended.

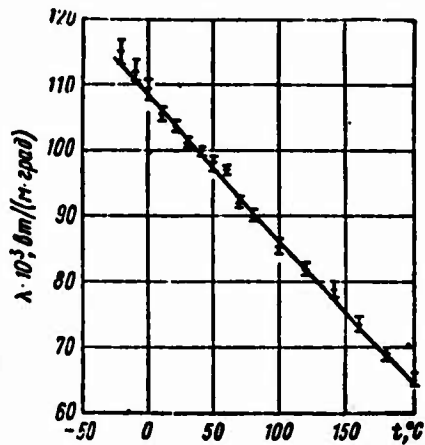


Fig. 57. Temperature dependence of the thermal conductivity of liquid carbon tetrachloride on the saturation line (smoothed values). Designation:  $\text{Вт}/(\text{м} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ .

In the greatest temperature region the thermal conductivity of carbon tetrachloride vapors was measured in the works of N. B. Vargaftik, L. S. Zaytsevov and L. V. Yakush [220].

Table 59. Recommended values of the thermal conductivity of liquid carbon tetrachloride on the saturation line.

$t, ^\circ\text{C}$	$\lambda \cdot 10^3, \frac{\text{Вт}}{\text{м} \cdot \text{град}}$	$\Delta, \%$	$\delta', \%$	$t, ^\circ\text{C}$	$\lambda \cdot 10^3, \frac{\text{Вт}}{\text{м} \cdot \text{град}}$	$\Delta, \%$	$\delta', \%$
-20	113	1,5	1,1	100	86,4	1	4,7
-10	110,8	1,5	1,2	110	84,8	1,5	5,3
0	108,7	1	1,4	120	82,8	1,5	6,0
10	106,5	1	1,6	130	79,7	1,5	6,7
20	104,8	0,4	1,8	140	77,5	1,5	7,3
30	101,9	0,5	2,2	150	75,3	1,5	8,1
40	99,7	0,5	2,5	160	73,1	1,5	8,9
50	97,5	0,6	2,7	170	71,0	1,5	9,8
60	95,8	0,7	3,1	180	68,8	1,5	10,7
70	93,8	0,9	3,4	190	66,8	1,5	11,7
80	90,8	0,9	3,8	200	64,8	1,5	12,9
90	88,8	1	4,2				

Designation:  $\text{Вт}/(\text{м} \cdot \text{град}) = \text{J}/(\text{m} \cdot \text{deg})$ .

The results obtained are in comparatively good agreement with the data of Masia and Alvares [221], and the maximum divergence amounts to ~2%. There is significantly greater difference — up to 7% — between the results of [220] and the data of Moser [167]. This can be explained in part by the fact that for the relative measurements Moser took an inaccurate value for the thermal conductivity of air (it differs by 3% from the currently accepted value). Another reason for the divergence may be the fact that in Moser's experiment the temperature of the wall of the measuring cell was not measured directly, but was assumed to be equal to the temperature of the thermostat.

Table 60. Recommended-values of the thermal conductivity of carbon tetrachloride vapors.

$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$	$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$	$T, ^\circ K$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$
300	6,9	425	10,9	525	13,7
325	7,7	450	11,6	550	14,4
350	8,5	475	12,3	575	15,1
375	9,3	500	13,0	600	15,8
400	10,1				

Designation:  $\text{вт/(м} \cdot \text{град)} = \text{W/(m} \cdot \text{deg)}$ .

Considering the aforesaid, as the most reliable data on the thermal conductivity of carbon tetrachloride vapors we accept the results of [220]. The smooth values for the thermal conductivity are given in Table 60. The degree of error may be taken as equal to 2%.

### Ethyl Alcohol

The investigations on the thermal conductivity of ethyl alcohol, enumerated in Table 61, conformed to the criteria formulated in the preface. The data enumerated in the table refer to 100% ethyl alcohol. In those cases where the results of individual authors were taken for alcohol with a noticeable water content, the corresponding values were enumerated for 100% alcohol. For the correction for water content the following formula was used:

$$\lambda = \lambda_c P_c + \lambda_s P_s - (\lambda_s - \lambda_c) \alpha P_s P_c, \quad (68)$$

where P is the weight concentration of the substance, and the subscripts "c" and "a" refer to alcohol and water, respectively [226]. The coefficient  $\alpha$  was taken as equal to 0.59 in conformance with the results of work [226]. To the values, into which corrections for water content were introduced, a weight of 0.5 was ascribed in the averaging. This same weight was ascribed to the data of the works of Tsederberg [224], Venart [208], Challoner [201] in accordance with the author's evaluation of the accuracy, and also to the data of the works of Mason [215], Tufeu, et al. [211] according to the reasons laid down for toluene and for carbon tetrachloride.

The results of the weighted average at various temperatures together with the region of error  $\Delta$ , found from formula (62), are depicted in Fig. 58. In the entire temperature region these values within the limits of  $\Delta$  may be approximated by the linear dependence, the equation of which has the form

$$\lambda \cdot 10^3 = 172.3 - 0.23_t [W/(m \cdot \text{deg})]. \quad (69)$$

The smoothed data on thermal conductivity of ethyl alcohol, recommended as the most reliable, are shown in Table 62 along with an evaluation of the degree of error  $\Delta$ .

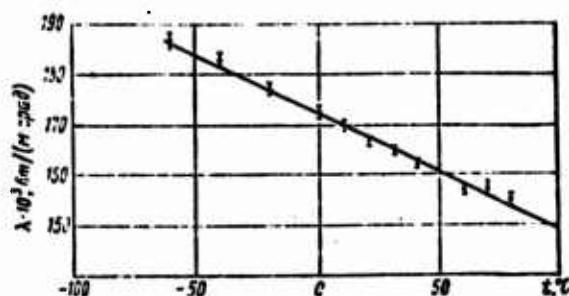


Fig. 58. The temperature dependence of the thermal conductivity of liquid ethyl alcohol on the saturation line (smoothed values).

Designation:  $\text{Вт}/(\text{м} \cdot \text{град}) = W/(m \cdot \text{deg})$ .

Table 61. Investigation of the thermal conductivity of liquid ethyl alcohol.

Author	Year	Liter- ature source	Method	Temperature, °C	$\lambda_{20} \cdot 10^3$ W/(m·deg)
Vargaftik	1949	[198]	Heated filament	31-68	173
Cherneyeva	1950	[222]	"	-75 to +70	160
Kerzhentsev	1951	[62,213]	"	10-243	169.5
Riedel	1951	[223]	Coaxial cylinders	-70 to +60	168
Mason	1954	[215]	The same	20-50	163.5
Filippov	1954- 1960	[188,185]	The same	15-90	163.5
Sakiadis, Coates	1955	[182]	Flat layer	40-75	-
Tsederberg	1956	[224]	Heated filament	-60 to +60	164
Challoner, Powell	1956	[55]	Flat layer	0-40	170
Challoner, et al.	1958	[201]	Coaxial cylinders	25-50	169.5
Frontas'yev, Gusakov	1959	[186]	Flat layer (optical)	20	164
Grassman, et al.	1962	[225]	Heated filament (non- stationary variant)	-50 to +50	170
Venart	1965	[208]	Coaxial cylinders	54	-
Tufeu, et al.	1966	[211]	The same	0-78	175



In this same table there are shown the results of precalculation of the recommended values of thermal conductivity for the thermal conductivity of alcohol with a concentration of 95.6 wt. % (azeotropic mixture). Precalculation was done with the aid of formula (68). As the effective values of thermal conductivity of water with negative temperatures the data found in work [226] were used. The degree of error of the values  $\lambda_{95.6}$  amounts to ~2%.

Table 62. The recommended values of the thermal conductivity of liquid ethyl alcohol on the saturation line.

$t, ^\circ\text{C}$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$	$\Delta, \%$	$\lambda_{95.6} \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$	$t, ^\circ\text{C}$	$\lambda \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$	$\Delta, \%$	$\lambda_{95.6} \cdot 10^3$ $\text{вт/(м} \cdot \text{град)}$
-60	186.5	1.1	194	20	168	0.6	176
-50	184	1	191	30	165.5	0.6	174
-40	182	0.9	189	40	163.5	0.6	172
-30	179.5	0.9	186	50	161	0.6	170
-20	177	0.9	184	60	158.5	0.7	168
-10	175	0.9	182	70	156	0.9	166
0	172.5	0.7	180	80	154	1	164
10	170	0.7	178				

Designation:  $\text{вт/(м} \cdot \text{град)} = \text{W/(m} \cdot \text{deg)}$ .

The change in the thermal conductivity of liquid alcohol under pressure, according to the data of the experiment of V. V. Kerzhentseva in a temperature range from 0 to 80°C for  $p = 100$  atm, amounts to  $3.5 \pm 0.5\%$ , and for  $p = 150$  atm is equal to  $6 \pm 1\%$ .

The dependence of thermal conductivity of ethyl alcohol vapors on the temperature at pressures close to atmospheric has been studied by a few authors by the heated filament method.

The first measurements in the range  $t = 0\text{-}100^\circ\text{C}$  were carried out in 1913 by Moser [167]. In 1939 P. I. Shushpanov [227] published data on the thermal conductivity of five normal alcohols, including ethyl alcohol, at  $t = 52\text{-}128^\circ\text{C}$ . Later V. V. Kerzhentsev [213] and V. N. Mel'nikova [228] determined the thermal conductivity of ethyl alcohol of temperatures up to  $350\text{-}380^\circ\text{C}$ . Fos, et al. [229] measured, using a relative heated filament method, the thermal conductivity for alcohols, and for ethyl alcohol they obtained data at  $t = 100^\circ\text{C}$ . Finally, recently A. A. Tarzimanov and

V. Ye. Mashirov [170] studied the coefficient of thermal conductivity of vapors of six normal alcohols, including the temperature range from 89 to 405°C for ethyl alcohol.

Moser [167], and Fos, et al. [229] calibrated equipment with air. As the base they adopted the reduced values of the thermal conductivity of air; therefore, the data of these investigators for ethyl alcohol have been adjusted by 3.0 and 5.5%, respectively.

Attention is drawn to the considerable divergences between the results of the experiments of various authors at temperatures close to normal boiling temperature. In connection with this, let us stop on the following problem.

It is usually assumed that pressures close to atmospheric the coefficient of the thermal conductivity of gases (vapors) does not depend on the pressure, i.e., the thermal conductivity value, for instance, with  $p = 0.5$  and  $1.0$  bar is one and the same. For nonpolar substances, such as the *n*-alkanes, this is indeed so. With polar compounds, especially at temperatures close to the boiling point, a significant change in the thermal conductivity is observed depending on the pressure. The probable reason for this is the formation of associations, the quantity of which depends on the temperature and pressure [170].

Moser [167], P. I. Shushpanov [227] and V. N. Mel'nikova [228] conducted experiments at pressures below atmospheric, and therefore these data cannot refer to  $p = 1$  bar.

In work [170] calculated equations are advanced for the thermal conductivity of normal alcohols with consideration of the formation of complexes. Here the divergence of the experimental data, including also points at low pressures, from the calculated ones basically do not exceed 2% (Fig. 59).

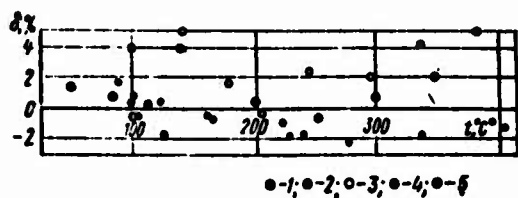


Fig. 59. Divergence of the experimental data on the thermal conductivity of ethyl alcohol vapors at  $p \leq 1$  bar from the calculated values [170]: 1 - Shushpanov [227]; 2 - Kerzhentseva [62, 214]; 3 - Mel'nikova [228]; 4 - Fos, et al. [229]; 5 - Tarzimanov, Mashirov [170].

As the most reliable data on the thermal conductivity of ethyl alcohol vapors (100%) we accept the data of work [170]. Table 63 shows the recommended values of the thermal conductivity; their probable error amounts to 1.5%.

Table 63. Recommended values of the thermal conductivity of ethyl alcohol vapors at atmospheric pressure.

$t, ^\circ\text{C}$	$\lambda \cdot 10^3$ $\text{BT}/(\text{M} \cdot \text{град})$	$t, ^\circ\text{C}$	$\lambda \cdot 10^3$ $\text{BT}/(\text{M} \cdot \text{град})$	$t, ^\circ\text{C}$	$\lambda \cdot 10^3$ $\text{BT}/(\text{M} \cdot \text{град})$
80	23,5	180	32,0	320	52,6
90	23,1	200	34,7	340	55,8
100	23,4	220	37,4	360	59,1
110	23,9	240	40,5	380	62,4
120	24,8	260	43,4	400	65,8
140	27,0	280	46,4	420	69,2
160	29,5	300	49,4		

Designation:  $\text{BT}/(\text{M} \cdot \text{град}) = \text{W}/(\text{m} \cdot \text{deg})$ .

## Water

### Ordinary Water $\text{H}_2\text{O}$

The basic experimental works on the study on the thermal conductivity of water are enumerated in Table 64. Until 1930 the thermal conductivity of water had been measured at atmospheric pressure and temperatures from 24 to  $90^\circ\text{C}$ . There was only the single work of Bridgman [230], in which the effect of pressure up to 12,000 atm on the thermal conductivity of water at  $t = 30$  and  $70^\circ\text{C}$  was studied. A review of all these investigations was done in the works of Barratt, Nettleton [236] and Powell [237].

Table 64. Investigation of the thermal conductivity of water.

Author	Year	Liter- ature source	Method	Temperature, °C	Pressure, bar
Bridgman	1923	[230]	Coaxial cylinders	30-75	1-12,000
Schmidt, Sellschopp	1932	[231]	The same	9-269	1-75
Timrot, Vargaftik	1940	[232]	Heated filament	28-331	1-400
Riedel	1940- 1954	[199] [238]	Flat layer Coaxial cylinders, spherical layer	20-80	1
Schmidt, Leidenfrost	1955	[57]	Coaxial cylinders	32-72	1
Gilliann, Lamm	1955	[73]	Heated filament (nonstationary)	4-20	1
Challoner, Powell	1958	[201]	Flat layer	1-80	1
Riedel	1959	[233]	Coaxial cylinders	30-110	1-8000
Vargaftik, Oleshuk	1959	[234]	Heated filament	21-350	1-217
Fritz, Poltz	1962	[45]	Flat layer	25	1
Le-Meindre, Johannin, Vodar	1964- 1968	[235]	Coaxial cylinders	37-370	1-500

The thermal conductivity of water at high temperatures (up to 270°C) and pressure (up to 75 atm) was measured by Schmidt and Sellschopp [231] by the coaxial cylinders method. It was discovered that the thermal conductivity of water passes through the maximum. Later, D. L. Timrot and N. B. Vargaftik [232, 234], by the heated filament method, determined the thermal conductivity of water to higher temperatures (up to 350°C) at pressures of up to 217 atm and confirmed the results of the experiments obtained in work [231] on the presence of a maximum for the thermal conductivity of water.

Recently a great volume of experimental data on the thermal conductivity of water at temperatures from 37 to 370°C and pressures from 1 to 500 atm has been obtained by Bogor and coworkers [235]. These measurements were carried out using the method of coaxial cylinders. Fritz and Poltz [45] conducted experiments with various widths of the layer of water (0.5-2 mm) in order to clarify the effect of natural radiation of water on thermal conductivity. The measurements were carried out by the method of a flat layer at only one temperature (25°C). The experiments showed that the measured values for the thermal conductivity do not depend on the thickness of the layer; the authors explain this by the high absorptive capacity of water in the infrared region of the spectrum.

A number of other investigators [57, 73, 199, 200, 238], in order to refine the data on the thermal conductivity of water in the low temperature region carried out additional measurements by various methods. Riedel [199, 238] for measurements at  $t$  from 20 to 80°C used three different methods: flat layer, spherical layer, and coaxial cylinders. Gilliann and Lamm used the nonstationary method of a heated filament in the temperature range from 4 to 20°C, while Lawson and Lovel used the method of coaxial cylinders for the temperature region from 30 to 110°C and pressures up to 8000 atm.

The basic experimental works on the thermal conductivity of water vapor are shown in Table 65. Just as for water, in the experiments various methods were employed. In the high pressure region (up to 300 bar) and high temperatures (up to 450°C) the measurements for the thermal conductivity of water vapor using the heated filament method were carried out by D. L. Timrot and N. B. Vargaftik [21, 239], and then up to 700°C and 500 atm - by N. B. Vargaftik and A. A. Tarzimanov [240]. Keyes and Vines [242], for a number of years studied the thermal conductivity of water vapor by the coaxial cylinders method. The results of their experiments refer to pressures of 1-180 atm and temperatures as high as 370°C. Thermal conductivity close to the saturation line was studied by A. A. Tarzimanov [241]. The method of a regular regime for measuring the thermal conductivity of water vapor at high pressures was employed by M. P. Vukalovich and L. I. Cherneyeva [243]. In the region of parameters of state, in which the thermal conductivity depends basically on the pressure and temperature (at temperatures of 350-450°C and pressures of 200-400 atm) measurements were conducted by Kh. I. Amirkhanov and A. P. Adamov [244]. Their data in this region are the only ones (the method of a flat horizontal layer was employed).

At atmospheric pressure and high temperatures there are a number of works by N. B. Vargaftik and coworkers [245, 129] and by Geier, Schafer [25]. These measurements were carried out by the heated filament method. Among the results of experiments of [245, 129] and [25] there are the basic divergences, which increase in proportion to the increase in temperature. The problem of these divergences is examined in detail in the works of N. B. Vargaftik and N. Kh. Zimina [245], where it has been demonstrated that the reason for the underestimated data of Geier and Schafer is their disregard of the correction for the temperature jump, which essentially affects the results of measurements of the thermal conductivity at high temperatures. The very careful measurements conducted recently by Brain [247] on the thermal conductivity of water vapor up to  $t = 600^{\circ}\text{C}$  by the coaxial cylinders method have completely confirmed the results of the experiments of [245, 129].

Table 65. Investigation of the thermal conductivity of water vapor.

Author	Year	Liter- ature source	Method	Temperature, °C	Pressure, bar
Timrot, Vargaftik	1935	[21]	Heated filament	70-250	1
Vargaftik, Timrot	1939	[239]	"	250-450	1-300
Vargaftik, Oleshchuk	1946	[129]	"	52-783	1
Vargaftik, Gmirnova	1956	[37]	Coaxial cylinders, heated filament	176-505	1
Vargaftik, Tarzimanov	1959- 1960	[240]	Heated filament	320-720	5-500
Vines	1960	[27]	Coaxial cylinders	270-550	1
Geler, Schafer	1961	[25]	Heated filament	100-1760	1
Tarzimanov	1962	[241]	"	230-420	25-175
Keyes, Vines	1963	[242]	Coaxial cylinders	139-370	1-180
Vukalovich, Cherleyeva	1963	[243]	Coaxial cylinders, nonstationary	550-660	100-1500
Amirkhanov, Adamov	1963	[244]	Flat layer	350-450	200-400
Vargaftik, Ziminna	1964	[245]	Heated filament	330-300	1
Venart	1965	[246]	Coaxial cylinders	130-250	1-40
Brain	1968	[247]	The same	170-603	1

NOT REPRODUCIBLE

At the Sixth International Conference (1963) there was a careful examination of an entire collection of experimental data on the thermal conductivity of water and water vapor. On the basis of the most reliable experimental data an international table was compiled for the thermal conductivity of water and water vapor for the range  $t = 0-700^{\circ}\text{C}$  and  $p = 1-500$  bar. Moreover, calculated equations were adopted, according to which these tables were compiled.

For the thermal conductivity of water these tolerances were established:

$\pm 2\%$  in the region  $0 < t \leq 300^{\circ}\text{C}$ ;  
 $\pm 5\%$  in the region  $300 < t \leq 350^{\circ}\text{C}$ .

For water vapor at  $p = 1$  bar the tolerances amount to:

$\pm 3\%$  in the region  $100 \leq t \leq 400^{\circ}\text{C}$ ;  
 $\pm 4\%$  in the region  $400 \leq t \leq 700^{\circ}\text{C}$ ;

when  $p > 1$  bar the tolerance is equal to  $\pm 6\%$ .

For the region close to critical ( $350-450^{\circ}\text{C}$  at  $p = 200-500$  bar), since the experimental data were obtained only in one work [244], the tolerance was established at  $\pm 10\%$ .

All the material on thermal conductivity, which were examined at the Sixth International Conference on the properties of water and water vapor, are described in detail in the reports of N. B. Vargaftik and M. P. Bukalovich [3], Kestin and Whitelaw [248], and Mayninger and Grigull [249]. In these reports and the book of M. P. Vukalovich, S. L. Rivkin, A. A. Aleksandrov [250] there are also block diagrams and international tables and equations for the thermal conductivity of water and water vapor. One should note that for the thermal conductivity of water in a wide temperature range of  $0-300^{\circ}\text{C}$  the tolerance has been established at  $\pm 2\%$ . In



connection with the fact that water is of great interest, as a sample substance which is often used for calibrating instruments with respect to thermal conductivity, it is advisable to examine the possibility of adopting a lower tolerance for the values of thermal conductivity of water in a more narrow temperature range. For the temperature range from 0-200°C various authors have obtained a significant quantity of experimental values for thermal conductivity. Figure 60, taken from work [248], shows divergences in the experimental data from the international tables. From the overall number of 320 experimental points divergences up to 1% exist in 92% of the points, and those up to 1.2% - 98% of the points. Thus, for the basic mass of the experimental data obtained by various authors, divergences from the generalizing equation represent a value on the order of 1%. The root mean square divergence is less than 1%. As concerns the effect of natural radiation for thermal conductivity, the experiments of Poltz [45] demonstrated that at temperatures of 25°C the thermal conductivity of water does not depend on the thickness of the layer ( $L = 0.5-2$  mm), i.e., the effect of natural radiation is disregardably small. The calculations show that up to temperatures of 200°C at  $L \approx 0.5$  mm the effect of radiation may be not greater than 0.2%, which is connected with the large value of the thermal conductivity of water. Therefore, it is possible to recommend for the thermal conductivity of water in the temperature range of 0 to 200°C a tolerance of  $\pm 1\%$ . In this temperature range values of the thermal conductivity of water may be used as standard data with a tolerance of  $\pm 1\%$ . Tables 66 and 67 show the values of thermal conductivity of water and water vapor, calculated from the equations adopted by the international conference. For the range close to critical, for which the international conference did not adopt calculation equations, the tables were compiled from the equation of S. L. Rivkina [251], an equation which well describes the international block tables and the experimental data in the region.

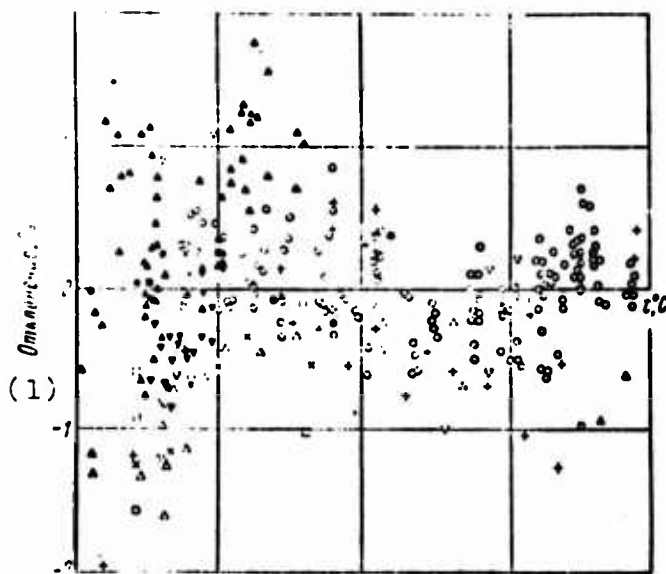


Fig. 60. Divergences of the experimental data on the thermal conductivity of water from the international tables.

KEY: (1) Deviation, %.

Table 66. Recommended values of the thermal conductivity of water and water vapor on the saturation line.

t, °C	$\lambda \cdot 10^3$ , $\text{вт}/(\text{м} \cdot \text{град})$		t, °C	$\lambda \cdot 10^3$ , $\text{вт}/(\text{м} \cdot \text{град})$	
	(1) жидкости	(2) пара		(1) жидкости	(2) пара
0	569	17,6	190	671	35,7
10	586	18,2	200	664	37,5
20	602	18,8	210	657	39,4
30	617	19,4	220	648	41,5
40	630	20,1	230	639	43,9
50	643	20,9	240	629	46,5
60	653	21,6	250	617	49,5
70	662	22,3	260	604	52,8
80	669	23,1	270	589	56,6
90	675	23,9	280	573	60,9
100	680	24,8	290	557	66,0
110	683	25,8	300	540	71,9
120	685	26,7	310	522	79,1
130	687	27,8	320	503	87,8
140	687	28,8	330	482	98,9
150	686	30,0	340	460	113
160	684	31,3	350	435	130
170	681	32,6	360	401	150
180	676	34,1	370	338	183

KEY: (1) Liquid; (2) Vapor.

Designation:  $\text{вт}/(\text{м} \cdot \text{град}) = \text{I}/(\text{m} \cdot \text{deg})$ .

Table 67. Recommended values of the thermal conductivity of water and water vapor at various temperatures and pressures.

t, °C	$\lambda \cdot 10^3, \text{ W/(m} \cdot \text{deg)}, \text{ with } p, \text{ bar}$															
	1	20	40	60	80	100	150	200	210	220	230	240	250	300	400	500
0	569	570	572	574	575	577	581	585	586	586	587	588	589	592	599	606
10	568	569	570	572	574	575	580	583	584	585	586	587	588	591	597	604
20	603	605	607	608	610	612	616	620	620	621	622	623	623	627	634	640
30	617	620	622	623	625	627	631	634	635	636	637	637	638	642	648	654
40	630	633	635	637	638	640	644	648	648	649	650	650	651	654	661	666
50	643	645	647	648	650	651	655	659	660	660	661	662	662	666	672	678
60	653	655	657	658	660	661	665	669	670	670	671	672	672	676	682	687
70	662	664	665	667	668	670	674	677	678	679	679	680	681	684	690	695
80	669	671	673	674	676	677	681	684	685	686	686	687	688	691	697	702
90	675	677	679	680	682	683	687	690	691	691	692	693	693	696	702	708
100	21,5	682	684	685	686	688	691	694	695	696	696	697	698	701	707	713
110	25,2	686	687	688	690	691	694	698	698	699	700	700	701	704	710	716
120	26,0	688	689	691	692	693	697	700	700	701	702	702	703	706	712	718
130	26,9	689	690	692	693	694	698	701	702	702	703	703	704	707	714	720
140	27,7	689	690	692	693	694	698	701	701	702	703	703	704	707	714	720
150	28,6	688	689	690	692	693	696	700	700	701	702	702	703	706	713	720
160	29,5	685	687	688	690	691	694	698	698	699	700	700	701	705	711	718
170	30,4	682	683	685	686	688	691	695	696	696	697	698	698	702	709	716
180	31,3	677	679	680	682	683	687	691	692	692	693	694	695	698	706	713
190	32,2	672	673	675	677	678	682	686	687	688	688	689	690	694	702	709
200	33,1	665	667	668	670	672	676	681	681	682	683	684	685	689	697	704
210	34,1	657	659	661	663	665	670	674	675	676	677	678	678	683	691	699
220	35,1	40,0	650	652	654	656	662	667	668	669	670	671	672	676	685	693
230	36,1	40,3	640	643	645	647	653	658	660	661	662	663	664	669	678	686
240	37,1	40,8	629	632	634	637	643	649	650	652	653	654	655	660	670	679
250	38,1	41,4	616	619	622	625	632	639	640	642	643	644	645	651	662	671
260	39,1	42,1	48,9	606	609	612	620	628	630	631	632	634	635	642	653	663
270	40,1	42,9	48,7	590	594	598	607	616	617	619	621	622	624	631	643	653
280	41,2	43,8	48,8	58,1	578	582	593	602	604	606	608	609	611	619	633	643
290	42,3	44,7	49,1	58,8	580	585	577	587	590	592	594	595	597	606	622	633
300	43,3	45,7	49,6	56,1	66,9	545	559	571	573	576	578	580	582	592	609	622
310	44,4	46,7	50,3	55,8	64,7	523	539	553	555	558	561	563	566	577	596	610
320	45,5	47,7	51,0	55,9	63,3	75,2	516	532	535	538	541	544	547	560	582	597
330	46,7	48,8	51,8	56,2	62,5	72,0	491	509	513	516	520	523	526	541	566	583
340	47,8	49,9	52,7	56,7	62,1	69,9	462	483	488	491	495	499	503	520	548	568
350	49,0	51,0	53,7	57,3	62,1	68,8	104	454	458	463	467	472	476	496	529	552
360	50,1	52,1	54,7	58,0	62,3	68,1	94,8	420	425	430	435	440	445	468	501	537
370	51,3	53,2	55,7	58,8	62,7	67,8	89,3	163	206	392	385	396	406	437	479	514
380	52,5	54,4	56,7	59,7	63,3	67,8	85,9	129	147	170	185	209	322	398	453	490
390	53,6	55,5	57,8	60,6	64,0	68,1	83,6	115	126	140	150	165	188	338	423	465
400	54,8	56,7	58,9	61,6	64,7	68,6	82,2	107	115	124	134	144	156	262	388	439
410	56,0	57,9	60,1	62,6	65,6	69,1	81,2	102	108	114	124	132	141	206	348	411
420	57,3	59,1	61,2	63,7	66,5	69,8	80,8	98,3	103	108	116	123	130	177	307	382
430	58,5	60,3	62,4	64,8	67,5	70,6	80,6	95,7	99,8	104	109	116	122	160	271	352
440	59,7	61,5	63,6	65,9	68,5	71,4	80,6	94,1	97,6	101	105	110	116	148	241	323
450	61,0	62,8	64,8	67,0	69,5	72,4	81,0	93,3	96,0	99,2	103	106	111	139	217	297
460	62,2	64,0	66,0	68,2	70,6	73,3	81,5	92,4	95,0	97,9	101	104	108	131	198	274
470	63,5	65,3	67,2	69,4	71,7	74,3	82,0	92,1	94,5	97,0	99,7	103	106	125	181	253
480	64,8	66,5	68,5	70,6	72,9	75,4	82,7	92,1	94,2	96,5	99,0	102	104	120	172	236
490	66,0	67,8	69,7	71,8	74,0	76,5	83,5	92,2	94,2	96,4	98,7	101	103	118	163	220
500	67,3	69,1	71,0	73,0	75,2	77,6	84,3	92,6	94,4	96,4	98,5	101	103	116	155	207
520	69,9	71,7	73,5	75,5	77,6	79,9	86,2	93,7	95,3	97,1	98,9	101	103	113	142	186
540	72,5	74,3	76,1	78,1	80,1	82,3	88,2	95,2	96,6	98,2	99,8	102	103	112	136	170
560	75,2	76,9	78,7	80,6	82,7	84,7	90,4	96,9	98,3	99,7	101	103	104	112	123	159
580	77,8	79,6	81,4	83,3	85,2	87,3	92,7	98,8	100	101	103	104	106	113	131	153
600	80,5	82,3	84,1	85,9	87,8	89,8	95,1	101	102	103	105	106	107	114	130	149
620	83,2	85,0	86,7	88,6	90,5	92,4	97,6	103	104	105	107	108	109	116	130	147
640	85,9	87,7	89,5	91,3	93,2	95,1	100	105	106	108	109	110	111	117	131	147
660	88,7	90,4	92,2	94,0	95,8	97,7	103	108	109	110	111	112	113	119	132	146
680	91,4	93,1	94,9	96,7	98,5	100	105	110	111	112	113	115	116	121	133	147
700	94,2	95,9	97,7	99,5	101	103	108	113	114	115	116	117	118	124	135	148

NOT REPRODUCIBLE

Table 68. Investigation of the thermal conductivity of heavy water.

Author	Year	Liter- ature source	Method	Temperature, °C	Pressure, bar
Meyer, Eigen	1953	[252]	Flat layer	10-60	1
Challoner, Powell	1956	[55]	" "	2-80	1
Vargaftik, Oleshchuk, Belyakova	1959	[253]	Heated filament	25-355	1-208
Ziebland, Burton	1960	[254]	Coaxial cylinders	75-260	24-294
Vargaftik, Oleshchuk	1962	[255]	Heated filament	145-500	1-250
Vargaftik, Zaytseva	1963	[256]	" "	107-500	1
Bakker, Brokkau	1964	[147]	" "	108-250	1
Le Neindre, Johannin, Vedar	1964- 1968	[235]	Coaxial cylinders	40-370	1-1000

## Heavy Water D<sub>2</sub>O

The thermal conductivity of heavy water has been studied in the liquid and gas phases. The most detailed investigations have been carried out for the liquid phase. Data on the experimental works are shown in Table 68. During the period from 1953-1956 various authors [55, 252] measured the thermal conductivity at temperatures from 2 to 80°C. Then, by the heated filament method in work [253] the thermal conductivity of liquid D<sub>2</sub>O was measured at temperatures from 24° to 355°C and pressures only slightly exceeding saturation pressure. In work [254], by the method of coaxial cylinders during the study of the effect of pressure on thermal conductivity, experimental data at  $t = 75-260^\circ\text{C}$  and  $p = 24-294$  atm were obtained. At the same time Vodar and coworkers published the results of measurements of the thermal conductivity in the liquid phase at  $t = 60-360^\circ\text{C}$  and  $p = 1-1000$  atm. The results of experiments of all the authors correspond well with one another in the range of temperatures from room temperature to 260°C; divergences amount to 2%. These divergences increase in proportion to the rise in temperature and with  $t = 300^\circ\text{C}$  go as high as 5%.

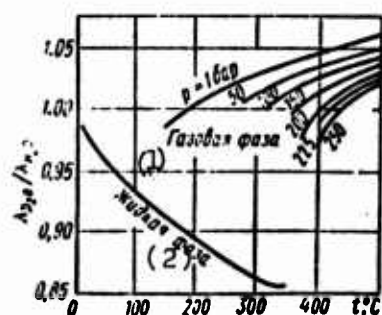


Fig. 61. Dependence of the relationship of the thermal conductivity of D<sub>2</sub>O to the thermal conductivity of H<sub>2</sub>O ( $\lambda_{D_2O}/\lambda_{H_2O}$ ) on the temperature.

KEY: (1) Gas phase; (2) Liquid phase.

The first investigations of the thermal conductivity of heavy water in the gas phase were conducted at atmospheric pressure in the temperature range from 100 to 500°C [256] and at  $t = 108-260^\circ\text{C}$  in work [147]. The results of these works are in complete agreement

with one another. In the region of high pressures a single work [255] was done, in which measurements were made at pressures from 1 to 250 atm in a temperature range from 145 to 500°C.

Table 69. The relationships of the thermal conductivity of  $D_2O$  and  $H_2O$  for the liquid phase on the saturation line.

$t, ^\circ C$	$\lambda_{D_2O}/\lambda_{H_2O}$	$t, ^\circ C$	$\lambda_{D_2O}/\lambda_{H_2O}$	$t, ^\circ C$	$\lambda_{D_2O}/\lambda_{H_2O}$
10	0,988	130	0,925	250	0,881
20	0,975	140	0,922	260	0,875
30	0,969	150	0,919	270	0,870
40	0,961	160	0,916	280	0,865
50	0,954	170	0,911	290	0,862
60	0,952	180	0,906	300	0,859
70	0,947	190	0,905	310	0,855
80	0,944	200	0,904	320	0,851
90	0,938	210	0,900	330	0,848
100	0,933	220	0,896	340	0,844
110	0,930	230	0,891	350	0,852
120	0,927	240	0,887		

Table 70. The relationships of the thermal conductivity of  $D_2O$  and  $H_2O$  for the gas phase at various temperatures and pressures.

$t, ^\circ C$	$\lambda_{D_2O}/\lambda_{H_2O}$ with p, bar					
	1	100	150	200	225	250
100	0,97	—	—	—	—	—
150	0,985	—	—	—	—	—
200	1,000	—	—	—	—	—
250	1,010	—	—	—	—	—
300	1,020	—	—	—	—	—
320	1,024	—	—	—	—	—
340	1,028	0,997	—	—	—	—
360	1,032	1,012	0,998	—	—	—
380	1,036	1,023	1,008	0,972	—	—
400	1,040	1,026	1,010	1,002	0,981	0,971
420	1,044	1,027	1,016	1,008	1,001	0,994
440	1,047	1,035	1,024	1,013	1,007	0,999
460	1,050	1,037	1,028	1,019	1,014	1,008
480	1,053	1,039	1,030	1,025	1,018	1,016
500	1,055	1,041	1,034	1,027	1,023	1,021

The results obtained showed that in the liquid phase the thermal conductivity of  $D_2O$  is less than the thermal conductivity of  $H_2O$ , wherein the difference increases in proportion to the rise in temperature. For the gas phase the ratio  $\lambda_{D_2O}/\lambda_{H_2O}$  is a function of temperature and pressure.

Let us note that the temperature conductivity of  $D_2O$  was measured by almost all the authors using the same equipment as for the measurements of the thermal conductivity of  $H_2O$ . Therefore, the ratios  $\lambda_{D_2O}/\lambda_{H_2O}$  do not contain systematic errors and have a sufficiently high degree of accuracy — the degree of error has a value on the order of 0.5-1%. These values are given in Table 69 and 70 and in Fig. 61.

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