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LIQUID THERMAL CONDUCTIVITY RESEARCH AT MOSCOW UNIVERSITY

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Аннотация—Статья представляет краткий обзор работ по исследованию теплопроводности жидкостей, выполненных в Московском университете. Описаны 9 экспериментальных методов исследования, в значительной мере новых. Приведены результаты измерений теплопроводности 83 органических жидкостей. Обсуждаются закономерности концентрационной и температурной зависимости теплопроводности растворов, в том числе бинарных жидких систем вблизи критической точки. Приведены результаты исследования изменений теплопроводности при переохлаждении и кристаллизации жидкостей. Кратко изложены результаты исследования теплопроводности жидких металлов.

NOMENCLATURE

λ,	thermal conductivity [kcal/m h degC];
a,	thermal diffusivity [cm^2/s];
ρ,	density, [g/cm^3];
M,	molecular weight;
c,	weight concentration.

THE PAPER is a brief review of experimental research which has been carried out at the Moscow State University, at the Chair of Molecular Physics, Physical Department, headed by A. S. Predvoditelev. These works are contributions to the series of researches aimed at an investigation into the nature of the liquid state and primarily at revealing the mechanism of thermal motion. The behaviour of thermal conductivities of the following different groups of substances has been studied: normal and associated organic liquids and their mixtures, inorganic substances and their solutions, metal melts. The aim of the research was to find general laws of temperatures and concentration behaviour with thermal conductivity, to formulate the relation between the value of thermal conductivity and physico-chemical properties of the material, to compare thermal conductivities of the substance in liquid and solid states (including supercooling).

In this work great attention is given to the development of the experimental technique, particularly, to the development of a series of measurement methods which would be convenient for practical applications. This was achieved by the use of various relative methods. Application of the relative methods allows us to avoid the determination of the heat flux, which simplifies essentially both the design of the devices and the measurement procedure. Besides, the measurement of relative values does not involve any noticeable increase of errors since at present relative data are available on heat conductivity of a number of pure substances which may be used as reference standards.

1. MEASUREMENT METHODS

For convenience of the description we classify the methods of measurements into two categories: the class of steady-state methods and the class of unsteady-state methods. We shall begin the description of each class with the methods with plane isotherms, and then we shall discuss the methods with cylindrical isotherms.

A. Steady-state methods

1. The device which is based on the well-known plane-layer method of Christiansen is described in paper [1]. The test cell of the device consists of a plane copper heater; a thin layer of the tested material which is placed between the heater and a copper disk; a layer of the reference material (glass) between that disk and another lower disk used as a cooler. Measurements of thermal conductivity are carried out by records of the temperature differences due to heat flux which passes first through the layer of the test material and then through the standard one. As a precaution against heat losses from the lateral surface, a guard ring is used. Temperature differences are measured by differential thermocouples imbedded in channels of the appropriate copper disk.

The measuring system is placed into an autoclave that allows measurements at pressures up to 100 atm and in a temperature range from the room temperatures up to 300°C. For calibration of the device, substances with known thermal conductivities are used.

The device may be used for measurement of thermal conductivity of both gases and liquids, the error being within 2–3 per cent.

The main advantage of the device in comparison with the similar installations used for absolute measurements lies in the absence of the necessity to use guard heaters for the elimination of heat losses from the lateral surfaces and the top. Thus the design of the device is simplified and the measurements require less time.

The disadvantage of the device is its large size. In this respect the method discussed is inferior to the well-known hot-wire technique. However, the use of this relative method of a plane layer has in a number of cases essential advantages over other methods, particularly for the measurements of highly viscous substances, plastic and polymer materials. The use of the modified device for study of the behaviour of thermal conductivity of melts is described in [2].

2. Another modification of the relative plane-layer method is developed with a special purpose of measuring thermal conductivity of very small quantities of liquids [3]. In Fig. 1 a schematic drawing of such a device is shown.

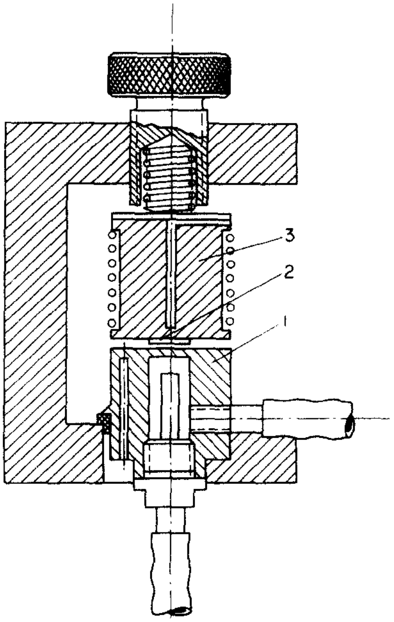

FIG. 1.

A drop of liquid fills a flat narrow gap between the thermostat surface of a cooler (1) and the metal-covered surface of a plane semi-conductor pellet (2) of a diameter of about 1 cm. This pellet is soldered to a copper cylinder (3) which is provided with a heater. If in this system a temperature difference exists, at the surfaces of the semi-conductor element thermal e.m.f. arises whose value depends on the thermal conductivity of the test liquid, other things being equal. Thus, this device calibrated with liquids of which thermal conductivity is known may serve as an instrument for the measurement of thermal conductivity of liquids. To avoid the effect of the temperature difference between the heater and cooler on the instrument readings, for calibration and measurements the ratio of the thermal e.m.f. of the semi-conductor element to the temperature difference between the heater and cooler measured by the thermocouple should be used rather than the e.m.f. itself. This ratio remains constant even when the temperature difference is several times larger or smaller. Thus, the procedure consists in measuring two electromotive forces. The main advantage of the instrument is that very small quantities of liquid are necessary for the measurement and that the procedure consumes little time. The disadvantage is the difficulty or impossibility of its application to volatile liquids which quickly evaporate out of the slot.

3. The third variety of the relative plane-layer method is based on quite a new principle.

In this method the junction of the thermocouple may be displaced normally to a thin liquid layer (see Fig. 2). This is a characteristic feature of the technique. A junction (1) together with another junction (2) which is placed at the liquid interface forms a differential thermocouple. The junctions of another differential thermocouple (3 and 4) are placed at the surfaces of a glass plate below the liquid layer. The differential thermocouples are connected in such a way that their electromotive forces are subtracted from each other. With a downward temperature gradient, the readings of the thermocouple will be zero in a certain position only which depends linearly on the thermal conductivity of the tested liquid. Thus in this method measurements are carried out by readings of the micrometer screw controlling displacement of the thermocouple corresponding to zero reading of the galvanometer. Used for non-volatile substances, the instrument produces an error below 2–3 per cent [3].

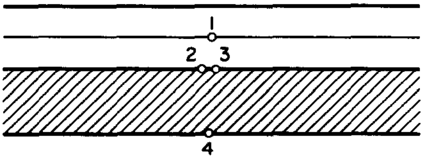

FIG. 2.

Extreme simplicity of measurements allows this method to be recommended especially for engineering application.

4. The next steady-state method belongs to a class with cylindrical symmetry of the temperature field. The method is a relative measurement variant of the hot-wire method which is widely used for measuring thermal conductivity [4].

A measuring cell is essentially the same as an ordinary one. It consists of a taut wire placed along the axis of a capillary. Every possible precaution should be provided to avoid temperature changes in the capillary. The procedure is the following. The measuring cell is connected as one arm of the Wheatstone bridge. With a certain inlet voltage, the bridge is balanced by the resistance of one of its arms. Then the inlet voltage is changed and the bridge is unbalanced due to the change of the wire temperature. From the measured values of this unbalance and the inlet voltage, we may determine the thermal conductivity of the tested material, if identical measurements have also been made with a material of known thermal conductivity.

The advantages of this method over the usual absolute one is as follows. First, the procedure involves no measurements of geometrical sizes of the cell. Moreover, it demands no careful choice of a capillary and centering a wire that is usually a very difficult operation. Finally, the relative nature of the measurements involves no calibration of platinum resistance and determination of zero resistance of the instrument. The advantages mentioned are peculiar to all relative variants of the hot-wire method. The variant discussed possesses an additional essential advantage: the measured quantities can be obtained with the accuracy of three or four significant figures. In the ordinary hot-wire method the situation is quite different. The temperature of the wire (as well as of the wall) is determined directly from the resistance which requires careful measurements within five or six significant figures.

The technique described may equally be applied to liquids and gases. The error with necessary corrections is 1–2 per cent.

5. The peculiarity of another modification of the hot-wire technique is the use of two identical measuring tubes connected as two arms of the Wheatstone bridge exactly the same way as in gas analysers. The bridge is balanced when all tubes are filled with the standard liquid. If one tube is then filled with the tested liquid, the magnitude of the unbalance will be directly associated with the difference of the reverse of the thermal conductivities of the test and standard liquids. Such a compensating circuit allows taking records of extremely small changes in thermal conductivities or the measurement of appreciable differences of thermal conductivities with very small temperature differences across the thickness of the liquid layer, viz. up to tenths or even hundredths of a degree. This device therefore allows measurements of thermal conductivity in the critical region of binary liquid mixtures (see below). The procedure discussed is rather complicated and demands careful control of temperature. The method is best employed for precision-measurements in a narrow temperature range.

6. The last of the steady-state methods to be discussed is a relative modification of the coaxial cylinder technique [3–5].

This method will be discussed in more detail since it was used in the majority of our works.

The sectional view of the instrument is shown in Fig. 3. The whole apparatus is made of glass. The test liquid fills the gap (1) between the internal (2) and external (3) tubes. The internal tube is filled with mercury in which a heater element is completely immersed (a nichrome wire in a two-channel porcelain straw) and the junction of a differential thermocouple (5). The second junction is at a temperature of the thermostat liquid circulating in a jacket (6). The measurements consist of the determination of the electromotive force of the thermocouple. e for a known voltage across the heater E. From general considerations it follows that at a fixed temperature for a certain instrument the quantity

$$x = e/E^2 \tag{1}$$

depends solely on the liquid thermal conductivity λ. In particular, if in the vicinity of the thermocouple the temperature field is purely radial (no noticeable axial gradients), this dependence should be of the form

$$(x - b)\lambda = c \tag{2}$$

where b is a coefficient including the temperature gradients in the glass walls and superheat of the wall relative to the thermostat liquid; c is the coefficient depending primarily on the geometry of the instrument. The quantities b and c should be found from calibrating runs with two substances. The dependence of these

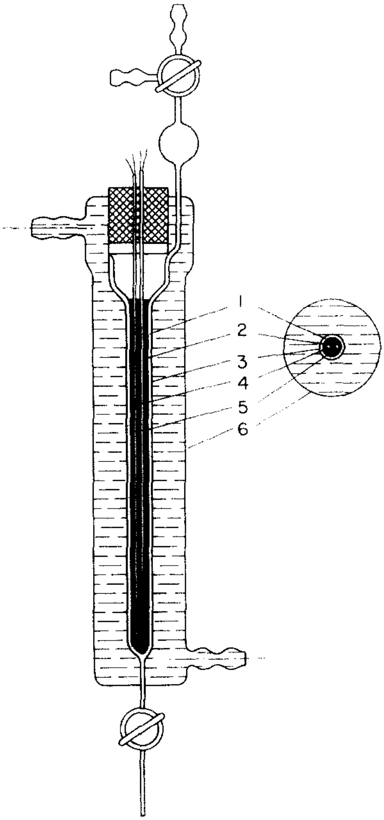

FIG. 3.

values on the temperature is rather weak and for calibration it is quite sufficient to have temperature intervals of 20 degC.

A detailed analysis of the validity of formula (2) (smallness of the axial gradient effect) is carefully carried out. It was found with optimal dimensions of the instrument (the length of the mercury tube is ~70 mm, the diameter of the internal tube is 4 mm, the gap between the tubes is 0·5–1 mm, the thermocouple junction is at a distance of 25–30 mm above the lower end of the heater) formula (2) should be valid over quite a wide range of thermal conductivities from very small values (for gases) to the highest (for liquids). This is confirmed also by the results of the experimental study. In Table 1 are presented the values of constant C which are obtained with different calibrating substances and thermostat liquids (the values of b are different for different thermostat liquids).

Table 1

Thermostat liquid	Calibrating liquids	C
water	mercury + water	0·304
	mercury + toluene	0·308
	mercury + air	0·304
	mercury + argon	0·302
kerosene	water + toluene	0·305

The main advantages of the instrument are the simplicity of design and measuring procedure, short response time and small quantities of test materials. The instrument may be used without any adjustment for measurement of thermal conductivities of both gases and liquids. The essential advantage is that the instrument allows measurement of thermal conductivity of electrically conducting liquids as well as toxic and chemically aggressive substances. The precision of measurements with this instrument is from 1 to 3 per cent (absolute value), though the sensitivity is considerably higher. Small changes of thermal conductivity may be recorded up to one-hundredth per cent. This instrument is very convenient in the temperature range from room temperature to 100°C when water may be used as a thermostat liquid. The instrument may also be successfully used for measurements in a wider range of temperatures (from -30 to 200°C). The procedure described and some modifications of the method are widely used in scientific research and some applications (see, for example, [6–10]).

B. Unsteady-state methods

1. The first unsteady-state method to be discussed is the measurement of thermal diffusivity [11]. The method is based on the use of the so-called regular thermal regime of the second kind, i.e. a constant rate of heating at a stage when the effect of the initial conditions becomes negligible [12]. The essence of the method is the determination of thermal diffusivity from the constant temperature difference at two points in the fluid investigation.

The test fluid fills a flat gap between two metal surfaces. Inside the liquid layer and near one of the faces, are fixed flat resistance thermometers which are fabricated by burning silver paste into thin mica sheets (see Fig. 4). The thermometers are connected as arms of a bridge circuit balanced in a steady state so that unbalance of this circuit is proportional to the temperature difference of the gauges. To achieve a constant rate of heating (from some tenths of a degree to several degrees per minute) it was placed inside a thermally insulated vessel filled with water (2 l. in volume) provided with a mixer and a heater.

The measurement procedure with such an instrument is rather simple, but the accuracy of the results is not very high (of about 4 per cent).

2. Another non-steady method is the measurement of thermal activity [13]. This term was originally devised by Luikov [14] to call the quantity $\lambda/\sqrt{a}$ which is a combination of thermal conductivity λ and thermal diffusivity a. The method consists essentially in measuring temperature fluctuations of a small inertia gauge (strips of metal foil or wire) heated by

alternating current. The amplitude of these fluctuations depends on the coefficient of thermal activity of the medium surrounding the gauge, other things being equal. For the measurement of the fluctuation amplitude the gauge is connected as an arm of a Wheatstone bridge, balanced relatively to the voltage of the feeding frequency. The frequency of the e.m.f. at the bridge diagonal due to the temperature fluctuations of the gauge is three times that of the supply frequency. The signal of the three-fold frequency is increased by a selective amplifier and measured.

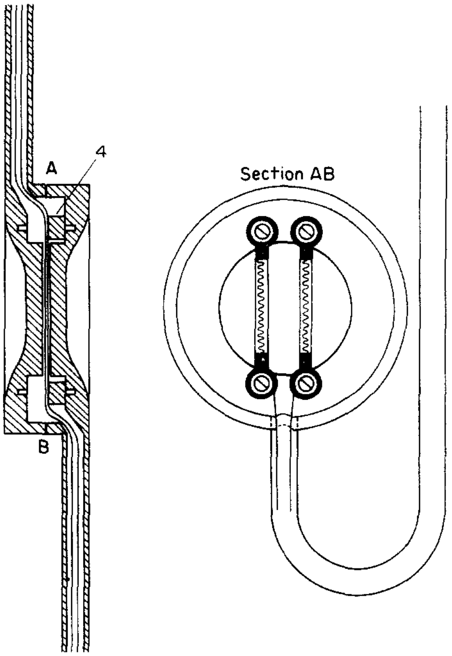

FIG. 4.

The gauge used in the work was a foil strip, several centimeters in length, 1 mm in width and 0·01 mm in thickness. The foil was placed into a small glass with the test liquid of which constant temperature was provided by a water flow from an ultrathermostat. The position of the foil in the glass may be arbitrary since the temperature waves at the frequencies of about 100 cm/s attenuated almost completely at a distance of 0·1 mm. This was also the reason why convective flows in the liquid had no effect on the results.

The experience with this method [13, 15] allows the conclusion to be made that the error in the coefficients of thermal activity is about 3 per cent. The main advantage of the method is simplicity of the test cell. For measurements, extremely small quantities of liquid may be used and the time for steady state to set in is very short.

A similar method is developed by American authors for gases [16, 17].

3. The method of simultaneous determination of series of properties of liquid metals (thermal conductivity, heat capacity and thermal diffusivity) was briefly reviewed in [18]. In that method radial temperature waves are used which arise in a test sample (a crucible with liquid metal) due to periodic electronic heating [19]. It is a combination of several methods developed earlier for measurement of thermal diffusivity [20–22] and heat capacity [22, 23]. The last modification of the device allows measurements of the group of thermal properties at temperatures up to 1800°K.

2. DISCUSSION AND RESULTS

2.1. *Thermal conductivity of organic liquids. Results.*

The author's results for thermal conductivity of eighty-three substances [25, 26] are summarized in Table 2. The majority of the data are obtained in a narrow temperature range in which thermal conductivity varies with temperature, following the linear dependence:

$$\lambda = \lambda_{30}[1 - \alpha(t - 30^\circ)] \quad (3)$$

In the table the values of λ_{30} and α are presented and the temperature range studied is shown.

For comparison of the results with the data of other authors, it is desirable to find the range of the values which may be considered the most

Table 2

Formula	Substances	Temperature range		kcal/m h degC	$\alpha\ 10^3$ deg C^{-1}
		lower	upper		
CCl_4	carbon tetrachloride	15	90	$0{\cdot}087_5$	2
$CHBr_3$	bromoform	10	90	0·087	2·1
$CHCl_3$	chloroform	15	70	0·101	1·8
CH_2O_2	formic acid	15	90	$0{\cdot}23_5$	—
CH_4O	methanol	15	90	0·175	1
$C_2H_4Br_2$	ethyl bromide (1·2-ethylen dibromide)	15	90	$0{\cdot}086_5$	1·3
$C_2H_4Cl_2$	ethylen dichloride (1·2-ethylene dichloride)	15	80	$0{\cdot}115_5$	1·5
C_2H_4O	acetaldehyde	10	30	$0{\cdot}159_5$	$2{\cdot}_6$
$C_2H_3ClO_2$	monochloracetic acid (supercooled)	40	90	0·145	non-linear
$C_2H_4O_2$	acetic acid	5	90	0·143	1
$C_2H_4O_2$	methyl-formate	10	40	0·163	1·2
C_2H_5Br	ethyl-bromide	15	45	$0{\cdot}087_5$	2
C_2H_5J	ethyl-iodide	20	70	$0{\cdot}077_5$	$1{\cdot}_0$
C_2H_5ON	acetamide	65	100	0·216	~0
C_2H_6O	ethanol	15	90	0·140	$1{\cdot}_9$
$C_2H_6O_2$	ethylen-glycol	15	90	0·220	−1·0
C_3H_6O	acetone	15	50	$0{\cdot}139_5$	$2{\cdot}_2$
$C_3H_6O_2$	ethyl-formate	15	50	0·134	(3)
$C_3H_6O_2$	methyl-acetate	10	50	0·13	2
C_3H_8O	propanol	15	80	0·120	1·4
C_3H_8O	*i*-propanol	10	80	0·244	1
$C_3H_8O_3$	glycerine	15	90	$0{\cdot}140_5$	$-2{\cdot}_3$
$C_4H_6O_2$	acetaldehyde	15	90	0·128	1·5
$C_4H_8O_2$	butyric acid	10	90	$0{\cdot}123_5$	0·9
$C_4H_8O_2$	ethyl-acetate	15	90	$0{\cdot}123_5$	2
$C_4H_8O_2$	propyl-formate	15	70	$0{\cdot}124_5$	1·7
$C_4H_{10}O$	butanol	15	90	0·123	1·4
$C_4H_{10}O$	*i*-butanol	15	90	0·115	1·0
$C_4H_{10}O$	diethylether	10	70	0·114	$2{\cdot}_3$
$C_5H_4O_2$	furfurol	15	90	0·152	1·0
C_5H_5N	pyridine	10	90	0·144	1·2
$C_5H_6O_2$	furfurol alcohol	10	90	$0{\cdot}154_5$	~0
$C_5H_8O_2$	acetyl acetone	10	90	0·132	1·0
$C_5H_{10}O$	isovalerianic aldehyde	10	90	0·113	1·9
$C_5H_{10}O_2$	butylformate	15	90	0·125	1·8
$C_5H_{10}O_2$	propylacetate	15	90	0·120	1·5
$C_5H_{11}O_2N$	isoamylnitrite	10	70	$0{\cdot}099_5$	1·5
C_5H_{12}	*i*-pentan	10	30	0·096	2
$C_5H_{12}O$	*n*-amyl alcohol	15	90	$0{\cdot}114_5$	0·9
$C_5H_{12}O$	*i*-amyl alcohol	15	90	$0{\cdot}114_5$	0·8
$C_6H_4Br_2$	*p*-dibromo-benzene (90°C)	87	100	$0{\cdot}081_5$	
C_6H_5Br	bromo-benzene	15	90	$0{\cdot}096_5$	1·5
C_6H_5Cl	chloro-benzene	15	90	0·109	1·5
C_6H_5F	fluoro-benzene	15	70	0·116	1·5
C_6H_5J	iodo-benzene	15	90	$0{\cdot}085_5$	1·0
$C_6H_5NO_2$	nitro-benzene	15	90	0·129	1·0
C_6H_6	benzene	15	70	$0{\cdot}123_5$	$1{\cdot}_8$
C_6H_6O	phenol (50°C)	40	90	$0{\cdot}124_5$	1
C_6H_7N	aniline	15	90	0·148	0·5
C_6H_{12}	cyclohexane	10	40	$0{\cdot}105_5$	1·8
C_7H_6O	benzoaldehyde	15	90	$0{\cdot}130_5$	0·8
C_7H_8	toluene	15	240	$0{\cdot}115_5$	1·75
C_7H_8O	benzil alcohol	15	90	0·135	0·5
$C_6H_{10}O$	cyclohexanon	20	90	$0{\cdot}118_5$	1·2
$C_6H_{10}O_3$	acetoacetic ester	15	90	0·134	1·0

Table 2—continued

Formula	Substances	Temperature range		kcal/m h degC	10^3 degC^{-1}
		lower	upper		
$C_6H_{12}O_2$	butyl acetate	15	90	0·116	1·9
C_6H_{14}	hexan	15	60	0·106	2·0
C_7H_8O	*o*-crezol	10	90	0·132	~0
C_7H_8O	*m*-crezol	10	90	0·128	
C_7H_8O	anizol	15	30	$0{\cdot}124_5$	0·9
C_7H_9N	*p*-toluidine (50°C)	50	100	0·141	1
C_7H_9N	*o*-toluidine	10	90	0·140	~0
$C_7H_{14}O_2$	amylacetate	15	90	0·109	1·7
$C_7H_{14}O_2$	*i*-amylacetate	15	90	0·111	1·8
C_7H_{16}	heptane	10	90	0·108	1·8
C_8H_8O	acetophenon	10	90	$0{\cdot}126_5$	0·4
C_8H_{10}	*o*-xylene	15	90	$0{\cdot}113_5$	1·3
C_8H_{18}	octane	30	40	$0{\cdot}109_5$	
C_8H_{18}	isooctane	15	90	0·085	1·8
$C_8H_{18}O$	octyl alcohol (secondary)	15	90	0·118	1·0
C_9H_7N	chinoline	15	90	0·126	0·8
C_9H_{12}	cumene	15	90	0·107	1·3
$C_9H_{20}O$	nonilic acid	15	90	0·128	1·1
$C_{10}H_7Br$	α-bromnaphthalene	15	90	$0{\cdot}094_5$	0·4
$C_{10}H_{15}N$	diethylaniline	15	90	0·116	0·7
$C_{13}H_{10}O_2$	salol (supercooled)	20	80	$0{\cdot}116_5$	~0
$C_{16}H_{22}O_4$	dibutyl phthalate	10	90	0·120	0·3
$C_{18}H_{36}O_2$	stearic acid (70°C)	70	100	0·148	0·7
	castor oil	15	90	0·154	0·5
	cylinder oil	15	90	$0{\cdot}117_5$	0·5
	vaseline oil	30	90	0·108	1·4
	turbine oil	40	80	$0{\cdot}109_5$	1·5
	transformer oil	30	—	0·112	—

reliable. To minimize the subjectivity of estimation, the following procedure was developed [26]. First, mean values of thermal conductivity were found for the materials for which not less than three data of different authors were available. (At that time there were about thirty substances of this kind.) Then deviations from the mean values were calculated for the data of each author. In the majority of cases deviations from the data of an individual author were not regular, and the accuracy of the corresponding data could be evaluated by the mean square deviation. The reverse values of the squared deviation were used as weight factors for the next weighted averaging of the same data, and then the procedure was repeated. The third approximation of this method produced as a rule the results which were almost the same as the previous approximation.

The method of averaging described allowed the author not only to obtain the data which may be considered as most reliable, but also to characterize in a definite way the data of each particular author. Ridel's data were found to be most reliable (the square mean deviation was 0·4–0·8 per cent). The mean error of the present author's data was 1·9 per cent. Tables of the most reliable thermal conductivity data in 1961 for 150 organic liquids, obtained with this method are presented in [26] and [27]. The author believes that at present it would be reasonable to repeat this work including the data of the recent publications.

The results of comparison of the data presented in Table 2 with the values obtained in subsequent works (see, for example [28–32]) allow to conclude that as a rule the present author's data agree with the results of other workers within 1 or 2 per cent.

Direct examination of the material presented in Table 2 allows a number of qualitative conclusions on the close correlation between the thermal conductivity and the molecular structure of the material. Thus the behaviour of thermal conductivity at a certain temperature in homologous series is not universal, although usually thermal conductivity decreases with increasing molecular weight. Thermal conductivity of substances with forked molecular chains are as a rule smaller than for isomers with non-forked chains. Substitution of hydrogen atoms by halogens decreases thermal conductivity. This effect increases from fluor to iodine and is more pronounced when a greater number of atoms is substituted. Presence of hydroxil groups in a molecule increases thermal conductivity as well as the introduction of nitro- and amino-groups.

The relations discussed above may be useful for estimation of thermal conductivity of compounds which are not yet studied, particularly of the type of freon and perfluor compounds.

The next step in the analysis of the available experimental data requires the introduction of the physical ideas about the mechanism of the process of heat transfer in liquids connected with various ideas about the nature of thermal motion.

Before the discussion of this fundamental problem we shall consider the experimental correlations of the temperature dependence of thermal conductivity, especially that such consideration allows conclusions useful for further discussions.

2.2. *Temperature dependence of heat conductivity in organic liquids*

Table 2 demonstrates that thermal conductivity of the overwhelming majority of substances in the temperature range up to 100°C decreases linearly with temperature. Glycerine and ethylen glycol alone have a positive temperature coefficient.

In the analysis of the laws of the behaviour of thermal conductivity with temperature, it seems useful to assume that the quantity which controls the behaviour of the thermal conductivity with changing temperature and pressure is the specific liquid volume.

According to Predvoditelev [33, 34], thermal conductivity of unassociated liquids should be related with the density by the equation

$$\lambda = B\rho^{\frac{4}{3}} \tag{4}$$

where B is the coefficient independent of the temperature.

For the verification of this relation the results should be used of the measurements of thermal conductivities which are obtained in the widest possible temperature range. Figure 5 furnishes data for toluene and shows the validity of formula (4). This formula may be also confirmed by measurements in a narrower temperature ranges. In Fig. 6 values of $\lambda_{t_1}/\lambda_{t_1}$ are compared with the values of $(\rho_{t_1}/\rho_{t_1})^{\frac{4}{3}}$ (each point corresponds to a particular substance). The fact that the points lay along the straight line at an angle of 45° illustrates the validity of formula (4).

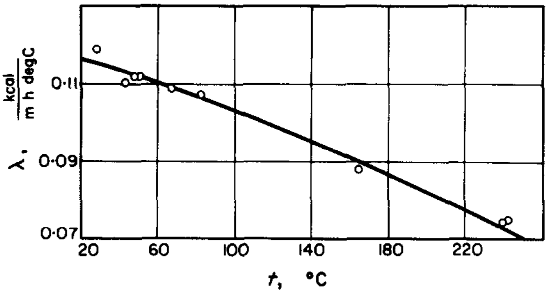

FIG. 5.

2.3. *Relation of thermal conductivity of organic liquids with other properties*

As it is known, attempts to develop the theory of thermal conductivity for liquids by successive usage of the apparatus of the statistical physics yield at present no satisfactory quantitative results. In the analyses of the relation of thermal conductivity with other properties two trends exist. The first is associated with the name of Bridgeman who considered the heat transfer by random acoustic waves to be similar to Debye's heat-conduction theory for a solid body. The other trend is represented by works of Predvoditelev who has developed an original approach to the description of collective motions in liquid [33–36].

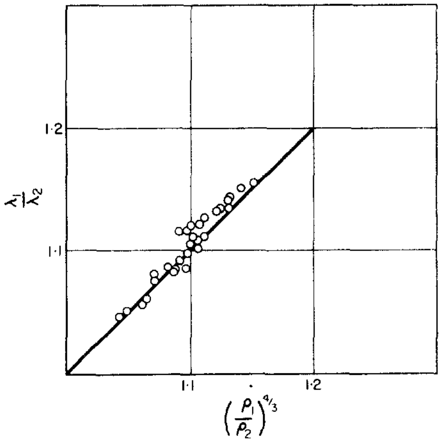

FIG. 6.

The vast material on thermal conductivity of organic liquids of different nature allowed the author to analyse the relation between thermal conductivity and those physical parameters of liquids which should reflect the mechanism of thermal motion and the heat-transfer processes. These parameters are the sound velocity (or exactly speaking, hypersound velocity) in the liquid, specific heat of a unit volume, mean intermolecular distance. Bearing in mind that the relation of thermal conductivity with these and other quantities are not so far definitely determined, the present author tackled the problem of these relation from the point of view of correlation between thermal conductivity and the properties mentioned above.

Thus examination of the correlation between thermal conductivity and the sound velocity allows us to see that close relation exists between these properties and to find that the regression line of the corresponding statistical group passes through the original of the coordinate system. Deviations from the most probable straight line λ/u = const. for the class of nonassociated substances with one exception (methyl-formate) is not above 20 per cent, and the mean square value is 9·8 per cent. For particular groups of substances the deviations are even smaller. Thus for ethers the mean square deviation is 8·5 per cent, for aromatic and cyclic hydrocarbons and their haloid derivatives is 5·6 per cent, for aliphatic hydrocarbons and their haloid substances is 7·3 per cent. Formulae of such kind may apparently be useful for the prediction of thermal conductivity of the liquids for which direct experimental data are absent.

Still closer relation is found between thermal diffusivity and acoustic velocity, especially, if the quantities in question are compared not at a prescribed, but at the fixed corresponding temperature. For the whole class of non-associated substances the mean square deviation is 6·7 per cent. In two cases only (carbon tetrachloride and ethyl-bromide) deviations are above 10 per cent; for the rest it is 5·3 per cent. A combination of thermal conductivity with specific heat capacity and density also enters into another important relation which is known in the West as Weber's formula and as Predvoditelev's formula in the Soviet Union [34]

$$a = \sqrt[3]{(M/\rho)} = c(T). \tag{5}$$

The square mean deviation for unassociated substances with this formula is 8·7 per cent.

2.4. *Thermal conductivity of solutions*

The concentration dependence of thermal conductivity of liquid solutions has been studied mainly by the method discussed in Section A.6. Thus studied were: twelve systems of unassociated components [37], ten systems with a single associated component [38], aqueous solutions of three alcohols [39], solutions of some salts and acids. Some typical curves are shown in Fig. 7.

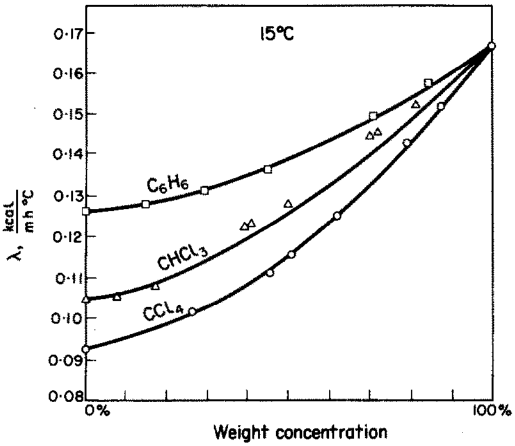

FIG. 7.

Negative deviations from the additivity and concave concentration curves are peculiar to concentration dependence of thermal conductivity of the systems considered (except, for example, aniline-acetic acid, characterized by chemism [40]). Simplest of all is the dependence of the thermal conductivity on weight concentrations. The deviations from additivity are described by a single parabolic formula

$$\lambda = \lambda_1 C_1 + \lambda_2 C_2 - \alpha C_1 C_2. \qquad (6)$$

The coefficient α which describes the value of the deviation from additivity correlates explicitly with the difference of thermal conductivities of the components. In particular, for solutions of the substances with very similar thermal conductivity, $\alpha \sim 0$. For solutions of unassociated substances, α is found to be almost directly proportional to $|\lambda_2 - \lambda_1|$:

$$\alpha = K|\lambda_2 - \lambda_1| \qquad (7)$$

$K = 0{\cdot}72$. For solutions of associated substances K ranges from 0·5 to 1, and for aqueous solutions from 0·3 to 0·7.

Formula (6) describes the concentration dependence of thermal conductivity with an accuracy close to that of the experimental data; the maximum deviations of the values predicted by the formula from the measured data is as a rule less than 3 per cent. This is illustrated by Fig. 7 where solid curves are plotted by formula (6) for $K = 0{\cdot}72$.

It should be noted that formulae (6) and (7) allow description of both concentration and temperature dependences of thermal conductivity of the solutions, since the coefficient K in equation (7) is actually independent of the temperature. The effect may be easily traced in the case of aqueous solutions of organic liquids where the components depends on the temperature in a different way. Figure 8 illustrates dependence of the thermal conductivity on concentration and temperature (aqueous solutions of isopropyl alcohol). Solid lines are calculated from formula (6).

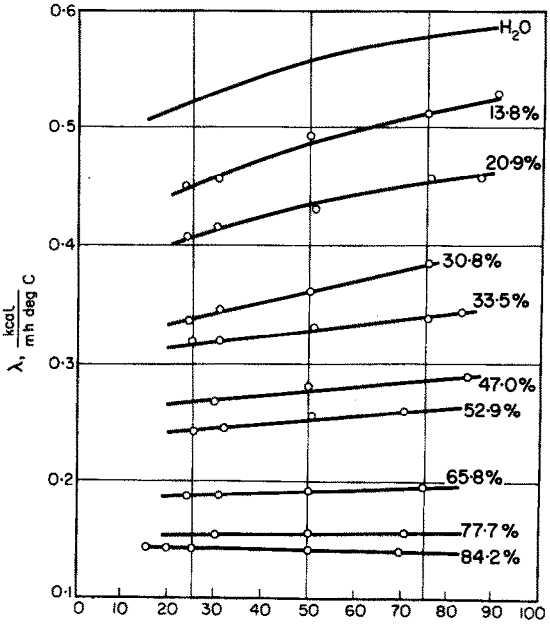

FIG. 8.

2.5. *Critical point thermal conductivity of liquid binary solutions*

Study of critical point thermal conductivity have been carried out with the aim to investigate the behaviour of the substance near the critical point "liquid–vapour" where thermal conductivity shows sharp maxima as reported in a number of references.

The procedure described in Section A.5 was used in this work since it allows measurements with extremely small temperature drops and the nearest possible approach to the critical point.

A specially developed system allowed the control of the temperature within ~0·001°C. Temperature drops in a layer of the tested fluid ranged from 0·01 to 0·3 degC, the temperature interval being 0·02–0·03 degC. Before each transition to a new temperature the system was carefully mixed. The results are obtained for the system nitrobenzene–hexane, nitrobenzene–heptane, methyl alcohol–hexane (upper critical point) and thriethylamine–water (lower critical point) [41]. Figure 9 illustrates the results (nitrobenzene–hexane). No anomalies of thermal conductivity at the critical point are revealed both for this system and others.

Plausible explanations of this effect are discussed in Skripov's work [42].

2.6. *Thermal conductivity of supercooled liquids*

Information about the behaviour of thermal conductivity of supercooled liquids may be obtained from the data on concentration dependence of thermal conductivity for solutions in the temperature range below the crystallization point of one or both components. Application of formulae (5) and (6) allows obtaining thermal conductivity of the appropriate component in a state which may be reasonably considered supercooled. The calculations on the basis of Ridel's experimental data are presented in reference [39]. Diagram in Fig. 10 illustrates that thermal conductivities in the state of supercooling follows the natural continuation of the line for the normal state. The results of the direct measurements of supercooled salol, monochloracetic acid, acetophenone, cresol and $Na_2S_2O_3 \cdot 5H_2O$ [15] lead to the same conclusion. Two typical curves are shown in Fig. 11.

Similar smooth curves are also found for thermal conductivity of salol and acetophenone [15].

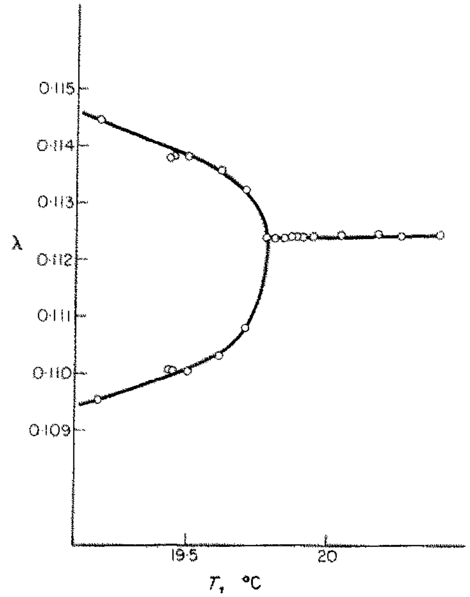

FIG. 9.

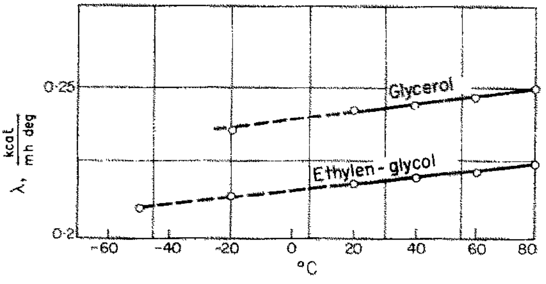

FIG. 10.

The results obtained lead to the conclusion that the heat-transfer mechanism in supercooled liquids is probably qualitatively the same as that for liquids in a normal state.

2.7. *Behaviour of thermal conductivity in fusion*

The study of the thermal conductivity of the same substance in solid and liquid states is useful for the investigation of the heat-transfer mechanism in liquids. The data obtained by one and the same method for both phases is of great value. Such measurements were carried out by the method described in Section A.6 [43]. Two typical curves are presented in Fig. 12; the curves for seven other substances are of the same shape. In all cases thermal conductivity of the solid phase exceeds that of the liquid phase. The difference between the thermal conductivity of the solid and liquid states for different substances varies considerably from a two-fold difference (hyposulphite) to a two per cent difference (cyclohexane). Thermal conductivity of solid stearic acid which has been studied in detail is found to be different. When cooling was rapid, the thermal conductivity of the phase was higher than during slow cooling. This difference may be attributed to the difference in the microstructure.

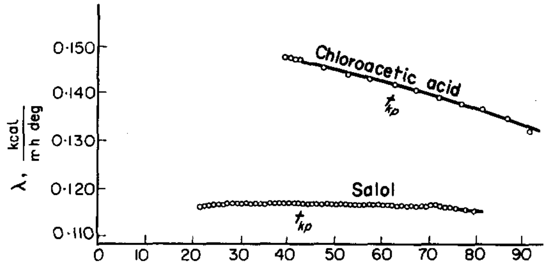

Fig. 11.

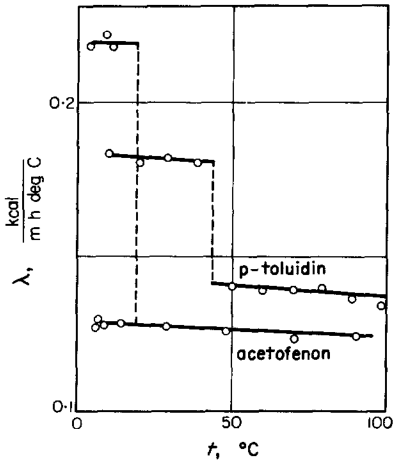

Fig. 12.

2.8. *Thermal conductivity of liquid metals*

The study of the laws of the behaviour of liquid metals is allied to the study of the other complex of thermal properties of solid and liquid metals at high temperatures [44, 18].

The main aim of this study is to find general laws of the behaviour of some properties in connection with the problem on thermal motion and transfer processes in solid and liquid metals.

The methods of measuring the combination of thermal conductivity, thermal diffusivity, heat capacity of liquid metals are described in Section B.3. Besides, the classical method of temperature waves developed by Angström was used. At present data have been obtained on lead, tin, bismuth, cadmium and copper.

In Fig. 13 thermal conductivities of tin and lead are shown. An almost complete independence of thermal conductivity from temperature is peculiar to these metals (for tin

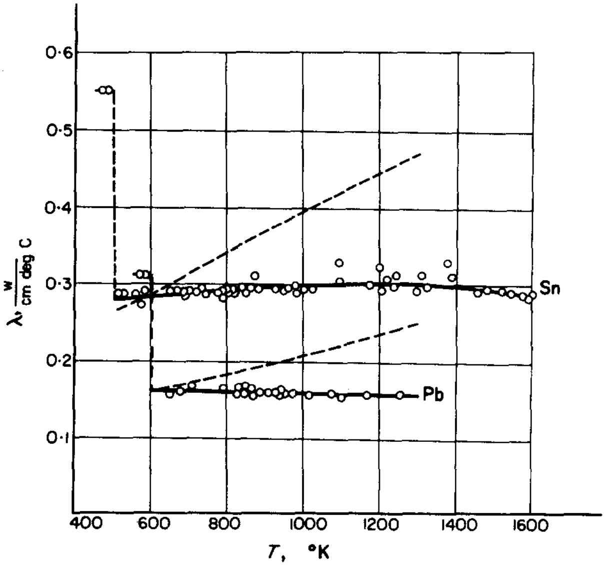

Fig. 13.

this effect was studied at temperature intervals over 1000°).

An increasing deviation from the Wiedemann–Franz law in the form of the decrease of Lorentz numbers is a characteristic feature of heat transfer in liquid metals. In Fig. 13 thermal conductivity curves corresponding to the case when the Wiedemann–Franz law is valid are shown by a dotted line. Near the fusion point the Lorentz constant for liquid metals is usually somewhat higher than for the solid phase [this apparently is connected to the fact that the decrease of the lattice component of thermal conductivity in fusion is proportionally smaller than the decrease of the electronic thermal conductivity. (see previous section)]. However with increasing temperature, the Lorentz number begins to decrease comparatively rapidly, passing rather quickly through the value of the "classical" Sommerfeld number. According to our observations such behaviour of the Lorentz number is typical for liquid metal, but we have refrained from discussing in this paper any possible explanations of this effect.

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Abstract—The paper is a brief review of works relating to thermal conductivities of liquids which have been carried out at the Moscow University. Nine essentially new experimental methods are described in the paper. Thermal conductivities of eighty-three organic liquids are reported. The laws are discussed of the dependence of thermal conductivity on the concentration and temperature of solutions including the cases of liquid binary systems in the critical region. The behaviour of thermal conductivity of liquids under super-subcooling and crystallization is presented. A brief discussion of thermal conductivities of liquid metals is given.

Résumé—L'article est une courte revue des travaux se rapportant aux conductivités thermiques des liquides qui ont été effectués à l'Université de Moscou. Neuf méthodes expérimentales essentiellement nouvelles sont décrites dans l'article.

Les conductivités thermiques de 83 liquides organiques sont présentées. On discute les lois reliant à la concentration et à la température la conductivité thermique de solutions parmi lesquelles des systèmes binaires liquides dans la région critique. On donne la variation de la conductibilité thermique de liquides surfondue et pendant la cristallisation, ainsi qu'une courte discussion des conductivités thermiques des métaux liquides.

Zusammenfassung—Es wird ein kurzer Überblick gegeben über Forschungsarbeiten, die an der Moskauer Universität über die Wärmeleitfähigkeit von Flüssigkeiten durchgeführt wurden. Neun wesentlich neue Versuchsmethoden sind in der Arbeit beschrieben. Die Wärmeleitfähigkeiten von 83 organischen Flüssigkeiten werden mitgeteilt. Gesetzmässigkeiten über den Einfluss von Konzentration und Temperatur auf die Wärmeleitfähigkeit von Lösungen einschliesslich flüssiger binärer Systeme im kritischen Bereich werden diskutiert. Der Verlauf der Wärmeleitfähigkeit von Flüssigkeiten bei Unterkühlung und Kristallisation wird angegeben. Die Wärmeleitfähigkeit flüssiger Metalle wird kurz diskutiert.