THERMAL CONDUCTIVITY OF LIQUID TETRACHLORIDES

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The thermal conductivity of liquid carbon, silicon, titanium, germanium, and tin tetrachlorides over the −20 to +60°C temperature range was measured by the transient relative null method with a hot wire.

The relation between the thermal conductivity of a liquid and its molecular mass was studied by Horrocks, McLaughlin, and Ubbelonde [1], who compared the thermal conductivities of liquids of different isotopic molecular contents: benzene and deuterobenzene, cyclohexane and deuterocyclohexane, etc. A shortcoming of this method is that the difference between the mass of a normal and an isotropically substituted molecule cannot be made large enough, usually less than 10%.

The object of this study was to analyze the effect of molecular mass on the thermal conductivity of liquids with the variation in molecular mass much wider than would be possible in the isotope substitution method, and to compare this effect with that of other molecular parameters. The study was made with tetrachlorides of group IV elements in the Periodic Table: CCl_4, $SiCl_4$, $TiCl_4$, $GeCl_4$, and $SnCl_4$ with their respective molecular masses in the ratio 1 :1.1 :1.23 :1.39 :1.72. These molecules have a simple structure:

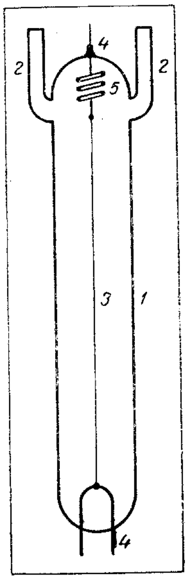

Fig. 1

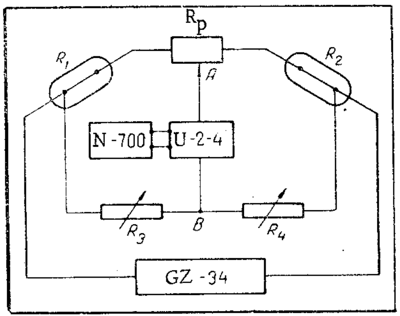

Fig. 2

Fig. 1. Schematic diagram of a test cell.

Fig. 2. Schematic diagram of the electrical apparatus: R_1, R_2 are the cells, R_3, R_4 are the resistance boxes, R_p is the tuning potentiometer, GZ-34 is the audio oscillator, U-2-4 is the instrument amplifier, and N-700 is the loop oscillograph.

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TABLE 1. Values of k_iM_i Obtained in Measuring the Ratio of Thermal Conductivities, CCl_4 to Toluene, and Results of Interpolation to kM = 0

T=1,6 °C		T=20 °C		T=40 °C	
$\frac{1}{\gamma_i}$	k_iM_i	$\frac{1}{\gamma_i}$	k_iM_i	$\frac{1}{\gamma_i}$	k_iM_i
1,0522	149,4	1,0522	173,0	1,0522	187,3
	151,9		174,4		188,5
	150,7		166,2		186,6
	147,6		165,6		184,7
	148,3		169,3		184,1
1,0318	126,5	1,0318	146,3	1,0318	171,6
	132,6		143,7		170,5
	132,1		143,2		167,6
	136,3		154,1		169,3
	128,2		150,6		167,0
1,0000	95,0	1,0000	111,9	1,0000	122,1
	99,6		115,7		120,4
	99,2		118,7		125,4
	96,8		113,3		116,9
	100,0		109,1		115,7
0,8514	—61,5	0,8842	—23,6	0,8842	—12,5
	—65,4		—27,3		—16,8
	—59,4		—22,2		—16,8
	—63,2		—29,1		—17,6
	—57,7		—23,1		—17,4
0,8842	—24,1	0,8514	—62,8	0,8514	—60,6
	—23,5		—63,8		—64,8
	—24,6		—65,8		—65,8
	—23,2		—68,5		—63,5
	—23,9		—68,5		—64,5
$\frac{1}{\gamma}=0,9082$ $s=0,0026$		$\frac{1}{\gamma}=0,9061$ $s=0,0033$		$\frac{1}{\gamma}=0,9004$ $s=0,0037$	

the chlorine atoms form a tetrahedron around the center atom. The shape of these molecules is nearly spherical. The character of the intermolecular forces is the same in all these liquids; it is determined by the interaction between electron shells in the chlorine atoms.

Experimental Part. The measurements were made by the relative null method with a hot wire under transient thermal conditions [2]. Specimens of the test liquid and the reference liquid were poured separately into two identical cells shown schematically in Fig. 1. The inside diameter of a glass cylinder (1) was 13 mm. Liquid was poured in through tubes 2 which had been fused into the cylinder at the top. A platinum wire 3 0.03 mm in diameter and 130 mm long stretching along the cylinder axis served as both heater and resistance thermometer. The electrical resistance of this wire was 6.66 Ω. The wire was silver-soldered to platinum leads 4. One of the leads terminated into a spring 5 of platinum wire 0.3 mm in diameter, by means of which wire 3 was held tight. The amount of tension was set by suspending a 5 g plummet on the lead which had been soldered to the cylinder last.

The cells were placed in an aluminum case inside a vessel with double walls. The vessel was thermally insulated on the outside. A liquid (water–alcohol solution of ethylene glycol) from a model TS-24 thermostat was circulated between the walls. The temperature inside the vessel was maintained at the necessary level within 0.05°C.

The electric circuit is shown schematically in Fig. 2. The two cell resistances R_1 and R_2 were connected here as separate arms of the bridge. The other two arms were variable resistances R_3 and R_4 adjustable so as to make the total resistance constant and equal to 511.0 Ω. Model R14 plug-type resistance boxes of class 0.1 accuracy were used here in the arms R_3 and R_4. Resistance R_p was here a special-purpose potentiometer made of constantan wire with a total resistance of 9 Ω and with a silver contact. The bridge drew 100 mA supplied from a 400 Hz oscillator model GZ-34. Into the diagonal branch with the indicating meter was also connected a model U2-4 instrument amplifier. The narrow-band sensitivity of this amplifier was 1 mV per full scale deflection. The amplified signal was recorded with a model N-700 oscillograph.

TABLE 2. Thermal Conductivity of Tetrachlorides, $\lambda \cdot 10^2$ W/m·°K

Temperature, °C	−20	−10	0	10	20	30	40	60
CCl_4	11,26	11,13	11,00	10,85	10,70	10,57	10,45	10,20
$SiCl_4$	—	—	—	10,14	9,99	9,87	9,76	—
$TiCl_4$	14,80	14,71	14,61	—	14,42	—	14,22	14,03
$GeCl_4$	11,00	10,83	10,72	10,54	10,39	—	10,15	9,90
$SnCl_4$	11,95	11,83	11,78	—	11,45	—	11,20	10,93

Following the procedure, the measurements consisted in finding an arms ratio $R_3/R_4 = \gamma$ at which the bridge circuit would become insensitive to a change in the resistances R_1 and R_2 of the platinum wires due to their heatup after energization with electric current. This ratio was calculated from measurements of the rate at which the magnitude of the bridge unbalance changed between various settings of the arms ratio γ_i. To each value of the arms ratio γ_i set by the resistance boxes R14 corresponded a definite setting on the potentiometer R_p. The potentiometer setting was matched by means of plugs in such a way that, as the bridge supply was switched on, the unbalance voltage changed from some maximum level (within the range of the instrument scale) down to zero. In the transient hot-wire method the unbalance voltage is proportional to the logarithm of the heatup time. The graph of voltage versus logarithm of time is a straight line. The slope of this line k_i multiplied by the bridge constant M_i (which depends on γ_i) is proportional to the difference between $1/\gamma_i$ in a given measurement and $1/\gamma$ corresponding to zero bridge sensitivity. The values of γ_i and the values of k_iM_i determined in tests were then used for calculating the unknown ratio γ for zero bridge sensitivity ($k = 0$). The ratio of thermal conductivities λ/λ_{ref}, test liquid to reference liquid, was calculated by the formula

$$\lambda/\lambda_{ref} = \gamma/\gamma_0, \tag{1}$$

with γ_0 denoting the arms ratio obtained in calibration tests with the reference liquid in both cells.

Evaluation of Errors. The errors of the transient hot-wire method have been thoroughly analyzed by Falcao in [3]. According to preliminary calculations by the formulas and the graphs in [3], all errors due to the cell geometry, the heatup time (approximately 5 sec), the heat convection, and the temperature drift were negligibly small under our test conditions. Most significant, much larger than the other errors, was the error due to stray heat leakage from the wire-heater terminals to the soldered joints. In absolute measurements by the hot-wire method with the same cell and the same test substances this error would be, according to [3], 0.9, 1.0, and 1.1% at 0.3, 1.0, and 5.0 sec after the current has been switched on. In relative measurements by the hot-wire method this error was largely compensated and equal to $\Delta\lambda/\lambda_{ref}$ ($\Delta\lambda = \lambda - \lambda_{ref}$), i.e., a fraction of the error in absolute measurements. For the test substances and carbon tetrachloride as the reference liquid this fraction amounted to 0.07, for carbon tetrachloride with toluene as the reference liquid this fraction was 0.26. Therefore, those errors were respectively 0.06, 0.07, 0.08 and 0.23, 0.26, 0.29%.

The errors in this method are: the error in determining the ratio of arm resistances in the bridge circuit, the error in setting the amplifier gain in the instrument by calibration, and the error in measuring the distances on an oscillogram. The first of these errors may be considered equal to double the error in the resistance box, namely 0.2%. The second and the third errors together are estimated as 2%. Of such a magnitude are also the errors in the test values of k_iM_i, from which the ratio $1/\gamma$ for a zero bridge sensitivity is calculated. The error $\delta(1/\gamma)$ in determining $1/\gamma$ is a function of the relation error $\delta(kM)/kM$ and of the interval $\Delta(1/\gamma) = 1/\gamma_i - 1/\gamma_i$ used for finding $1/\gamma$ by interpolation. If the interpolation is based on the results of two measurements only, then

$$\delta\left(\frac{1}{\gamma}\right) = \frac{\delta(kM)}{kM}\,\Delta\left(\frac{1}{\gamma}\right). \tag{2}$$

In our experiment the minimum interval $\Delta(1/\gamma)$ was 0.116, the maximum interval was 0.201 (Table 1). Therefore, the upper limit of error $\delta(1/\gamma)$ lay between $0.116 \cdot 2\% = 0.23\%$ and $0.201 \cdot 2\% = 0.40\%$.

For a statistical estimate of the error and for a complete checkout of this entire procedure, control measurements were made with liquids whose thermal conductivity had been checked many times against

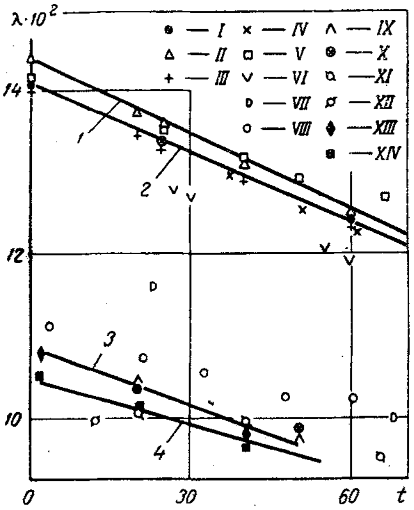

Fig. 3

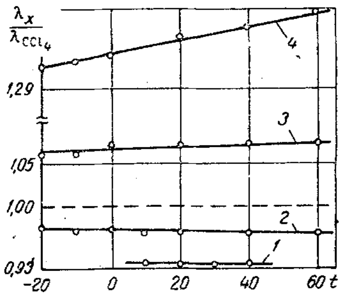

Fig. 4

Fig. 3. Comparison between the thermal conductivities ($\lambda \cdot 10^2$ W/m·°K) of toluene and CCl_4. Data for toluene according to: Riedel [4] (I), Challoner and Powell [5] (II), Ziebland and Burton [6] (III), Horrocks and McLaughlin [7] (IV), Vargaftik [8] (V), Rastorguev, Grigor'ev, and Bogatov [9] (VI). Most reliable estimates according to [5] (1), according to [10] (2). Data for CCl_4 according to Davis [11] (VII), Challoner and Powell [5] (VIII), Riedel [4] (IX), Schmidt and Leidenfrost [12] (X), Mason [13] (XI), Weber [14] (XII). Our calculations based on [5] (XIII and 3), on [10] (4). Temperature t (°C).

Fig. 4. Ratio of thermal conductivities, tetrachlorides to CCl_4: $\lambda_{SiCl_4}/\lambda_{CCl_4}$ (1), $\lambda_{GeCl_4}/\lambda_{CCl_4}$ (2), $\lambda_{SnCl_4}/\lambda_{CCl_4}$ (3), $\lambda_{TiCl_4}/\lambda_{CCl_4}$ (4). Temperature t (°C).

carbon tetrachloride and toluene. The ratio of the thermal conductivities, CCl_4 to toluene, was measured at temperatures 1.6, 20, and 40°C. In Table 1 are given the values of $1/\gamma_i$, the corresponding test values of k_iM_i, the sought values of $1/\gamma$ calculated by interpolation to $kM = 0$ by the method of least squares, and the standard deviation of test points from the straight interpolation line. For the parameter s, which characterizes the error of a single measurement, we obtained the values 0.0026, 0.0033, and 0.0037. This agreed with the earlier estimate of 0.23-0.40%. The error $\delta(1/\gamma)$ depends on the number of test points n used for interpolation and, at a given probability p, is equal to the product of $s/\sqrt{n-2}$ by the appropriate coefficient in the Student's equation.

The $\lambda_{CCl_4}/\lambda_{toluene}$ ratios according to formula (1) were compared with data published in the technical literature. The results of this comparison are given in Fig. 3. In the upper part has been plotted the thermal conductivity of toluene according to test values obtained by Riedel [4], Challoner and Powell [5], Ziebland and Burton [6], Horrocks and McLaughlin [7], Vargaftik [8], and Rastorguev, Grigor'ev, and Bogatov [9]. The straight lines 1 and 2 represent average values suggested as the most reliable ones: 1 based on the estimate by Challoner and Powell [5], 2 based on the estimate by McLaughlin [10]. In the lower part has been plotted the thermal conductivity of CCl_4 according to test values obtained by Davis [11], Challoner and Powell [5], Riedel [4], Schmidt and Leidenfrost [12], Mason [13], and Weber [14]. The straight lines 3 and 4 are based on our test points. If the values suggested in [5] and represented by line 1 are taken for the thermal conductivity of toluene as the reference liquid, then the values for the thermal conductivity of CCl_4 will fit on line 3. If the values suggested in [10] (line 2) are taken for toluene, then the values for CCl_4 will fit on line 4. Our data lie within the limits given by the various other authors.

Thermal Conductivity of Tetrachlorides. The test substances met the following specifications: CCl_4 grade GDR chemically pure (99.5% basic substance), $SiCl_4$ extra pure, $TiCl_4$ (99.5% basic substance), $GeCl_4$ and $SnCl_4$ chemically pure. The specimens were not additionally purified.

In Fig. 4 are shown the ratios of thermal conductivity, test liquids to CCl_4, with that of the latter taken as unity at all temperatures and indicated on the diagram by a dashed line. The absolute values of thermal conductivity were calculated with the values for CCl_4 taken from [5]. The results are shown in Table 2.

The results of measurements show that the thermal conductivity of liquids in the test series is not a monotonic function of the molecular mass. The thermal conductivity decreases from CCl_4 to $SiCl_4$ and then increases to a maximum for $TiCl_4$, after which it again decreases for $GeCl_4$ and increases for $SnCl_4$. A smooth change in the thermal conductivity will be noted only in a series of four test substances, namely of those whose center atoms belong to the same subgroup of group IV: the carbon group C, Si, Ge, Sn. The thermal conductivity of these substances can be represented as a quadratic function of the molecular mass. The inverse proportion between the thermal conductivity and the square root of the molecular mass applies only to the first two members of this series: CCl_4 and $SiCl_4$ with the thermal conductivity of $SiCl_4$ 1.07 times smaller and the square root of its molecular mass 1.05 times larger than those of CCl_4 respectively. Further along the series, the thermal conductivity does not decrease but increases and, as a result, the product of thermal conductivity by the square root of the molecular mass does not remain constant but increases as 1 :1.17 :1.41. These numbers indicate that the Horrocks–MacLaughlin–Ubbelohde theory [1] for isotopically substituted molecules cannot be extended to molecules of this class. Significant in our case is probably not only the mass but also other molecular parameters: their dimensions, the mean intermolecular distances, the elastic moduli of intermolecular forces, etc. The effect of these parameters other than the mass is evident in the thermal conductivity of $TiCl_4$, where the center atom belongs to another subgroup of group IV elements. The thermal conductivity of $TiCl_4$ differs greatly from that of the other four liquids and cannot be fitted on the same curve representing the thermal conductivity as a function of the molecular mass. The reason for this is that the parameters of a $TiCl_4$ molecule do not have the same values which a molecule of the same mass would have if it belonged to the carbon subgroup. Considering the differences between molecular radii and between intermolecular distances in the liquid tetrachlorides series as a function of the molecular mass, one notes that these parameters increase monotonically only as far as the tetrachlorides of the same subgroup are concerned. These same parameters of a $TiCl_4$ molecule drop out of this trend. Its radius is larger and the intermolecular distance is smaller than those of tetrachloride molecules in the carbon subgroup.

NOTATION

k	is the slope of the voltage versus logarithm of time curve;
M	is the bridge constant;
R	is the electrical resistance;
s	is the standard deviation of test points from the straight interpolation line;
γ	is the bridge arms ratio;
γ_0	is the bridge arms ratio at zero sensitivity during calibration with the same reference liquid in both cells;
Δ	is the difference between two values;
δ	is the error;
λ	is the thermal conductivity.

Subscript

i	denotes to measurement at a certain bridge arms ratio.

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