THERMAL CONDUCTIVITY OF TETRAMETHOXYSILANE, TETRAETHOXYSILANE, AND TETRAETHYL TIN

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The results of an investigation of the thermal conductivity and density of liquid tetramethoxysilane, tetraethoxysilane, and tetraethyl tin in the temperature range − 13.5° to +90°C are given.

In this work, which is a continuation of the research in [1, 2], we investigated the thermal conductivity and density of liquid $(CH_3O)_4Si$, $(C_2H_5O)_4Si$, and $(C_2H_5)_4Sn$ to find out how the thermal conductivity of liquids is affected by replacement of the halogen atom by the radicals CH_3O^-, $C_2H_5O^-$, and $C_2H_5^-$. The experimental apparatus and the measurement procedure are described in [1]. The investigations were carried out by the relative null hot-wire method in transient conditions [1]. The error of the relative thermal conductivity measurements was estimated as 0.4%. Toluene was used as a reference liquid. The absolute values of the thermal conductivity were calculated from the values recommended for toluene in [3].

The results of the measurements are given in Table 1. In the investigated temperature ranges the thermal conductivity can be expressed satisfactorily as a linear function of temperature,

$$\lambda = \lambda_0 - bt. \tag{1}$$

The coefficients in Eq. (1) were calculated from the experimental points by the method of least squares.

We measured not only the thermal conductivity, but also the density $\rho(t)$ of these liquids. The density was measured with a pycnometer, which was calibrated with water. The measurements for all the substances were made in the temperature range 0.6–60°C. The values of the density of water at different temperatures were taken from [4].

The main sources of error in the density measurements were the errors in weighing, in the determination of the liquid level in the pycnometer capillary, and temperature variation. The liquid was weighed on an analytical balance to an accuracy of 0.1 mg. The smallest mass of liquid used in the experiment was 50 g. Hence, the error in mass determination was $2 \cdot 10^{-4}$%. The liquid level in the pycnometer capillary was determined to within half a scale division, which gave a relative error of 10^{-3}%. The temperature of the liquid was kept constant to within 0.05°C with a TS-24 thermostat. The error due to change in temperature with the thermostat in operation was $6 \cdot 10^{-3}$%. This was the largest of all the errors and determined the accuracy of density measurement.

TABLE 1. Thermal Conductivity Values

Substance	$\lambda \cdot 10^2$, $W \cdot m^{-1} \cdot {}^\circ K^{-1}$							
	−13,5°	0°	10°	20°	40°	60°	80°	90°
$(CH_3O)_4Si$	—	—	16,26	16,09	15,57	14,86	14,36	14,09
$(C_2H_5O)_4Si$	14,43	14,19	—	13,59	13,16	12,69	12,18	11,99
$(C_2H_5)_4Sn$	13,83	13,61	—	13,13	12,61	12,22	11,67	11,47

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TABLE 2. Density of Liquids

Substance	$\rho(t)$, kg/m^3						
	0,6°	10°	20°	30°	40°	50°	60°
$(CH_3O)_4Si$	—	1051,45	1039,60	1027,34	1015,51	1002,91	990,26
$(C_2H_5O)_4Si$	955,39	945,51	935,05	924,29	914,05	903,99	894,67
$(C_2H_5)_4Sn$	1216,39	1205,19	1193,51	1181,51	1170,33	1158,44	1146,07

TABLE 3. Coefficients in Eqs. (1) and (2)

Substance	M	$\lambda_0 \cdot 10^2$, W/m·°K	$b \cdot 10^2$, W/m·°K^2	ρ_0, kg/m^3	a, kg/m^3·°K
$(CH_3O)_4Si$	152,2	16,69	0,028	1063,96	1,222
$(C_2H_5O)_4Si$	208,3	14,20	0,024	955,65	1,029
$(C_2H_5)_4Sn$	234,9	13,65	0,024	1217,05	1,177

The results of the measurements are given in Table 2. Throughout the investigated temperature interval the density is a linear function of the temperature and can be expressed by the equation

$$\rho(t) = \rho_0 - at. \tag{2}$$

The coefficients ρ_0 and a in Eq. (2) were calculated by the method of least squares.

Table 3 gives the values of the coefficients in Eqs. (1) and (2), and also the molar mass M. The root-mean-square error of the deviation of the experimental points from the straight line given by (2) was $2.5 \cdot 10^{-2}\%$ for tetramethoxysilane and $4.5 \cdot 10^{-2}\%$ for tetraethoxysilane.

Table 4 compares the thermal conductivities of the liquids investigated in the present work with the thermal conductivities of previously investigated tetrachlorides and tetrabromides. The data for $SiCl_4$, $GeCl_4$, and $SnCl_4$ and taken from [1] and those for $GeBr_4$ and $SnBr_4$, from [2]. An examination of these data shows that an increase in the mass of the particles surrounding the central atom leads to a reduction of the thermal conductivity of the liquid. This applies to all the investigated substances except $SiCl_4$. The failure of $SiCl_4$ to fit into the series tetramethoxysilane, silicon tetrachloride, and tetraethoxysilane can be attributed to the high thermal conductivity of the first and third compounds.

The atoms (groups of atoms) surrounding the central atom of the molecule affect the temperature dependence of the thermal conductivity. For tetrachlorides $\partial\lambda/\partial T$ is $2.0 \cdot 10^{-4}$ W·m^{-1}·°K^{-2} [1], and for tetrabromides of germanium and tin it is $1.2 \cdot 10^{-4}$ W·m^{-1}·°K^{-2} [2]. Tetraethoxysilane and tetraethyl tin molecules have practically the same environment. For these two liquids $\partial\lambda/\partial T$ has the same value — $2.4 \cdot 10^{-4}$ W·m^{-1}·°K^{-2}. Conversion of tetraethoxysilane to tetramethoxysilane by replacement of the ethyl group by the methyl group leads to a change in $\partial\lambda/\partial T$: for tetramethoxysilane it is $2.8 \cdot 10^{-4}$ W·m^{-1}·°K^{-2}.

From the obtained experimental thermal conductivity and density data for $(CH_3O)_4Si$, $(C_2H_5O)_4Si$, and $(C_2H_5)_4Sn$ we tried to establish a relationship between the thermal conductivity and the density of these liquids.

TABLE 4. Comparison of Thermal Conductivities of Liquids

Substance	M	$\lambda \cdot 10^2$, W·m^{-1}·°K^{-1}
$Si(CH_3O)_4$	152,2	15,57
$SiCl_4$	169,9	9,06
$Si(C_2H_5O)_4$	208,3	13,16
$GeCl_4$	214,4	9,42
$GeBr_4$	392,2	8,37
$Sn(C_2H_5)_4$	234,9	12,61
$SnCl_4$	260,5	10,40
$SnBr_4$	438,3	8,59

TABLE 5. Values of Coefficients in Equations and Errors

Substance	$B'\cdot 10^6$	n	$\sigma'\cdot 10^2$ from (4)	$B_0\cdot 10^6$	$\gamma\cdot 10^4$	$\sigma\cdot 10^2$ from (3')
$(CH_3O)_4Si$	4,45	1,51	3,5	15,33	2,8	3,7
$(C_2H_5O)_4Si$	1,29	1,69	0,3	15,04	3,7	2,2
$(C_2H_5)_4Sn$	0,33	1,82	2,5	10,48	4,8	1,8

The obtained experimental data were correlated with the aid of the Vargaftik formula,

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

and the formula proposed by Tsvetkov in [5]:

$$\lambda = B'\rho^{n}. \tag{4}$$

When formula (3) was used we found that the coefficient B was not constant, but depended on the temperature: it decreased approximately linearly with increase in temperature. In view of this we correlated the experimental data by using (3) in the form

$$\lambda = B_0(1-\gamma t)\,\rho^{\frac{4}{3}}. \tag{3'}$$

The results of mathematical correlation of the obtained data with the aid of formulas (3) and (4) are given in Table 5, which also gives the values of the coefficients B_0 and γ from (3'), B' and the index n in Eq. (4). This table also gives the root-mean-square deviations σ and σ' of the experimental points from the curves drawn from Eqs. (3') and (4).

Using the data of Table 5, we can draw the following conclusions.

1. Formulas (3') and (4) are equally suitable for representation of the obtained results.

2. In the investigated temperature range the variation of coefficient B with temperature for these substances is almost the same: the products $B_0\gamma = \partial B/\partial T$ for tetramethoxysilane, tetraethoxysilane, and tetraethyl tin have similar values and are $4.5\cdot 10^{-4}$, $5.5\cdot 10^{-4}$, and $5.0\cdot 10^{-4}$, respectively.

3. The variation of the coefficient B with temperature has also been investigated for tetrahalides [1, 2]. The density values for these liquids were taken from published data [4, 6-13]. The calculated value of $\partial B/\partial T$ was $2\cdot 10^{-4}$ for the tetrachlorides and $0.5\cdot 10^{-4}$ for the tetrabromides.

NOTATION

a	is the coefficient in Eq. (2);
b, B, B^1, B_0	are the coefficients in (1), (3), (3'), and (4);
n	is the index in (4);
γ	is the coefficient in Eq. (3');
λ	is the thermal conductivity;
λ_0	is the coefficient in Eq. (1);
ρ_0	is the coefficient in (2).

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