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### EXPERIMENTAL INVESTIGATION OF THE THERMAL CONDUCTIVITY OF FORMIATES AS A FUNCTION OF TEMPERATURE

R. A. Mustafaev and T. P. Musaev

UDC 536.22

Experimental temperature dependences of the coefficient of thermal conductivity of formiates at atmospheric pressure are obtained by the method of monotonic heating.

Data on the temperature dependence of the thermal conductivity of formiates (butyl formiate, propyl formiate, hexyl formiate, and octyl formiate) were obtained by the method of monotonic heating [1]. Chemically clean reagents were investigated. The liquids were first cleaned by distillation in a vacuum, after which their purity was estimated on a Tsvet-4 chromatograph at the Yu. Mamedaliev Institute of Petrochemical Processes of the Academy of Sciences of the Adzerbaidzhan SSR. The analysis showed that the content of the principal product in the reagents was not less than 99.2%.

The experiments were performed at atmospheric pressure at temperatures ranging from room temperature to the normal boiling temperature of the liquid. The molecular weights of the substances studied range from 70 to 186.

When measuring the coefficient of thermal conductivity of the liquids, one of the important problems is the elimination of the influence of convective heat transfer. For this reason, in designing the measuring cell, the construction, geometric dimensions, and temperature conditions were chosen taking this circumstance into account.

In calculating the thermal conductivity, all corrections that are essential for this method were introduced [1]. The maximum, relative, measurement error was estimated to be  $\pm 2\%$ . The reproducibility of the experimental data, obtained at a given temperature, is about 0.8%.

No corrections for heat transfer by radiation in the substances that we investigated were introduced. The experimental results obtained on the temperature dependence of the thermal conductivity  $\lambda$  of the liquids investigated are presented in Table 1.

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Ch. Il'drym Azerbaidzhan Polytechnical Institute, Baku. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 46, No. 5, pp. 773-776, May, 1984. Original article submitted March 14, 1983.

TABLE 1. Experimental Values of the Thermal Conductivity  $\lambda \cdot 10^4$  W/m·K of Formiates as a Function of Temperature

Propyl formiate		Butyl formiate		Hexyl formiate		Octyl formiate	
T, K	$\lambda$	T, K	$\lambda$	T, K	$\lambda$	T, K	$\lambda$
300,4	1449	300,4	1370	315,4	1348	300,2	1376
315,4	1395	307,7	1351	322,7	1345	307,4	1357
322,7	1327	314,2	1325	330,1	1315	314,2	1338
		321,3	1300	336,4	1290	322,1	1325
		330,4	1280	344,7	1270	330,4	1300
		337,5	1270	352,4	1268	337,6	1298
		344,7	1240	360,7	1215	344,8	1267
		351,9	1225	367,4	1210	351,7	1257
		360,7	1200	375,1	1175	359,9	1246
		367,2	1180	382,4	1164	367,4	1217
		375,2	1150	390,1	1149	375,7	1213
		382,4	1140	396,4	1135	382,8	1183
						390,6	1171
						397,9	1162

Formiates are polar liquids and therefore have a higher thermal conductivity than hydrocarbons and many other so-called normal liquids. This is related to the presence of directed intermolecular hydrogen bonds in the latter liquids.

According to the theory of chemical structure, the properties of any compound are determined by its composition, the structure of its constituent molecules, their dimensions and mass, as well as the configuration of the molecules, i.e., by the mutual spatial arrangement of the atoms in the molecule. For this reason, in order to understand the regularities occurring in the behavior of the coefficients of thermal conductivity we shall examine the dependence of  $\lambda$  on the mass of the molecule (the number of carbon atoms  $n_c$  in the molecule).

Study shows that the nature of the indicated dependence for the polar liquids that we studied differs from the analogous dependence for normal liquids (n-alkanes, n-alkenes, etc.). For normal liquids the coefficient of thermal conductivity increases with increasing molecular mass [1], but for the liquids that we examined, the opposite dependence occurs: the coefficient of thermal conductivity decreases with increasing molecular mass. This dependence is well illustrated in Fig. 1.

As is evident from the figure, significant changes in the coefficients of thermal conductivity from one homolog to another are characteristic for the first terms of the series. For the first terms of the series  $\lambda$  changes quite sharply, but as the carbon chain increases in length, the influence of the mass of the molecules on the coefficient of thermal conductivity decreases, and for large values of M there is a tendency for  $\lambda$  to increase.

The point is that in polar liquids the hydrogen bond can play a significant role in heat transfer for the first terms of the series. It should also be noted that the hydrogen bond also affects the temperature coefficient of thermal conductivity.

Modern theory of the liquid state does not yet permit establishing the temperature dependence for calculating  $\lambda$ . For this reason, it is useful to develop simplified semiempirical and empirical methods for calculating the thermal conductivity. In recent years, this has been performed by a number of authors, as a result of which relationships between  $\lambda$  and other physical parameters of the liquid have been proposed. A common inadequacy of these formulas is the fact that they are either approximate and encompass a narrow temperature interval or are useful for calculating  $\lambda$  of separate individual liquids without any attempts at including in a single formula definite classes of substances.

The most effective law is the law of corresponding states, which is based on the theory of similarity, which determines the criterional relationships in which the individual characteristics become general characteristics for different properties and processes.

Based on the theory of similarity we seek a unified temperature dependence of the coefficient of thermal conductivity in the dimensionless form:

$$\frac{\lambda}{\lambda_{cr}} = F(\tau),$$

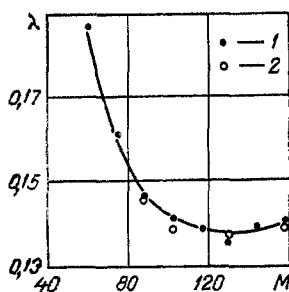


Fig. 1

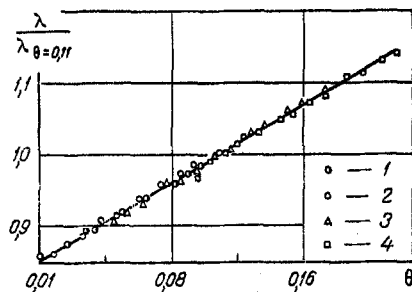


Fig. 2

Fig. 1. Dependence of the coefficient of thermal conductivity of formiates on the molecular mass: 1) according to data in [3]; 2) our data.  $\lambda$ , W/m·K.

Fig. 2. The dependence  $\lambda/\lambda_{\theta=0.11}=F(\theta)$  for formiates: 1) propyl formiates; 2) butyl formiates; 3) hexyl formiate; 4) octyl formiate.

where  $\tau = T/T_{cr}$  is the reduced temperature;  $\lambda_{cr}$  is the coefficient of thermal conductivity at the critical temperature  $T_{cr}$ .

Unfortunately, there are no data on  $\lambda_{cr}$  for most liquids in the literature, and their determination by means of extrapolation of available data to higher temperatures is not always reliable. For this reason, in order to establish the generalized dependences for the thermal conductivity of the class of formiates, it is useful to select a different temperature, which, as also the critical temperature, would be identically characteristic for all other terms.

It is well known that the physical properties of substances are determined primarily by the magnitude of the intermolecular interaction forces and the binding energies of molecules. An increase in the binding energy is usually accompanied by an increase in the boiling temperature.

The stronger the bond between the molecules, the higher the boiling temperature  $T_{boil}$  for a given substance is. Starting from this, for this temperature we chose the temperature of boiling of the liquid at atmospheric pressure and all starting experimental data were analyzed in the coordinates

$$\frac{\lambda}{\lambda_{\tau=0.8}} = F(\tau),$$

where  $\lambda_{\tau=0.8}$  is the coefficient of thermal conductivity at the reduced temperature  $\tau = T/T_{boil} = 0.8$ . An analysis of the experimental data with the help of this dependence shows that the experimental points for all liquids investigated fall on a single straight line, which can be described by the equation  $\lambda = \lambda_{\tau=0.8} (1.593 - 0.75\tau)$ .

Our investigations showed that good results for generalizing experimental data can be obtained if the quantity  $\theta = (1-\tau)/(1+\tau)$  is used as the reduced temperature. This relation permits including a wider range of materials and describing them with a single equation.

It follows from Fig. 2 that the dependence  $\lambda/\lambda_{\theta=0.11}=F(\theta)$  is a straight line, which is common for all formiates investigated.

The values of the coefficient of thermal conductivity for all formiates investigated can be calculated from the equation

$$\lambda_{\tau} = \lambda_{\theta=0.11} (0.851 + 1.355\theta). \quad (1)$$

The disagreement between the experimental values and the values calculated from this formula is not more than  $\pm 1.1\%$ .

The thermal conductivity of light homologs of the formiates that we studied (ethyl formiate, amyl formiate, and heptyl formiate) has been studied systematically by Mukhamedzhanov and Usmanov [2]. Recommended values of  $\lambda$  for the substances indicated are presented in [3]

based on the analysis of the data in [2]. A comparison of the values of the coefficient of thermal conductivity calculated according to this formula for light homologs with the recommended values [3] showed that the disagreement between the experimental values and the computed values does not exceed +2.1%. Therefore, the proposed formula (1) also describes with adequate accuracy the available experimental data on the thermal conductivity of light homologs of the formiates that we studied. Thus there is the possibility of calculating  $\lambda = f(T)$  for formiates that have not been studied or are difficult to study experimentally, thereby avoiding laborious and expensive investigations.

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#### NONISOTHERMAL TRANSFER PROCESSES IN A SINGLE COMPONENT GAS

T. N. Abramenko

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Expressions relating the true thermal conductivity coefficient of a gas to the effective value measured by various experimental methods are obtained.

All of the methods used for experimental determination of gas thermal conductivity are based on the principle of heat transfer from a solid surface preheated to the required temperature and maintenance of a temperature gradient within a system containing the gas to be studied.

Existing thermal conductivity measurement methods can be divided into two classes:

- 1) pressure gradient present in system ( $\rho = \text{const}$ ): non-steady-state heated filament method, steady-state plane layer and thermal conductivity column methods;
- 2) constant gas pressure ( $\rho \neq \text{const}$ ): non-steady-state shock tube method, steady-state heated filament method, etc.

All these methods only permit determination of an effective thermal conductivity which is never equal to the true value because of various side effects.

With consideration of the classification presented above, we will examine nonisothermal transfer processes within a single component gas, neglecting viscous momentum transfer. The linear phenomenological expressions relating energy and mass-transfer processes in any single component system will be written in the form [1]

$$\vec{J}_M = L_{11}\vec{X}_M + L_{12}\vec{X}_U, \quad \vec{J}_U = L_{21}\vec{X}_M + L_{22}\vec{X}_U. \quad (1)$$

If the gas is ideal and the specific volume of the system is practically constant ( $\rho = \text{const}$ ,  $p \neq \text{const}$ ), then we can express the thermodynamic forces in the form of [1]

$$\vec{X}_U = -\nabla T/T^2, \quad \vec{X}_M = -\frac{v\nabla p}{T} + \frac{h\nabla T}{T^2}. \quad (2)$$

Considering Eq. (2), we rewrite Eq. (1):

$$\vec{J}_M = -\frac{L_{11}k}{mp}\nabla p + \left(\frac{5}{2}\frac{L_{11}kT}{m} - L_{12}\right)\frac{\nabla T}{T^2}, \quad (3)$$

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Applied Physics Institute, Academy of Sciences of the Belorussian SSR, Minsk. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 46, No. 5, pp. 776-781, May 1984. Original article submitted August 15, 1983.