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A FORMULA RELATING THE THERMAL CONDUCTIVITY OF LIQUIDS TO THE SOUND VELOCITY IN THEM

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On the basis of experimental data an analytical relationship is obtained between the thermal conductivity of liquids and sound velocity in them for wide temperature and pressure ranges.

The theory of the liquid state which is being developed at present requires thorough and comprehensive studies of the thermophysical and acoustic properties of liquids using various methods. Studies of the above-mentioned properties at different temperatures and pressures will give answers to many questions in the theory of the liquid state about the structure and nature of molecular interaction in liquids. However, such studies encounter various difficulties due to the high temperatures and pressures and specific properties of the liquids. It is of practical interest to find an interrelationship between these properties that can be used to determine other physical properties of liquids when one of the properties is known. In this connection, the relationship between the thermal conductivity of liquids and sound velocity is of interest. It is found that these properties have a lot in common in their manifestation.

One of the trends in the theory of heat conduction of liquids is use of Debye's concept of the character of thermal motion in liquids in the form of hydroacoustic vibrations of a continuous medium (phonons), which are responsible for heat transfer in liquids. On the basis of different versions of the heat conduction theory based on this transfer mechanism, Pashskog, Bridgeman, Borovik, Cordos, Filippov, Mamedov, and others have obtained formulas [1-6] which are characterized by the common property of direct proportionality between thermal conductivity and sound velocity in homogeneous liquids:

$$\lambda = \alpha u \,, \tag{1}$$

where α is a constant expressed in terms of the various physical parameters of the liquid and u is the sound velocity.

The existence of direct proportionality between thermal conductivity and sound velocity in liquids is primarily supported by the similarity of the mechanisms of these processes. Analysis of experimental data on the dependence of thermal conductivity and sound velocity on temperature and pressure shows their identical behavior as the temperature and pressure change. The temperature coefficients of thermal conductivity and sound velocity are negative, except for anomalous liquids. The effect of pressure is similar: both the thermal conductivity and the sound velocity increase as the pressure grows.

The identity of the temperature and pressure dependences on the thermal conductivity and sound velocity in liquids is favorable for determination of a relationship between these properties.

The main disadvantage of relations such as (1) is that their practical use requires prior knowledge of α, which is determined either in terms of the isobaric heat capacity and density of the liquid or in terms of molecule size, intermolecular spacing, etc., i.e., it is also necessary to determine the physicochemical and thermomechanical properties of the liquid. Because of this, the possibilities of relation (1) are greatly reduced. Moreover, in spite of a sound theoretical basis, calculations by these formulas give great errors and are almost unsuitable with high state

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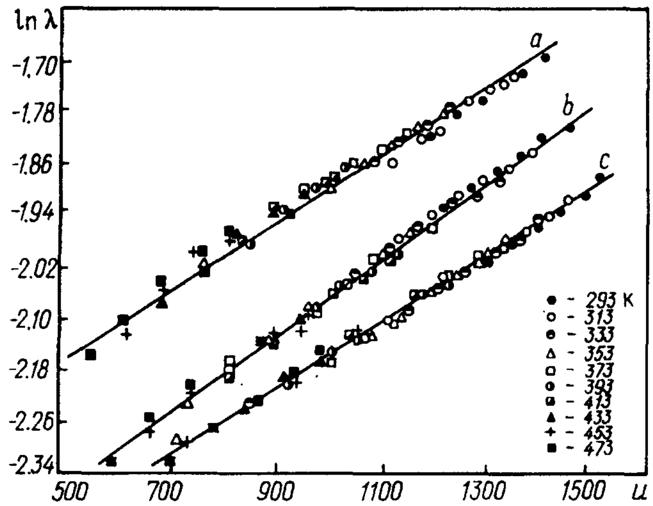

Fig. 1. Plot of ln λ on sound velocity in liquid ketones: a) dimethyl ketone; b) methyl ethyl ketone; c) methyl hexyl ketone. u, m/sec.

parameters. This does not mean, however, that hydroacoustic theory is inapplicable to the heat conduction phenomenon, since this relation is more complicated than equations of the type of (1).

Works [7-10] contain results of experimental studies of heat conduction of a homologous series of n-ketones in the temperature range of 300–670 K at pressures of from 0.1 to 49 MPa. Information about acoustic properties, in particular, the sound velocity, for some n-ketones studied here (dimethyl ketone, methyl ethyl ketone, and methyl hexyl ketone) has also been published [11-13].

Therefore, it is of great interest to determine a direct relationship between thermal conductivity and sound velocity over wide temperature and pressure ranges.

Analysis of available experimental data has shown that at constant temperatures and pressures the relationship between thermal conductivity and sound velocity is described in semilogarithmic coordinates by a straight line (Fig. 1). As can be seen from the figure, for each liquid all the points lie quite well along one straight line, and their spread around the line is within 2%.

In general form, the relationship between thermal conductivity and sound velocity can be presented as

$$\ln \lambda\,(P,\,T) = \ln A + Bu\,(P,\,T)\,, \tag{2}$$

where B is the slope of the straight line. A simple formula follows from (2):

$$\lambda\,(P,\,T) = A \exp\,[Bu\,(P,\,T)]\,. \tag{3}$$

Analysis of the parameter A shows that it greatly depends on the number of carbon atoms n_C in the molecule. It is easy to determine the following relation

$$A = C + \frac{D}{n_C^3}\,,$$

where $C = 0.065$ W/m·K; $D = 0.57$ W/m·K.

Thus, for the entire homologous series of n-ketones the relationship between λ and u can be expressed as

$$\lambda\,(P,\,T) = \left(0.065 + \frac{0.57}{n_C^3}\right) \exp\,[5.5\cdot 10^{-4}\,u\,(P,\,T)]\,. \tag{4}$$

The accuracy of this formula in the description of experimental data can be seen from Fig. 2, where experimental data on λ of dimethyl, diethyl, and methyl hexyl ketones are compared with λ calculated by this formula over wide temperature and pressure ranges.

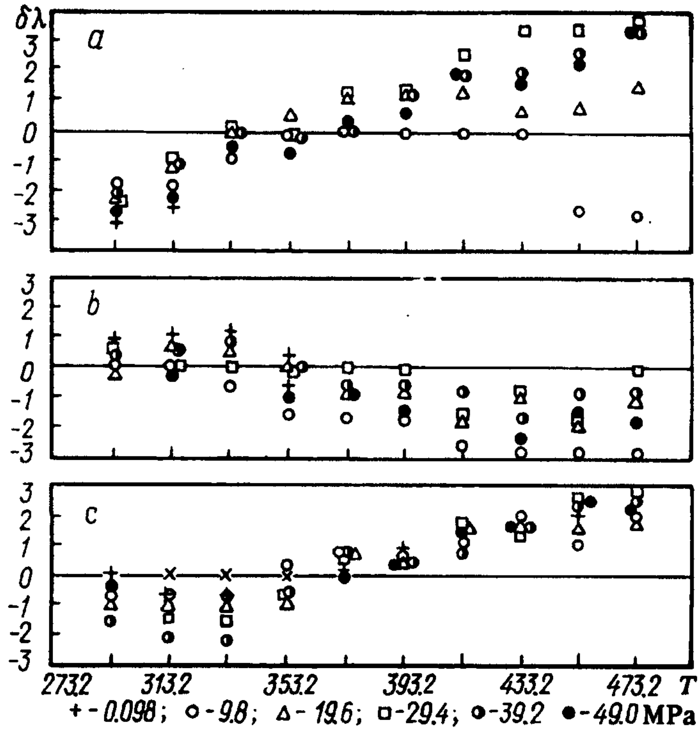

Fig. 2. Comparison of experimental thermal conductivities with calculations ($\delta\lambda = [(\lambda_e - \lambda_c/\lambda_e]\cdot 100\%$): a)-c) see Fig. 1. T, K.

Formula (4) can also be used for solution of the inverse problem of determining the sound velocity in n-ketones as a function of temperature and pressure. It should be noted that in this case error of sound-velocity determination will be at least 3%.

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