LITERATURE CITED

1. W. M. Congdon, AIAA Paper No. 74-702 (1974).
2. B. M. Pankratov, Yu. V. Polezhaev, and A. K. Rud'ko, Interaction of Materials with Gas Flows [in Russian], Mashinostroenie, Moscow (1976).
3. A. S. Senchenkov, Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza, No. 4 (1976).
4. A. S. Senchenkov, Inzh.-Fiz. Zh., 30, No. 3 (1976).
5. R. Ya. Kucherov and L. É. Rikenglaz, Zh. Eksp. Teor. Fiz., 57, No. 1(7) (1959).
6. N. A. Anfimov, Izv. Akad. Nauk SSSR, Mekh. Zhidk. Gaza, No. 1 (1966).

CORRELATION OF THE TEMPERATURE COEFFICIENT OF LIQUID HEAT CONDUCTION AND THE SPEED OF SOUND

G. G. Spirin

UDC 536.22

Underlying the correlation under consideration are the known relationships between the temperature coefficients of the heat conduction, the density, and the speed of sound

$$\frac{d\lambda}{dT}\frac{1}{\lambda}=n\frac{d\rho}{dT}\frac{1}{\rho}, \tag{1}$$

$$\frac{d\rho}{dT}\frac{1}{\rho}=m\frac{dv}{dT}\frac{1}{v}, \tag{2}$$

where n and m are constants.

These relationships express the connection between the heat conduction and the density [1, 2] and the known Rao rule [3] in differential form.

It should be noted that (1) and (2) can be written in dimensionless form

$$\frac{d\left(\frac{\lambda}{\lambda_c}\right)}{d\left(\frac{T}{T_c}\right)}\frac{1}{\left(\frac{\lambda}{\lambda_c}\right)}\Bigg/\frac{d\left(\frac{\rho}{\rho_c}\right)}{d\left(\frac{T}{T_c}\right)}\frac{1}{\left(\frac{\rho}{\rho_c}\right)}=f_1\left(\frac{T}{T_c}\right)=n, \tag{3}$$

$$\frac{d\left(\frac{\rho}{\rho_c}\right)}{d\left(\frac{T}{T_c}\right)}\frac{1}{\left(\frac{\rho}{\rho_c}\right)}\Bigg/\frac{d\left(\frac{v}{v_c}\right)}{d\left(\frac{T}{T_c}\right)}\frac{1}{\left(\frac{v}{v_c}\right)}=f_2\left(\frac{T}{T_c}\right)=m. \tag{4}$$

In this form they express the similarity between the reduced temperature coefficients of the heat conduction and density on the one hand, and the temperature coefficients of the density and the speed of sound on the other.

It follows from (1) and (2) that

$$\frac{d\lambda}{dT}\frac{1}{\lambda}=nm\frac{dv}{dT}\frac{1}{v}. \tag{5}$$

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 36, No. 4, pp. 591-596, April, 1979. Original article submitted May 11, 1978.

0022-0841/79/3604-0384$07.50

In order to go over to the speed of sound directly in (5), we write the expression for the hydrodynamic speed of sound

$$v^2 = -V^2 \left(\frac{\partial P}{\partial V}\right)_T \frac{C_P}{C_V}. \tag{6}$$

which can be converted to the form [4]

$$\frac{Mv^2}{T_c} = -\frac{MV_c P_c}{T_c} \frac{V}{V_c} \frac{P}{P_c} \frac{V}{P} \left(\frac{\partial P}{\partial V}\right)_T \frac{C_P}{C_V}, \tag{7}$$

where $MV_cP_c/T_c = R/K$ (R is the universal gas constant and K is a critical coefficient which is a constant for fluids subject to the law of corresponding states), and each of the factors in (7) is a constant in the corresponding states.

Therefore, (7) can be written as

$$\frac{Mv^2}{T_c} = \varphi(\theta), \tag{8}$$

where $\varphi(\theta)$ is the reduced temperature function ($\theta = T/T_c$) independently of the nature of the liquid. Bakker [5] first turned attention to the fact of the similarity of Mv^2/T_c.

Following [4], we rewrite [8] in the form

$$v = \frac{T_c^{1/2}}{M^{1/2}} f(\theta),$$

where

$$f(\theta) = \varphi^{1/2}(\theta),$$

and we differentiate with respect to the dimensionless temperature

$$\frac{dv}{d\theta} = \frac{T_c^{1/2}}{M^{1/2}} \frac{df(\theta)}{d\theta}.$$

Taking into account that

$$\frac{dv}{d\theta} = T_c \frac{dv}{dT},$$

we finally obtain

$$\frac{dv}{dT} = \frac{1}{T_c^{1/2} M^{1/2}} \frac{df(\theta)}{d\theta}. \tag{9}$$

Since the function $f(\theta)$ is almost linear (at least this is valid for the range $0.45 < \theta < 0.9$), it may then be considered that

$$\frac{df(\theta)}{d\theta} = l,$$

where l is a constant.

Therefore, (9) can be written in the form

$$\frac{dv}{dT} = \frac{l}{T_c^{1/2} M^{1/2}}. \tag{10}$$

Combining (5) and (10), we obtain the final expression

$$\frac{d\lambda}{dT} \frac{1}{\lambda} = \frac{A}{T_c^{1/2} M^{1/2} v} \tag{11}$$

($A = nml$ is a constant for all liquids).

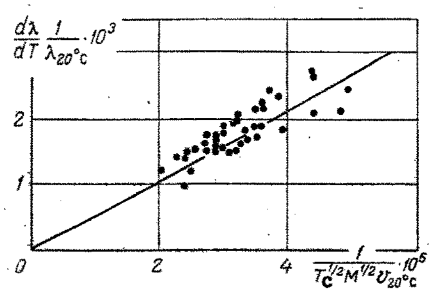

Fig. 1. Dependence of the temperature coefficient of the heat conduction of a number of normal liquids on the values of $1/T_c^{1/2}M^{1/2}v$.

This expression (11) is based on the similarity of a number of liquid properties. It is known that the most utilized form of thermodynamic similarity is the law of corresponding states. According to similarity theory, the equation of state connecting the dimensionless pressure (P/P_c), volume (V/V_c), and temperature (T/T_c) should have the form

$$\Phi\left(\frac{P}{P_c}, \frac{V}{V_c}, \frac{T}{T_c}, C_1, C_2, C_3, \ldots\right) = 0, \tag{12}$$

where Φ is a universal function for all liquids and the dimensionless parameters C_1, C_2, C_3, . . . (they are called the defining criteria) reflect the individual liquid properties.

It is shown in [6] that only one defining criterion is sufficient to describe the thermodynamic properties of liquids. In this case, liquids with nearby values of the defining criterion form a group of thermodynamically similar substances. Such liquids will be sufficiently rigorously subject to the law of corresponding states.

In the general case, the right side of (11) should contain a dependence on the defining criterion. It can only be neglected if it is barely evident. There are definite foundations for such neglect. Indeed, (11) is a corollary of (1), (2), and (10), each of which transmits the liquid properties sufficiently satisfactorily without taking account of the defining criterion, as tests show. The best results of applying (11) should be expected for a description of the homological series whose numbers are, as a rule, more similar in the thermodynamic similarity criterion. It is understood that the magnitude of the coefficient A should be corrected for the theoretical and experimental results to agree, at least for one representative of the series.

The analysis of a number of correlations, including those slightly dependent on the defining criterion, was performed by L. P. Filippov [7]. In particular, he obtained a relationship connecting the speed of sound and the temperature coefficient of the density which was ideologically similar to (11).

The main criterion for the legitimacy of using (11) to compute the temperature coefficients of organic liquids is, in the long run, the agreement between the theoretical and experimental results. Experimental values of the temperature coefficients of a number of normal liquids and their corresponding computed values $1/T_c^{1/2}M^{1/2}v$ are shown in Fig. 1. In order to eliminate the subjective factor in the selection of the liquids, those normal liquids are represented in the figure for which there would simultaneously exist data on the speed of sound from [8] and on the heat conduction from [9]. Experimental results on the heat conduction which we obtained by the method of measurement in the irregular thermal mode stage were used for three liquids [10] (carbon tetrachloride, methylene dioxane and chloride). In all, 39 normal liquids referring to different classes of chemical compounds are represented in the figure: limited and unlimited hydrocarbons, aromatic compounds, ketones, halogen substitutes, esters, etc.).

It is seen from the figure that the dependence of $d\lambda/dT \cdot 1/\lambda$ on $1/T_c^{1/2}M^{1/2}v$ is quite sufficiently definite; in particular, it can be made specific in the form

$$\frac{d\lambda}{dT}\,\frac{1}{\lambda_{20°C}} = \frac{540}{T_c^{1/2}M^{1/2}v_{20°C}}. \tag{13}$$

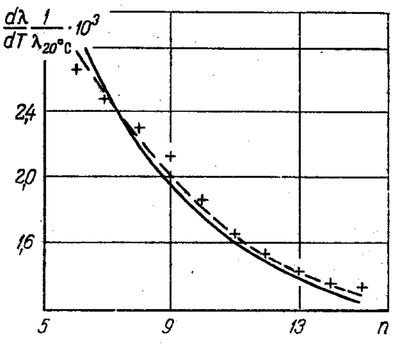

Fig. 2

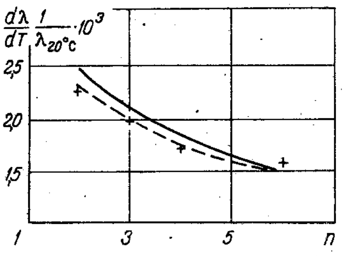

Fig. 3

Fig. 2. Dependence of $d\lambda/dT \cdot 1/\lambda$ of limited hydrocarbons on the number of carbon atoms n: solid curve is a computation using (11), A = 675, and the dashes represent experiment [9].

Fig. 3. Dependence of $d\lambda/dT \cdot 1/\lambda$ of iodine-substituted limited hydrocarbons on the number of carbon atoms: solid curve is a computation using (11), A = 623, while the dashes represent experiment [9].

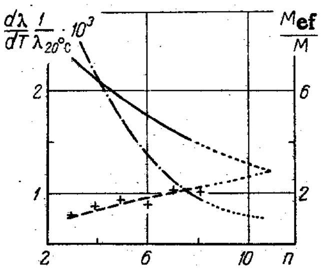

Fig. 4. Dependence of $d\lambda/dT \cdot 1/\lambda$ of limited single-base acids (solid curve is a computation using (13), while the dashed-curve is experiment [9]) and the quantity M_{ef}/M (dash-dot) on the number of carbon atoms. Shown dotted is the extrapolation of data on the dependence in the area of large values of n [9].

This relationship can be recommended for approximate estimates of the temperature dependence of the heat conduction of normal liquids. The maximum discrepancy between theory and experiment does not exceed 25% for a more than twofold change in the temperature coefficient of the liquid heat conduction.

We obtain more accurate results when (11) is applicable for homological series. Computed values of the temperature coefficients of the heat conduction of limited hydrocarbons (from hexane to pentadecane) and iodine-substituted limited hydrocarbons are shown in Figs. 2 and 3. The computation is in satisfactory agreement with experiment [9]. The computational dependence truly transmits the change in the temperature coefficient of the heat conductance with the growth of the molecular mass.

Utilization of the known connection between the speed of sound and the parachor is useful in estimating the temperature dependence of the heat conduction of normal liquids. Because of this dependence, the temperature coefficient of the heat conduction will be expressed in terms of the parachor, and since this latter can be calculated by knowing the structure of the molecule, then this affords a possibility of predicting the temperature dependence of the heat conduction of normal liquids by starting from the structure of their molecules.

As is known, the parachor is understood to be the quantity

$$[P] = \frac{M}{\rho_l - \rho_v} \sigma^{1/4}. \tag{14}$$

It is essential that the parachor be an additive quantity, i.e., that value of the parachor of the entire molecule can be written in the form of a sum of constants referred to its structural elements. Computation of the parachor by means of (14) can differ from a computation based on the analysis of the structural formula by 2% on the average.

As Altenburg [11] has shown

$$v = B \frac{[P]^2}{M^2} \rho^2 \sqrt[6]{\frac{1}{\rho^2 M}}, \tag{15}$$

where B is a constant. Combining (11) and (15) we obtain

$$\frac{d\lambda}{dT} \frac{1}{\lambda} = C \frac{M^{3/2} \sqrt[6]{\rho^2 M}}{T_c^{1/2} [P]^2 \rho^2}, \tag{16}$$

where C = A/B is a constant.

Naturally (16) is approximate. In particular, this is related to the fact, as shown in [4], that (15) does not take account of the change in the ratio of the specific heats C_P/C_V when going from one liquid to another. Meanwhile, (16) yields a functional dependence of the temperature coefficient of heat conduction of a liquid on those of its fundamentally important characteristics as the molecular weight, the density, the critical temperature, and a parachor parameter associated with the molecule structure. Consequently, (16) can be used to predict the temperature history of the heat conduction of normal liquids and to generalize data on heat conduction.

Let us examine the question of the legitimacy of using (11) and (16) on associated liquids. Experimental results from [9] and values computed in conformity with (13) are shown for the temperature coefficients of the heat conduction for limited single-base acids in Fig. 4. Besides the large quantitative discrepancy between the computational and experimental results, a qualitative discrepancy occurs: the computed values decrease with the growth of the molecular weight, while the experimental results increase.

The main reason that the associated liquids are not subject to the relationship (11), is apparently the change in molecular weight because of the formation of molecules or associate complexes. In substance, in order for the experimental value of the temperature coefficient of the heat conduction to be reflected correctly, the value of the molecular mass of the associate and not of one molecule should figure in (11) as in the computation. A similar explanation of the significant departure of alcohols from the regularities (8) is undertaken in [4]. The differences in the results in a domain remote from the critical point and their agreement approaching it are related to the formation and destruction of associates as the temperature rises.

The difference between the experimental and computed results permits estimation of the effective molecular or average weights of the associates formed in the liquid. The dependence of the relative value of the effective molecular mass on the number of carbon atoms in the molecule is shown in Fig. 4 for the considered case of single-base limited acids. This quantity decreases abruptly as the molecular weight grows. As follows from extrapolation of the data in the figure to the domain of high molecular weights, the effective mass agrees with the mass of one molecule at n = 11, i.e., there are no associates in practice.

The data in Fig. 4 have a simple interpretation. As the mass of a single molecule increases, the effective mass of the associate decreases; this factor is defining, and the temperature coefficient of the heat conduction grows. However, as the degree of association diminishes further, the tendency to diminish the temperature coefficient of the heat conduction because of the growth of the molecule mass in conformity with (11) becomes defining.

NOTATION

λ	is the coefficient of heat conduction, W/m · deg;
T	is the temperature, °K;

v	is the speed of sound, m/sec;
M	is the molecular weight, g;
P	is the pressure;
V	is the specific volume;
C_P/C_V	is the ratio of the specific heats;
σ	is the coefficient of surface tension.

Subscripts

c	is critical;
l	is liquid;
v	is vapor;
ef	is effective.

LITERATURE CITED

1. A. S. Predvoditelev, in: P. P. Lazarev (A Memorial) [in Russian], Izd. Akad. Nauk SSSR, Moscow (1956).
2. N. B. Vargaftik, Doctoral Dissertation, All-Union Institute of Heat Engineering, Moscow (1950).
3. Rama Rao, Ind. J. Phys., 14, 109 (1940).
4. V. F. Nozdrev, Molecular Physics Application of Ultrasonics, Gordon (1963).
5. Bakker, J. Phys. Chem., 21, 126 (1896).
6. L. P. Filippov, Vestn. Mosk. Gos. Univ., No. 2 (1956).
7. L. P. Filippov, in: Physics and Physicochemistry of Liquids [in Russian], No. 1, Moscow State Univ. (1972).
8. Tables of Physical Quantities. Handbook [in Russian], Atomizdat, Moscow (1976).
9. G. Kh. Mukhamedzyanov and A. G. Usmanov, Heat Conduction of Organic Liquids [in Russian], Khimiya, Leningrad (1971).
10. B. I. Il'in, A. V. Gurskaya, V. F. Salokhin, and G. G. Spirin, Vysokomol. Soedin., 17, Ser. A, No. 8 (1975).
11. K. Altenburg, Kolloid. Z., 122, No. 4 (1951).

INVESTIGATION OF TRANSITION BOILING UNDER NONSTATIONARY COOLING CONDITIONS

I. I. Berlin, É. K. Kalinin,
and V. V. Kostyuk

UDC 536.423.1

The method of nonstationary cooling is extensively used at present to investigate boiling. This method was applied successfully in a study of film boiling of cryogenic liquids [1-3]. Processing the test data in this case consists of determining the heat flux q and the heat-exchange surface temperature T_W according to the known dependence of the temperature at the site of thermocouple installation T_0 on the time τ. The values of q and T_W were determined either from the heat balance equation [3], or by the method of a regular regime [1], or from the solution of the inverse problem of heat conduction [2]. All the methods mentioned yield the same formula to compute the heat flux in an investigation of film boiling on working sections for which the condition $Bi < 0.1$ is satisfied:

$$q = -\rho c\delta \frac{dT_0}{d\tau}. \tag{1}$$

The method of nonstationary cooling is used in a number of papers [3, 4, 5] to investigate transition boiling. However, in this case a computation by means of (1) can result in substantial methodological errors because of the rapid change in the coefficient of heat transfer and the nonuniformity of the temperature field. It is

---

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 36, No. 4, pp. 597-602, April, 1979. Original article submitted June 13, 1978.