

MODIFIED TATE EQUATION FOR CALCULATING THE HEAT CONDUCTION OF LIQUID ETHERS

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Results of an experimental study of the heat conduction of liquid ethers in a wide range of temperatures and pressures are presented. The experimental data are generalized in the form of a Tate equation.

The thermal conductivities of liquid and gaseous ethers (diethyl, dipropyl, dibutyl, dihexyl, diheptyl, and dioctyl) have been studied in [1–5] in the ranges of temperatures $T = 287.4–723.2$ K and pressures $P = (0.98–490) \cdot 10^5$ Pa.

The thermal conductivities of liquid and gaseous ethers were measured by the method of a cylindrical bicalorimeter of regular thermal regime by isotherms in a layer with a thickness of 0.36 and 0.55 mm. The temperature drop at the boundary of the test layer varied from 1.31 to 0.65 K.

The thickness of the test layer and the temperature drop on its boundary were chosen so that there was no convective heat transfer in the experiments. The product $Gr \cdot Pr$ was less than 1000 throughout the ranges of temperatures and pressures studied. The absence of convection was also checked by measurement of the thermal conductivity coefficient with different temperature drops on the boundary of the test layer. The similar results obtained confirmed the absence of convection in the experiments. The total relative error in the measured thermal conductivities amounts to 4.2%.

As the temperature rises, the effect of the pressure on the value of the thermal conductivity of liquid ethers increases. For example, whereas a change in pressure from $48 \cdot 10^5$ to $490 \cdot 10^5$ Pa at 293 K increases the thermal conductivity of dioctyl ether by 16%, at 723 K this change is as high as 35%.

At present, Tate equations are widely used for describing the thermal properties of various liquids [6–10]. They were applied mainly to saturated hydrocarbons in a limited temperature range. It should be noted that the dependence $C(T)$ is weaker than $B(T)$, and therefore the authors of the works mentioned concluded that $C(T)$ remains approximately constant up to the boiling temperature.

New works [11, 12] have appeared in which the Tate equation was verified in wider temperature ranges, and as a result it was found that $C(T)$ was not a constant value but depended on temperature.

The Tate equation was used to calculate the thermal conductivity of liquid ethers. The differential form of this equation is as follows:

$$-\left(\frac{\partial \lambda}{\partial P}\right)_T = \frac{C}{B + P} \quad (1)$$

After integration of Eq. (1), we obtain

$$\frac{\lambda - \lambda_0}{\lambda} = C \ln \left[\frac{B + P}{B + P_0} \right], \quad (2)$$

where λ_0 is the thermal conductivity of the investigated object at $P_0 = 98 \cdot 10^5$ Pa; λ is the thermal conductivity of the investigated object at pressure P ; C , B are coefficients of the equation.

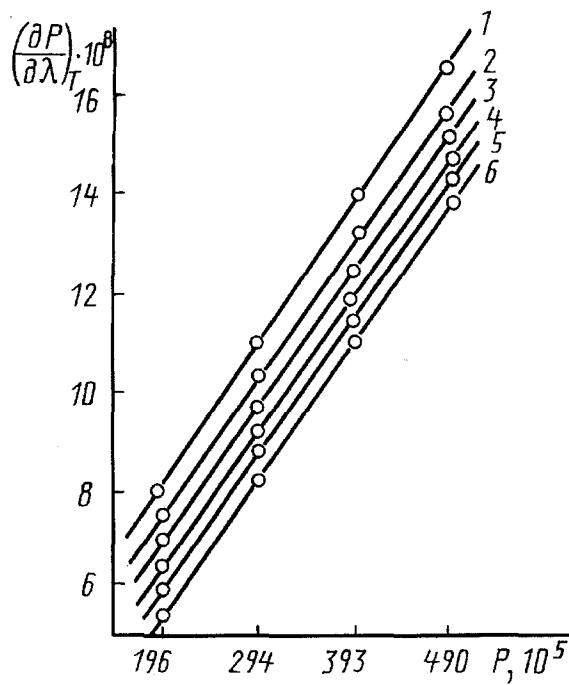


Fig. 1. The relation $(\partial P/\partial \lambda)_T = f(P)$ for liquid dibutyl ether at $T = \text{const}$: 1) 293.3; 2) 377.0; 3) 445.1; 4) 516.2; 5) 559.8; 6) 626.2 K. $(\partial P/\partial \lambda)_T$, K·sec; P , Pa.

For derivation of a calculation equation for liquid ethers from experimental data at various temperatures and pressures, the lines $T = \text{const}$ were constructed in the plane $[P - (\partial p/\partial \lambda)_T]$:

$$\left(\frac{\partial P}{\partial \lambda}\right)_T = f(P). \quad (3)$$

As can be seen from Fig. 1, the lines $T = \text{const}$ are straight and are described by the equation [6]

$$-\left(\frac{\partial P}{\partial \lambda}\right)_T = \frac{B}{C} + \frac{P}{C}, \quad (4)$$

where P is the external pressure, MPa; λ is the thermal conductivity, W/(m·K).

From an analysis of the coefficients B and C it is evident that they are functions of temperature, i.e., $B = B(T)$, $C = C(T)$. Therefore, Eq. (4) can be written as:

$$-\left(\frac{\partial P}{\partial \lambda}\right) = \frac{B(T)}{C(T)} + \frac{P}{C(T)}. \quad (5)$$

The values of $B(T)$ and $C(T)$ were processed in the form of the following functional relations:

$$\frac{B}{B_1} = f\left(\frac{T}{T_1}\right), \quad (6)$$

$$\frac{C}{C_1} = f\left(\frac{T}{T_1}\right), \quad (7)$$

where B_1 and C_1 are the values at T_1 ($T_1 = 413$ K); B and C are the values at T . Figure 2 shows that relations (6) and (7) are valid.

The curves in Fig. 2 are described by the equations

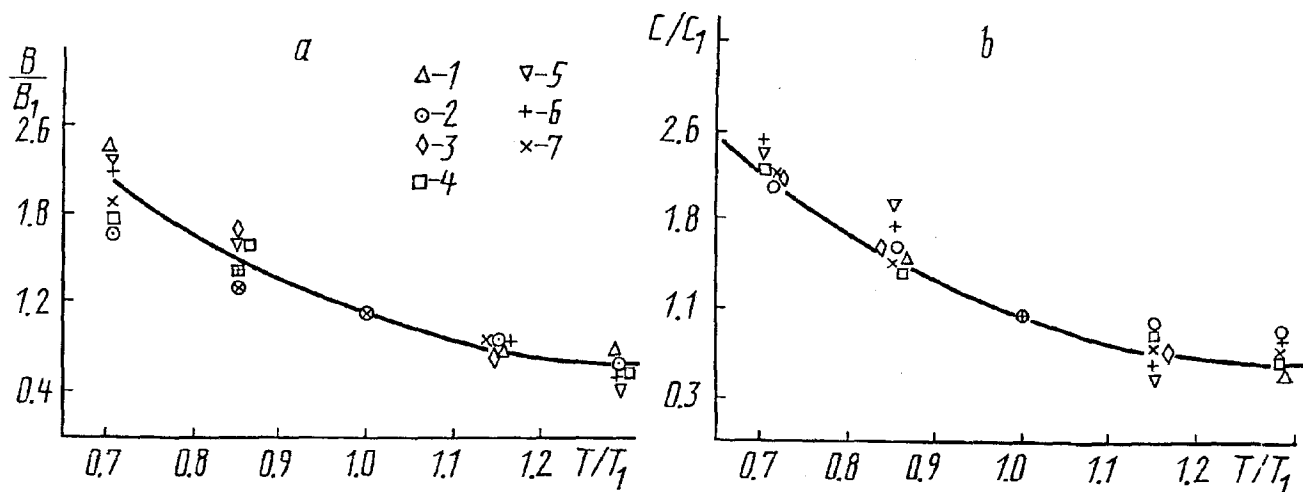


Fig. 2. Plot of B/B_1 (a) and C/C_1 (b) versus relative temperature T/T_1 for the ethers: 1) diethyl; 2) dibutyl; 3) dihexyl; 4) dipropyl; 5) diamyl; 6) dioctyl; 7) diheptyl.

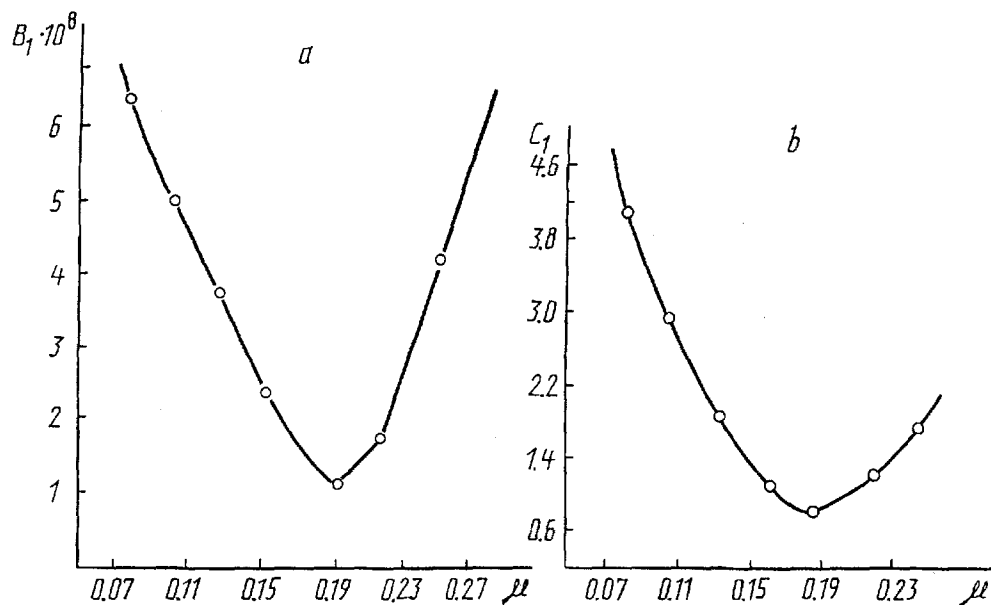


Fig. 3. Plot of B_1 (a) and C_1 (b) versus molar mass μ of ethers. μ , kg/mole.

$$B = \left[2.93 \left(\frac{T}{T_1} \right)^2 - 8.78 \left(\frac{T}{T_1} \right) + 6.84 \right] B_1, \quad (8)$$

$$C = \left[4.68 \left(\frac{T}{T_1} \right)^2 - 11.92 \left(\frac{T}{T_1} \right) + 8.25 \right] C_1. \quad (9)$$

The coefficients B_1 and C_1 for the ethers studied are a function of the molar mass μ . The dependence of B_1 and C_1 on μ is shown in Fig. 3. The curves in Fig. 3 are described by the following expressions:

$$B_1 = 4.41 \cdot 10^{10} \mu^2 - 1.6 \cdot 10^{10} \mu + 1.62 \cdot 10^9, \quad (10)$$

$$C_1 = 260.9\mu^2 - 99\mu + 10.3. \quad (11)$$

With (10) and (11) we obtain from Eqs. (8) and (9):

$$B = \left[2.93 \left(\frac{T}{T_1} \right)^2 - 8.78 \left(\frac{T}{T_1} \right) + 6.84 \right] \times (4.41 \cdot 10^{10} \mu^2 - 1.6 \cdot 10^{10} \mu + 1.62 \cdot 10^9), \quad (12)$$

$$C = \left[4.68 \left(\frac{T}{T_1} \right)^2 - 11.92 \left(\frac{T}{T_1} \right) + 8.25 \right] \times (260.9\mu^2 - 99\mu + 10.3). \quad (13)$$

From Eq. (2)

$$\lambda = \frac{\lambda_0}{1 - C \ln \left[\frac{B + P}{B + P_0} \right]}, \quad (14)$$

and with account for (12) and (13), Eq. (14) is written in the form

$$\lambda = \lambda_0 \left\{ 1 - \left[4.68 \left(\frac{T}{T_1} \right)^2 - 11.92 \frac{T}{T_1} + 8.25 \right] \times (260.9\mu^2 - 99\mu + 10.3) \ln \frac{D + P}{D + P_0} \right\}^{-1}, \quad (15)$$

where

$$D = \left[2.93 \left(\frac{T}{T_1} \right)^2 - 8.78 \frac{T}{T_1} + 6.84 \right] \times (4.41 \cdot 10^{10} \mu^2 - 1.6 \cdot 10^{10} \mu + 1.62 \cdot 10^9).$$

Equation (15) describes experimental thermal conductivities of ethers in the ranges of temperatures $T = 290-723$ K and pressures $P = 14.5-98.1$ MPa with an average error of 5%.

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