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GENERALIZATION AND ANALYTIC DESCRIPTION OF THERMAL CONDUCTIVITY

OF PARAFFIN AND AROMATIC HYDROCARBONS AND THEIR MIXTURES

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UDC 536.2

Experimental data on thermal conductivity of liquid binary mixtures of aromatic hydrocarbons with n-hexane are generalized.

At present unified theoretical expressions satisfactorily describing the thermal conductivity λ of liquids and gases as a function of temperature and pressure do not exist. Therefore the authors employed the cylindrical tricolorimeter method of [1, 2] to measure λ of aromatic hydrocarbons and their liquid binary mixtures with n-hexane. It was possible to generalize the measurement results by quite reliable equations.

The simplest sufficiently accurate expression was the Tait isotherm equation [3]. The authors of [4, 5] changed the form of the Tait equation and used it to describe thermal conductivity of liquids.

Since the analytical solution of the Tait isotherm equation presents definite difficulties, the authors of [6] derived two simple equations to calculate the coefficients of the former. The analytical description of the present data on thermal conductivity of individual hydrocarbons was performed with the first equation

$$\lambda_{p,T} = \lambda_T + \frac{Ap}{1 + Bp}, \quad (1)$$

TABLE 1. Values of Quantities Appearing in Eqs. (2) and (3)

Material	Values of A_0, α, T_0			Coeffs. k_i for calc. of A			
	$A_0 \cdot 10^{-6}$	$\alpha \cdot 10^{-6}$	T_0, K	$k_1 \cdot 10^{-6}$	$k_2 \cdot 10^{-6}$	$k_3 \cdot 10^{-6}$	$k_4 \cdot 10^{-6}$
Benzene	468	1,6686	298,15	1042	-4,373	432,09	-975,867
Toluene			198,15				
Orthaxylene			273,15				
Metaxylene	265	2,2	248,15	328	-0,162	77,25	-117,03
Paraxylene	355	1,772	298,15				

Material	Values of A_0, α, T_0			Coeffs. k_i for calc. of B			
	$A_0 \cdot 10^{-6}$	$\alpha \cdot 10^{-6}$	T_0, K	$k_1 \cdot 10^{-6}$	$k_2 \cdot 10^{-6}$	$k_3 \cdot 10^{-6}$	$k_4 \cdot 10^{-6}$
Benzene	468	1,6686	298,15	0	-0,4921	20,932	-28,205
Toluene			198,15				
Orthaxylene			273,15				
Metaxylene	265	2,2	248,15	5,3	-0,9732	45,540	-67,112
Paraxylene	355	1,772	298,15				
				256,49	-1,852	142,11	-311,56
				2	-0,1479	11,933	-14,767

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TABLE 2. Coefficients of Eq. (5)

Coefficients	Benzene, toluene	Ortho-, meta-, and paraxylene
λ_{τ_0}	1,33	1,278
m_1	0,5533	0,619
m_2	0,1927	0,4654
m_3	0,0108	-0,3148
τ_0	0,5552	0,668

TABLE 3. Values of A' and B' for Mixtures

Conc., %	Mixture	A'	B'	Max. error $\Delta = \frac{\lambda_{cal} - \lambda_{exp}}{\lambda_{exp}} 100\%$
	Benzene-n-hexane			
25	C ₆ H ₆ + 75 % C ₆ H ₁₄	0,081	1	1,1
50	C ₆ H ₆ + 50 % C ₆ H ₁₄	0,0937	1,0167	1,2
75	C ₆ H ₆ + 25 % C ₆ H ₁₄	0,0944	1,079	2,6
	Toluene-n-hexane			
25	C ₆ H ₆ + 75 % C ₆ H ₁₄	0,0873	0,9526	1,3
50	C ₆ H ₈ + 50 % C ₆ H ₁₄	0,0930	0,8938	2
75	C ₆ H ₈ + 25 % C ₆ H ₁₄	0,0960	0,8721	3,1
	Orthoxylene-n-hexane			
25	C ₈ H ₁₀ + 75 % C ₆ H ₁₄	0,0857	0,9725	1,5
50	C ₈ H ₁₀ + 50 % C ₆ H ₁₄	0,0868	0,9954	2,4
75	C ₈ H ₁₀ + 25 % C ₆ H ₁₄	0,0887	0,974	3
	Metaxylene-n-hexane			
25	C ₈ H ₁₀ + 75 % C ₆ H ₁₄	0,0829	0,9824	1,8
50	C ₈ H ₁₀ + 50 % C ₆ H ₁₄	0,0880	0,9333	1,8
75	C ₈ H ₁₀ + 25 % C ₆ H ₁₄	0,0881	0,9443	3
	Paraxylene-n-hexane			
25	C ₈ H ₁₀ + 75 % C ₆ H ₁₄	0,0821	0,9541	1,9
50	C ₈ H ₁₀ + 50 % C ₆ H ₁₄	0,0852	0,9246	1,7
75	C ₈ H ₁₀ + 25 % C ₆ H ₁₄	0,0857	0,9148	4,1

where

$$A = \frac{\Delta\lambda_1(1 + Bp_1)}{p_1}; \quad B = \frac{p_1\Delta\lambda_2 - p_2\Delta\lambda_1}{p_1p_2(\Delta\lambda_1 - \Delta\lambda_2)}$$

A FORTRAN program for a Minsk-32 computer was written to calculate the coefficients A and B.

The functions $A = f(T)$ and $B = f(T)$ for the various hydrocarbons over the temperature range studied were not identical: for benzene, para- and metaxylene $A(T)$ was practically rectilinear, while for toluene and orthaxylene it was curvilinear. For all hydrocarbons studied $B(T)$ was curvilinear.

The rectilinear dependence was described by an equation of the type

$$A = A_0 + \alpha\Delta T, \quad (2)$$

where A_0 is the value of A at $\Delta T = 0$; α is a temperature coefficient, and $\Delta T = T - T_0$.

For the curvilinear dependence a convenient equation is one of the type

$$Z = \sum_{i,j} k_i \Delta T^{j-1}, \quad \left\{ \begin{array}{l} i = 1, 2, 3, 4 \\ j = 1, 2, \frac{3}{2}, \frac{4}{3} \end{array} \right\}, \quad (3)$$

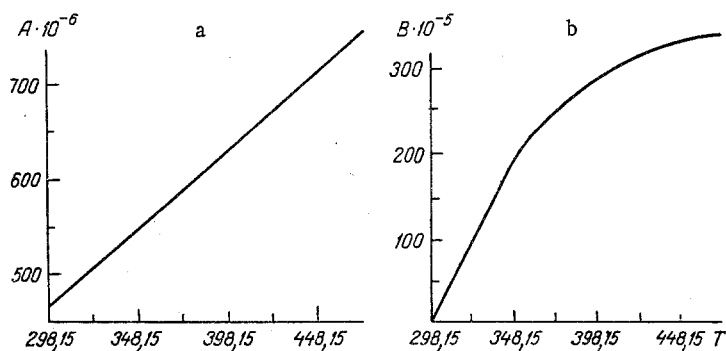


Fig. 1. Temperature dependence of coefficients A (a) and B (b) for benzene. A, W/m·K·MPa; B, l/MPa; T, K.

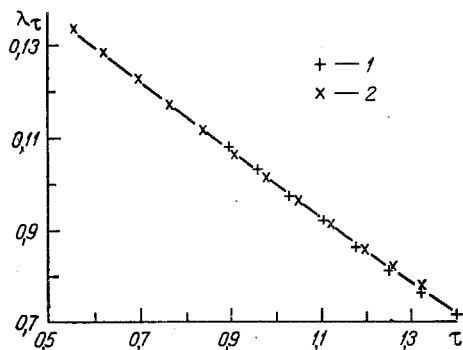


Fig. 2

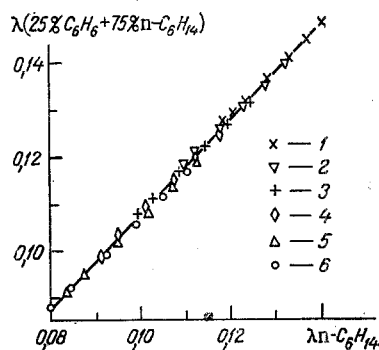


Fig. 3

Fig. 2. Dimensionless thermal conductivity vs dimensionless temperature for benzene (1) and toluene (2).

Fig. 3. Interrelationship of thermal conductivities of mixture (25% benzene + 75% n-hexane) and n-hexane at identical temperatures and pressures of 0.1-50 MPa: 1) 303.15 K; 2) 343.15; 3) 383.15; 4) 423.15; 5) 463.15; 6) 483.15 K.

where $Z = A$ or B .

The coefficients of Eqs. (2) and (3) are presented in Table 1. As an example, Fig. 1 shows temperature dependence of the coefficients A and B for benzene.

To calculate λ_p, T with Eq. (1) it is necessary to define the value of λ_T . The analytical description of aromatic hydrocarbon thermal conductivity along the saturation line was done with the equation

$$\lambda_T = \lambda_0 \exp \left(- \sum_{i=1}^{\infty} m_i \Delta T^i \right), \quad (4)$$

where λ_0 is the hydrocarbon thermal conductivity at $\Delta T = 0$; m_i are coefficients.

Data on hydrocarbon thermal conductivity above the boiling temperature were obtained by extrapolation.

Equation (4) describes the experimental data with a maximum error of $\pm 0.3\%$.

Relying upon the law of corresponding states we used the dependence for the thermal conductivity of aromatic hydrocarbons along the saturation line. For the generalization, equations of the form

$$\lambda_{\tau} = \lambda_{\tau_0} \exp \left(- \sum_{i=1}^3 m_i \Delta \tau^i \right) \quad (5)$$

were chosen, where λ_{τ_0} is the thermal conductivity at temperature $\Delta \tau = 0$; $\Delta \tau = \tau - \tau_0$.

Since λ_{cr} was not studied, for the dimensionless thermal conductivity in place of the ratio λ/λ_{cr} the ratio $\lambda/\lambda_{0.6T_{cr}}$ was used. The coefficients of Eq. (5), as determined with the Minsk-32 computer, are presented in Table 2. Figure 2 shows the generalizing curve $\lambda_{\tau} = f(\tau)$ for benzene and toluene.

Knowing the values of the λ_T coefficients, we can use Eqs. (2), (3), and (1) to calculate $\lambda_{p,T}$.

Equation (1) describes our experimental data with a maximum error of $\sim 0.9\%$.

Methods of comparative calculation are of great practical interest, since from values of the thermal conductivity of one of the hydrocarbons they permit calculation of λ of mixtures of given mass concentrations.

To generalize the experimental data on mixture λ the comparative calculation method of Karapetyants [7] was used, according to which one and the same property of two materials is compared at different parameter values. This method corresponds to the approximate linear equation

$$G_M = A' + B'G_N, \quad (6)$$

which compares values of the property G of materials M and N at an identical but differing from point to point value of the parameter.

A generalization of the thermal conductivity of all the liquid binary mixtures and the components of which they were composed was carried out according to Eq. (6). Absolute values of the thermal conductivity coefficient of the individual hydrocarbons and mixtures were used. The λ values of n -hexane were taken from [8].

As an example, Fig. 3 shows the interrelationship of the thermal conductivity of a mixture of 25% benzene +75% n -hexane (by mass) and the thermal conductivity of n -hexane at identical temperature and pressures of 0.1-50 MPa. It is evident that the dependence of the mixture thermal conductivity on n -hexane thermal conductivity is rectilinear.

Table 3 presents values of the coefficients A' and B' and maximum errors in the data calculated by Eq. (6) for each of the mixtures.

In the generalization, data on thermal conductivity of aromatic hydrocarbons and their mixtures with n -hexane were taken from [9, 10].

NOTATION

k_i, m_i , coefficients; λ_{τ} , dimensionless thermal conductivity, $\lambda_{\tau} = \lambda_T/\lambda^*$; λ^* , thermal conductivity at temperature $0.6T_{cr}$.

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