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THERMAL CONDUCTIVITY OF METHYL AND BUTYL PROPIONATES AT VARIOUS TEMPERATURES AND PRESSURES

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UDC 536.2

Experimental data are presented on the thermal conductivities of methyl and butyl propionates in the liquid and gaseous phases, including the saturation line, over the temperature range 300-600°K and pressures of 0.1-50 MPa.

The thermal conductivity of the propionates was studied by the coaxial cylinder method in the stationary regime [1]. Gap thickness in the experimental cell was 0.55 mm for the liquid phase and 0.36 mm for the gaseous phase. Temperature was measured by a 10-Ω platinum resistance thermometer (PTS No. 2000, constructed at VNIIFTRI). Pressure was generated and measured by a class 0.5 piston manometer, type MP-600.

Experimental uncertainties of the thermal conductivity results were ±(1.4-2.7)% at a confidence level $\alpha = 0.95$. Purity of the methyl propionate was 99.65%, and that of the butyl propionate 99.76% by weight (measured with "Tsvet-4" chromatograph).

Thermal conductivity was measured along isotherms with temperature steps of 30-35°K and pressure steps of 5-10 MPa. Thermal conductivity of the ethers was studied in the liquid and gaseous phases, including the saturation line. The λ values determined are presented in Tables 1 and 2.

An estimate of the radiant component of propionate λ was performed by studying IR absorption spectra in the wavelength range 2.5-25 μm with an IK-20 infrared spectrometer at 20°C. Analysis of the spectra obtained revealed that the transparency range is narrow and lies within the limits 3.5-5 μm, which corresponds to the maximum of the Planck function, while at temperatures from 116 to 580°K wide intense absorption bands are observed. Calculation of λ_{rad} under these conditions was carried out in the gray approximation [2-6]. The absorption spectra were recorded with a layer thickness $d = 0.02$ mm, with absorption intensities exceeding 60%, so that the propionates are among the strongly absorbing media. Calculation of the mean absorption coefficient was carried out with Rosseland's formula by the method described in [4]. The resulting value for methyl propionate was $\overline{K}_R = 14.8\ \text{m}^{-1}$.

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TABLE 1. Thermal Conductivity of Liquid Methyl Propionate λ, W/(m•°K)

Temperature T, °K	Pressure P, MPa						
	0,1	5	10	20	30	40	50
300	0,143	0,145	0,147	0,150	0,154	0,157	0,160
325	0,136	0,138	0,140	0,144	0,148	0,152	0,155
350	—	0,133	0,135	0,138	0,142	0,146	0,150
375	—	0,127	0,129	0,133	0,137	0,141	0,145
400	—	0,122	0,124	0,127	0,131	0,136	0,140
425	—	0,116	0,118	0,122	0,126	0,130	0,136
450	—	0,110	0,112	0,116	0,121	0,125	0,129
475	—	0,104	0,106	0,110	0,115	0,120	0,124
500	—	0,098	0,100	0,105	0,110	0,115	0,120

Saturation line				Vapor					
Liquid		Vapor		0,1 MPa		1,0 MPa		2,5 MPa	
T, K	λ	T, K	λ	T, K	λ	T, K	λ	T, K	λ
365,0	0,126	372	0,0154	380	0,011	516	0,034	516	0,037
391,0	0,119	447	0,025	426	0,022	562	0,040	572	0,043
416,0	0,114	490	0,032	475	0,028	608	0,045	603	0,046
445,0	0,107	515	0,039	503	0,035				
469,0	0,100	526	0,043						
494,0	0,089								

At a cylindrical layer thickness significantly less than the cylinder curvature, heat transfer occurs just as in a plane specimen [2, 7]. In the various modifications of the coaxial cylinder method in which the gaps filled by the liquids comprise fractions of a millimeter while the cylindrical surfaces have radii of 15-20 mm, the relationships describing cylindrical symmetry transform to the corresponding equations for a plane layer [7]. Calculation of λ_{rad} in the gray approximation for a plane layer, performed according to the recommendations of [8, 9], showed that at temperatures of 300-500°K the values of $\lambda_{rad}/\lambda_{eff}$ for the propionates lay in the range 0.7-3.8%.

In calculating λ of the gaseous state, the propionates were considered to absorb little of the medium's infrared radiation. The radiation correction was performed by the technique of [2].

The thermal conductivity of liquid methyl and butyl propionate had been studied previously at atmospheric pressure up to the boiling temperature and along the saturation line by the heated filament method [10, 11], with the experimental uncertainty of the λ measurements being estimated at ±1.5%. The divergence between the present data and those of the literature lies within the limits of experimental error. The present methyl propionate λ values are below those of [10] by 2.0% at 300°K, and by 1.8% at 325°K; the λ value of butyl propionate is higher than that of [10] at 300°K by 1.9%, and by 0.8% at 350°K.

An earlier study of thermal conductivity of the propionates [12] showed that their thermal conductivities decrease with temperature, with temperature having the greatest effect on λ in the first members of the series, growth in number of carbon atoms causing a decrease in the intensity of the function λ—f(T). With increase in pressure the effect of temperature upon λ is attenuated, while the thermal conductivity itself increases with pressure, although with increase in number of carbon atoms in the compound the effect of pressure on λ also decreases.

In contrast to normal liquids, the thermal conductivity of complex propionate ethers, like that of alcohols, decreases with increase in molecular mass. The density has a similar dependence upon μ.

At a fixed temperature, with increase in molecular mass λ of gaseous propionates decreases, which corresponds to molecular-kinetic considerations. The thermal conductivity λ of propionates in the gaseous phase increases with temperature and becomes more temperature sensitive. This phenomenon is related to pyrolysis which occurs at high temperatures, decomposing molecular complexes into individual molecules, which is accompanied by heat liberation from the chemical reactions.

Our earlier study of P—V—T dependences of the propionates [12] made it possible to study the dependence of excess thermal conductivity on density. It was established that in the

TABLE 2. Thermal Conductivity of Liquid Butyl Propionate λ, W/(m•°K)

Temperature, T, °K	Pressure P, MPa						
	0,1	5	10	20	30	40	50
300	0,138	0,140	0,142	0,144	0,148	0,152	0,156
325	0,132	0,134	0,136	0,139	0,143	0,147	0,152
350	0,126	0,129	0,131	0 135	0,139	0,143	0,147
375	0,120	0,123	0,126	0,130	0,134	0,139	0,143
400	—	0,118	0,121	0,125	0,129	0,132	0,139
425	—	0,114	0,117	0,121	0,126	0,130	0,134
450	—	0,107	0,110	0,115	0,120	0,125	0,130
475	—	0,102	0,106	0,110	0,115	0,120	0,125
500	—	0,096	0,099	0,105	0,111	0,116	0,121
525	—	0,091	0,95	0,101	0,106	0,112	0,117
550	—	0,087	0,091	0,097	0,102	0,107	0,113
575	—	0,083	0,087	0,093	0,098	0,104	0,110
600	—	0,079	0,083	0,089	0,094	0,101	0,107

Saturation line				Vapor					
Liquid		Vapor		0,01 MPa		1,0 MPa		2,0 MPa	
T, K	λ	T, K	λ	T, K	λ	T, K	λ	T, K	λ
431	0,108	433	0,020	420	0,017	585	0,036	590	0,038
444	0,106	465	0,024	454	0,022	603	0,038	617	0,041
470	0,100	516	0,0295	498	0,026	629	0,040	642	0,043
483	0,097	565	0,037	525	0,030	650	0,043	675	0,046
497	0,094	588	0,047			675	0,0455		
512	0,091								
550	0,091								
570	0,080								

coordinates $\Delta\lambda-\rho$ there is a certain layering of the general curve over isobars. Deviation of points from the averaged curve comprises 4-5%, while the isobars are shifted relative to each other, apparently in connection with the ambiguous dependence of excess thermal conductivity upon density. Processing was performed in the density range 550-920 kg/m^3, temperature range 425-600°K, and pressure range 0.1-50 MPa. The equations of the averaging curves are described by the polynomials

$$\Delta\lambda = \sum_{i=0}^{3} d_i (\rho/1000)^i , \tag{1}$$

where $\Delta\lambda$ is the excess thermal conductivity, W/(m•°K); ρ is the density, kg/m^3.

The values of the coefficients d_i are as follows: for methyl propionate $d_0 = 0.16794$, $d_1 = -0.57110$, $d_2 = 0.73062$, $d_3 = -0.15421$; for butyl propionate $d_0 = -0.04235$, $d_1 = 0.23368$, $d_2 = 0.38998$, $d_3 = 0.42160$.

The character of the dependence $\Delta\lambda-\rho$ is identical for all the materials studied (methyl, butyl, amyl, and isoamyl propionates), which permits use of the following expression to generalize the dependence of excess thermal conductivity upon density:

$$\frac{\Delta\lambda_{P,T}}{\Delta\lambda_1} = \frac{\lambda_{P,T} - \lambda_T}{\lambda_{P_1,T_c} - \lambda_{T_c}} = \varphi\left(\frac{\rho_{P,T}}{\rho_1}\right), \tag{2}$$

where $\lambda_{P,T}$, $\rho_{P,T}$ are the thermal conductivity and density of the liquid and temperature T and pressure P, λ_T is the thermal conductivity of the vapor at the same temperature and atmospheric pressure; λ_{P_1,T_c}, and ρ_1 are the liquid thermal conductivity and density at the critical temperature and P = 10 MPa; λ_{T_c} is the thermal conductivity of the vapor at critical temperature and atmospheric pressure.

Graphical processing of the experimental data with Eq. (2) is shown in Fig. 1, from which it is evident that there is some scattering of the experimental points along the common curve. The equation of the generalized curve is described by the polynomial

$$\frac{\Delta\lambda_{P,T}}{\Delta\lambda_1} = \sum_{i=0}^{3} c_i \left(\frac{\rho_{P,T}}{\rho_1}\right)^i , \tag{3}$$

where $c_0 = -0.5258$, $c_1 = 2.2625$, $c_2 = -1.2460$, $c_3 = 0.5050$.

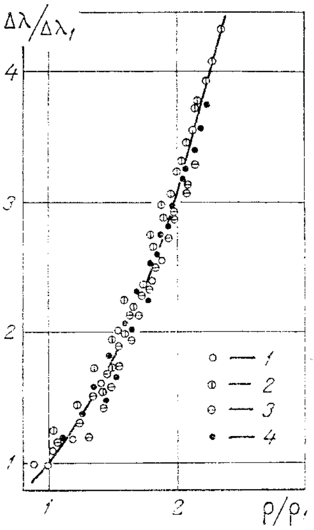

Fig. 1. Propionate thermal conductivity versus density in relative coordinates: 1) methyl; 2) butyl; 3) amyl; 4) isoamyl propionate

To calculate the thermal conductivity of normal-structure propionates Eq. (3) can be reduced to the form

$$\Delta\lambda_{P,T} = \sum_{i=0}^{2} m_i \mu^i \sum_{i=0}^{3} c_i \left(\frac{\rho_{P,T}}{\sum_{i=0}^{2} n_i \mu^i} \right)^i, \tag{4}$$

where μ is the molecular mass; $m_0 = 788.93077$; $m_1 = -1.46179$; $m_2 = -0.00252$; $n_0 = 0.5269$; $n_1 = -0.00033$; $n_2 = -0.00003$. This equation describes the experimental data on λ for the propionates with an error up to 5%, using only the molecular mass values of the compounds.

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QUESTION OF CONSTRUCTING TIKHONOV REGULARIZING ALGORITHMS FOR NON-ONE-DIMENSIONAL INVERSE PROBLEMS OF HEAT CONDUCTION

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Tikhonov regularizing algorithms are formulated and given a foundation for the multidimensional problem of determining the density of a finite heat source. Uniqueness of the solution is studied for one of the formulations of the problem.

1. One of the inverse problems in the theory of heat conduction is that of determining the characteristics of a finite heat source by means of certain data about the temperature field it generates – in particular, the problem of detecting defects in the lining of exothermal production reactors that originate during their utilization.

Since the inverse problem being considered is among the incorrect ones, a Tikhonov regularizing algorithm (RA) must be utilized for its solution [1]. The concept of an RA includes a broad class of stable algorithms and some have been developed or realized in [2, 3] for heat conduction problems. The most extensive domain of application, including the topic under consideration, has a general A. N. Tikhonov regularizing algorithm based on the solution of a certain auxiliary variational problem for a "smoothing" functional. The stabilizer [1] is the element of such a functional that governs the stability.

This algorithm was realized in [4, 5] for the solution of different one-dimensional inverse problems. The problem of determining a heat source is multidimensional. In this case the stabilizer construction given a mathematical foundation is sufficiently complicated, and the question occurs of a possible simplification so well founded as to denote a saving in machine computations in practice.

In this paper we limit ourselves mainly to a well-founded formulation of simplifications associated with the finiteness of the desired function. Here the starting point is the fact that according to [6] the problem of minimizing the Tikhonov smoothing functional governing the general RA can also include quantitative information about the desired solution of the problem. The boundary conditions for the desired function can be such information for the problem of a finite source.

Let us note that the general Tikhonov RA and the modifications proposed below are considered for utilization with an electronic computer, which corresponds to modern possibilities of engineering practice and its prospects.

2. Let us first consider the problem of a concentrated heat source, in which example we clarify the question of the correctness of the formulation as well as the possibility of simplifying the stabilizer. Here and henceforth, we limit ourselves to a consideration of an infinitely extended spatial model, which does not limit the generality of the algorithms being formulated for problems of appropriate dimensionality.

Let the temperature field u(x, t), $x = (x_1, x_2) \in E_2$ satisfy the conditions

$$k\Delta u + F(x,\ t) = c\rho\frac{\partial u}{\partial t},\ |x| < +\infty,\ 0 < t \leqslant T,\ |u| \underset{|x|\to\infty}{\to} 0,\ u|_{t=0} = 0, \tag{1}$$

where $F(x, t) = f(t)\delta(x, x_0)$, $\delta(x, x_0)$ is the Dirac function, and x_0 is the source location $f(t) \equiv 0$ for $t \leqslant 0$.

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