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EXPERIMENTAL INVESTIGATION OF THE THERMAL CONDUCTIVITY OF VAPOR—GAS MIXTURES WITH LOW VAPOR CONCENTRATION

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We give the results of an experimental investigation of the thermal conductivity of vapor—gas mixtures with low vapor concentration.

Determining the thermal conductivity of vapor—gas mixtures with low vapor concentration is of interest in studying, with the aid of a diffusion chamber, the early stages of the formation of aerosol particles when condensation processes take place [1].

An absolute heated-filament method (stationary variant) [2, 3] was used to investigate the thermal conductivity of mixtures of Ar (N_2) with vapors of C_2H_5OH, C_3H_7OH, C_3H_8O, C_6H_{14}, C_7H_{16}, and CCl_4 with an error not exceeding 1.5% in the 330-370°K temperature range. The vapor concentration in the mixture did not exceed 0.01-0.05 mole fraction.

The characteristics of the pure components were the following: Ar — brand A, with a 0.987 Ar content; N_2 — 0.99 N_2; the alcohols were brand KhCh. The vapor—gas mixtures were prepared at room temperature according to partial pressure with the aid of an MBP manometer in 10-liter tanks. The pressure of the mixture in the tank differed according to the vapor concentration and the temperature at which the investigation was carried out (see the saturation curves for the vapors, Figs. 1-2); however, the pressure was sufficient to repeat the experiment two or three times if necessary. With increasing vapor concentration in the mixture, there was a decrease in the total pressure of the vapor—gas mixture in the measuring cell (Table 1).

Determination of the thermal conductivities of Ar and N_2 at pressures of $(0.25\text{-}1.01)\cdot 10^5$ Pa showed (Table 2) that the differences in the thermal-conductivity values at the indicated pressures are within the error limits of the experiment.

Figures 1 and 2 show the variation of the thermal conductivity of mixtures of Ar (N_2) with vapors of C_2H_5OH, C_3H_7OH, C_3H_8O, C_6H_{14}, C_7H_{16}, and CCl_4 as a function of temperature in the 250-370°K range; the data for the 250-330°K range were obtained in experiments we conducted earlier [17]. It should be noted that the values of the thermal conductivity of the mixtures shown in Figs. 1-2 and the values for the pure components (Table 3) do not take account of the thermal-accommodation effect. An estimate of the temperature-jump correction to the measured thermal conductivity showed that for the mixture pressures shown in Table 1, the influence of the temperature jump does not exceed 0.27% for argon and 0.35% for nitrogen. The estimate was made according to the formula [6, 7].

$$\delta = \frac{100\lambda'\sqrt{T}}{r_1 \ln \frac{r_2}{r_1}} \frac{1}{P} \frac{2-a}{a} \sqrt{\frac{\pi M}{2R}} \left(\frac{c_v}{R} + \frac{1}{2}\right)^{-1}.$$

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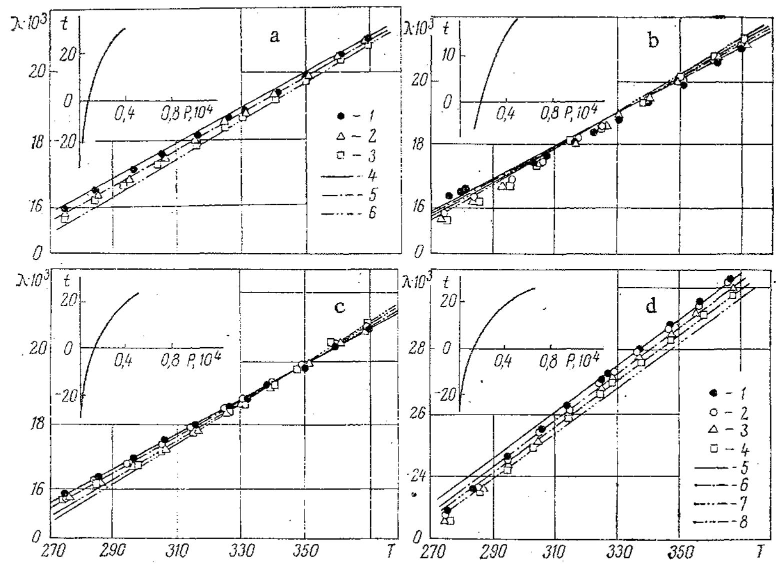

Fig. 1. Thermal conductivity of the mixture as a function of temperature: Ar—C_3H_8O: 1, 2, 3) experimental data for 0.01, 0.03, and 0.05 C_3H_8O; 4, 5, 6) theoretical data for the same C_3H_8O concentrations (a); Ar—C_2H_5OH: 1, 2, 3) experimental data for 0.01, 0.02, and 0.04 C_2H_5OH; 5, 6, 7, 8) theoretical data for the same C_2H_5OH concentrations (b); Ar—C_3H_7OH: 1, 2, 3, 4) experimental data for 0.01, 0.02, and 0.04 C_3H_7OH; 5, 6, 7, 8) theoretical data for the same C_3H_7OH concentrations (c); N_2—C_3H_7OH: 1, 2, 3, 4) experimental data for 0.01, 0.02, and 0.04 C_3H_7OH; 5, 6, 7, 8) theoretical data for the same C_3H_7OH concentrations (d). λ, W/m·°K; t, °C; T, °K; P, 10^4 Pa.

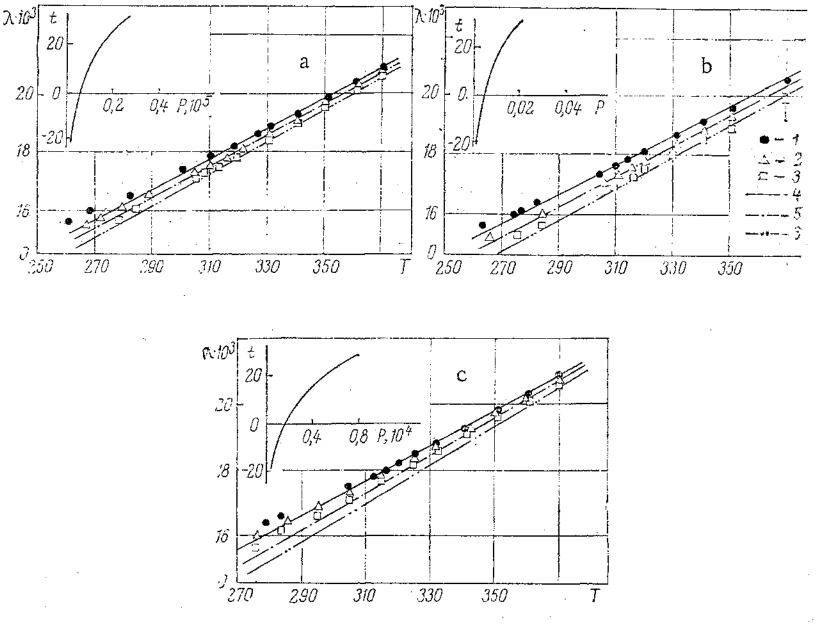

Fig. 2. Thermal conductivity of the mixture as a function of temperature: Ar—C_6H_{14}: 1, 2, 3) experimental data for 0.01, 0.03, and 0.05 C_6H_{14}; 4, 5, 6) theoretical data for the same C_6H_{14} concentrations (a); Ar—CCl_4: 1, 2, 3) experimental data for 0.01, 0.03, and 0.05 CCl_4; 4, 5, 6) theoretical data for the same CCl_4 concentrations (b); Ar—C_7H_{16}: 1, 2, 3) experimental data for 0.01, 0.03, and 0.05 C_7H_{16}; 4, 5, 6) theoretical data for the same C_7H_{16} concentrations (c). P, MPa for (b).

TABLE 1. Pressure of the Vapor—Gas Mixture in the Measuring Cell as a Function of the Vapor Concentration

Mixture	Vapor concentration (m.f.)	Pressure, P, 10^5 Pa	Mixture	Vapor concentration (m.f.)	Pressure, P, 10^5 Pa
Ar—C_2H_5OH	0,01	0,5	Ar—C_3H_8O	0,01	0,5
	0,02	0,3		0,03	0,35
	0,03	0,25		0,05	0,25
	0,04	0,2	Ar—C_6H_{14}	0,01	0,5
Ar—C_3H_7OH	0,01	0,5		0,03	0,4
	0,02	0,4		0,05	0,25
	0,03	0,25	Ar—C_7H_{16}	0,01	0,5
	0,04	0,2		0,03	0,3
N_2—C_3H_7OH	0,01	0,5		0,05	0,25
	0,02	0,3	Ar—CCl_4	0,01	0,5
	0,03	0,25		0,03	0,35
	0,04	0,2		0,05	0,2

TABLE 2. Values of the Thermal Conductivity of Ar and N_2 at T = 305.7°K and Various Pressures

Gas	Pressure, P, 10^5 Pa	$\lambda \cdot 10^3$, W/m· °K
N_2	0,25	25,65
	0,33	25,68
	0,5	25,72
	1,0	25,75
Ar	0,25	18,22
	1,0	18,26

By processing the experimental data using the method of least squares, we obtained approximate equations of the following form for the thermal conductivity of the investigated mixtures as a function of temperature:

$$\lambda = \sum_{i=1}^{n} a_i T^{i-1}. \tag{1}$$

The values of the coefficients of the polynomial (1) in the 270-370° temperature range are shown in Table 4, and the smoothed values of the thermal conductivity of the investigated mixtures are shown in Table 5. Figures 1 and 2 also show theoretical data on the thermal conductivity of the mixtures, obtained by the rigorous molecular-kinetics theory.

The values of the thermal conductivity of the mixtures containing molecules of a polyatomic gas (vapor) were calculated by the formula [8]:

$$\lambda_0 = \lambda^* + \sum_{i=1}^{2} \frac{\lambda_i - \lambda_i^*}{\sum\limits_{j=1}^{2} \frac{x_i}{x_j} \frac{D_{ii}}{D_{ij}}} . \tag{2}$$

The method for calculating the values of λ^*, λ_i, λ_i^*, D_{ii}, D_{ij} is given in [9]. The calculation was carried out by using the Lennard-Jones potential (12-6) for the nonpolar components (Ar, N_2, C_6H_{14}, C_7H_{16}, CCl_4) and (12-6-3) for the polar components (C_2H_5OH, C_3H_7OH, C_3H_8O) with the potential parameters as recommended in [8, 9] and also calculated according to the formula of [10], using the critical parameters $\varepsilon/k = 0.75\ T_{cr}$, °K, and $\sigma = (13.698\ T_{cr}/P_{cr})^{1/3}$, Å. The critical parameters were taken from [11].

TABLE 3. Experimental Data on the Thermal Conductivity of the Components of the Mixtures Investigated

	Our data			Data of other authors			
Substance	T, °K	P, 10^5Pa	$\lambda \cdot 10^3$, W/m· °K	T, °K	P, 10^5Pa	$\lambda \cdot 10^3$, W/m· °K	literature source
N_2	333,20	0,5	28,10	330	1	28,08	[5]
	341,63		28,65				
	351,50		29,41	350	1	29,3	[4]
	361,01		30,15				
C_2H_5OH	330,73	0,035	18,10				
	340,33		19,10	350	1	19,8	[5]
	350,82		20,16	353	1	22,5	[4], [14]
	362,76		21,25	360	1	21,6	[15]
	371,08		22,20	370	1	22,6	[15]
C_3H_8O	314,50	0,025	14,33				
	324,64		15,40				
	335,15		16,44				
	346,02		17,50				
	355,71		18,70				
	365,21		19,70				
C_7H_{16}	331,14	0,03	14,59				
	341,27		15,52				
	351,25		16,37	350	1	16,5	[5]
	361,52		17,22				
	373,77		18,27				
Ar	306,30	0,5	17,63	330	1	19,23	[13]
	318,04		18,36	330	1	19,2	[4]
	329,96		18,91	330	1	19,19	[5]
	342,34		19,55	332,6	1	19,3	[2]
	352,81		20,18				
	364,07		20,73				
	373,96		21,25				
C_3H_7OH	330,37	0,025	17,15				
	341,25		18,25				
	349,85		19,82				
	357,97		20,53				
	367,20		21,77	360	1	21,2	[16]
C_6H_{14}	332,30	0,03	15,67	350	1	17,6	[5]
	341,80		16,63	360	1	19,1	[13]
	350,00		17,65	370	1	20,2	[13]
	360,11		18,45				
	370,21		19,52				
CCl_4	336,30	0,03	8,03	330	1	7,70	[13]
	346,70		8,23	340	1	8,01	[13]
	355,59		8,59	350	1	8,34	[5], [13]
	364,79		8,90	360	1	8,66	[13]
	374,55		9,28	370	1	9,00	[13]

The thermal conductivity of the mixture in the stationary state is equal to $\lambda_\infty = \lambda_0 - \lambda_D T$, where $\lambda_{DT} = \frac{pD_{12}}{T} \alpha_T k_T$ is the contribution of the diffusion thermoeffect to the total thermal conductivity of the mixture. A knowledge of the value of $\lambda_D T$, and hence of λ_∞, is necessary for a correct comparison of the theoretical and experimental data. The calculations in [12] show that in the case of mixtures of gases whose molecules differ sharply in mass (for example, a mixture of He and Xe), $\frac{\lambda_{DT}}{\lambda_\infty} \cdot 100\%$ does not exceed 1.5%, and in the case of mixtures containing a polar gas, the value will be even less (of the order of 0.5%), which is within the limits of error of our experiment. Therefore in the calculations of the thermal conductivities of the mixtures investigated, we assumed that $\lambda_\infty = \lambda_0$.

A comparison of the experimental results with the theoretical results calculated by the Chapman–Enskog theory and using different force constants showed that the theoretical data

TABLE 4. Values of the Coefficients of the Polynomial (1) for the Thermal Conductivity of Vapor—Gas Mixtures

Mixture	Vapor concn.	Coefficients			
		$a_1 \cdot 10^2$	$a_2 \cdot 10^4$	$a_3 \cdot 10^6$	$a_4 \cdot 10^9$
Ar—C_3H_8O	0,01	0,394917	0,350527	0,0303139	
	0,03	0,299397	0,396528	0,0243792	
	0,05	0,141562	0,482942	0,0120251	
Ar—C_6H_{14}	0,01	1,17794	—0,0965249	0,0931343	
	0,03	1,44732	—0,313712	0,131833	
	0,05	1,38784	—0,286733	0,128121	
Ar—CCl_4	0,01	0,838280	0,120222	0,0570547	
	0,03	2,42091	—1,67644	0,696076	—0,73519
	0,05	0,149997	0,498353		
Ar—C_2H_5OH	0,01	1,756	—0,458737	0,150637	
	0,02	0,635712	0,172442	0,061987	
	0,03	0,657991	0,156357	0,0646786	
	0,04	0,723746	0,104316	0,0741982	
Ar—C_3H_7OH	0,01	0,471493	0,286700	0,0427032	
	0,02	0,622414	0,180368	0,0606873	
	0,03	0,602269	0,182921	0,0614612	
	0,04	0,741753	0,0823807	0,0787239	
Ar—C_7H_{16}	0,01	1,64858	—0,38294	0,135953	
	0,03	0,860463	0,0769198	0,0681922	
	0,05	0,537248	0,264199	0,0400679	
N_2—C_3H_7OH	0,01	—0,535043	1,2021	—0,0632993	
	0,02	—0,656113	1,26875	—0,0732688	
	0,03	—0,6852	1,129555	—0,0802079	
	0,04	—0,564443	1,22308	—0,0709205	

TABLE 5. Smoothed Experimental Values of the Thermal Conductivity of Vapor—Gas Mixtures

Mixture	Molar concn. of vapor	Thermal conductivity, $\lambda \cdot 10^3$ (W/m • °K) at temp. T, °K				
		330	340	350	360	370
Ar—C_3H_8O	0,01	18,82	19,37	19,93	20,50	21,07
	0,03	18,73	19,29	19,86	20,43	21,00
	0,05	18,66	19,23	19,79	20,36	20,93
Ar—C_6H_{14}	0,01	18,74	19,26	19,81	20,37	20,96
	0,03	18,47	19,05	19,64	20,27	20,91
	0,05	18,37	18,94	19,54	20,16	20,81
Ar—CCl_4	0,01	18,56	19,07	19,58	20,11	20,64
	0,03	18,27	18,78	19,28	19,77	20,23
	0,05	17,95	18,44	18,95	19,44	19,94
Ar—C_2H_5OH	0,01	18,81	19,38	19,97	20,58	21,21
	0,02	18,80	19,38	19,98	20,60	21,22
	0,03	18,78	19,37	19,97	20,59	21,23
	0,04	18,76	19,36	19,98	20,61	21,25
Ar—C_3H_7OH	0,01	18,83	19,40	19,98	20,57	21,17
	0,02	18,79	19,37	19,97	20,58	21,21
	0,03	18,75	19,35	19,95	20,57	21,21
	0,04	18,71	19,32	19,94	20,59	21,24
N_2—C_3H_7OH	0,01	27,43	28,20	28,97	29,72	30,46
	0,02	27,32	28,10	28,87	29,62	30,35
	0,03	27,17	27,93	28,67	29,40	30,10
	0,04	26,99	27,74	28,48	29,20	29,90
Ar—C_7H_{16}	0,01	18,65	19,18	19,73	20,32	20,93
	0,03	18,57	19,10	19,65	20,21	20,79
	0,05	18,45	18,99	15,53	20,08	20,63

calculated on the basis of potential parameters obtained from the formulas in [10] best described the experimental results.

For mixtures containing vapors of C_6H_{14}, C_7H_{16}, and CCl_4, whose interaction potential can be regarded approximately as spherically symmetric, there is satisfactory agreement between experiment and theory. The maximum deviation of the experimental from the calculated data, observed in the case of an Ar—C_7H_{16} mixture, does not exceed 1.2%. For mixtures of Ar—C_2H_5OH, Ar—C_3H_7OH, and N_2—C_3H_7OH the value of the deviation of the theoretical from the experimental data is within the limits of experimental error, and for Ar—C_3H_8O, at a concentration of 0.05 C_3H_8O, the theoretical results are 1.5% lower than the experimental.

NOTATION

δ, correction for the temperature jump, %; r_1, r_2, parameters of the measuring system, m; λ', value of the thermal conductivity obtained without considering the temperature jump, W/m·°K; α, coefficient of accommodation of the energy of the gas molecules and the surface; P, gas pressure, Pa; M, molecular mass of the gas, kg/mole; c_V, specific heat of the gas at constant volume, J/°K·mole; R, universal gas constant, J/°K·mole; λ^*, thermal conductivity of the mixture due to translational degrees of freedom; λ_0, thermal conductivity of a uniformly mixed mixture of gases (thermal conductivity at the initial instant of time), W/m·°K; λ_i, thermal conductivity of the i-th component of the mixture, W/m·°K; λ_i^*, thermal conductivity of the i-th component in the case when the internal degrees of freedom of a polyatomic gas (vapor) are frozen, W/m·°K; D_{ii}, D_{ij}, coefficients of self-diffusion and mutual diffusion, m²/sec; $\lambda_D T$, correction for the thermal conductivity due to thermal diffusion, W/m·°K; α_T, k_T, the thermal-diffusion constant and the thermal-diffusion ratio of the mixture, respectively.

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EXPERIMENTAL INVESTIGATION OF THERMAL CONDUCTIVITY AND THE TEMPERATURE JUMP IN DISSOCIATING GASES. VAPORS OF CARBONACEOUS ACIDS. I.

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UDC 536.212.2

We investigated the thermal conductivity of propionic acid vapor in the low-pressure range by means of measuring cells with different geometries.

The experimental investigation of the thermal conductivity of pure gases, nonreactive gas mixtures, and chemically reactive gases in the low-pressure range requires the introduction of a correction for the temperature jump at the interface between the gas and the surface of the measuring cell. This correction is due both to the geometric, i.e., characteristic, dimensions of the cell and to the structure of the gas molecules.

From an analysis it follows [1, 2] that the equation relating the measured value λ_{exp} and λ_{tr} of the thermal conductivity of the gas, independently of the structure of the gas and the nature of the intermolecular interactions, has the following form for the low-pressure range:

$$1/\lambda_{\mathrm{exp}} = 1/\lambda_{\mathrm{tr}} + AB_{\mathrm{ef}}/P, \tag{1}$$

where the expression AB_{ef}/P is the correction for the temperature jump. The term $A = (r_1 + r_2)/r_1 r_2 \ln(r_2/r_1)$ is the so-called geometric factor of a measuring cell with cylindrical geometry and radii r_1 and r_2 for the working surfaces, while B_{ef} is the temperature-jump factor, which is obviously related to the structure of the gas molecules, the nature of the intermolecular interactions, and the accommodation of the energy of the gas molecules at the surface of the cell.

In [1, 2] it was shown that in the special case of a gas which dissociates according to the scheme $A_2 \rightleftarrows 2A_1$ at relatively high rates of the direct and reverse reactions, B_{ef} as a function of the structure of the molecules, the composition of the mixture, and the energy of dissociation is given by the relation

$$B_{\mathrm{ef}} = \left(\frac{2 - \xi\alpha_{\mathrm{mix}}}{2}\right)\left\{\frac{X_1(T)}{B_1(T)} + \frac{X_2(T)}{B_2(T)} + \frac{\alpha(1-\alpha)}{B_{\mathrm{chem}}}\Psi(\sigma)\right\}^{-1}, \tag{2}$$

where the functions $B_1(T)$, $B_2(T)$, B_{chem}, and $\Psi(\sigma)$ are equal to

$$\frac{1}{B_1} = \frac{\alpha_{\mathrm{ef}1}}{8}\,\frac{(\gamma_1+1)}{(\gamma_1-1)}\,\frac{\bar{V}_1(T)}{T}; \quad \frac{1}{B_2} = \frac{\alpha_{\mathrm{ef}2}}{8}\,\frac{(\gamma_2+1)}{(\gamma_2-1)}\,\frac{\bar{V}_2(T)}{T}; \tag{3}$$

$$\frac{1}{B_{\mathrm{chem}}} = \frac{3}{32}\,\alpha_{\mathrm{ef}1}\beta_1\left[\frac{2Q_p(T)}{RT} - 1\right]\left[\frac{Q_p(T)}{RT}\right]\frac{\bar{V}_{12}(T)}{T}; \tag{4}$$

$$\Psi(\sigma) = \frac{X_1^2\sigma_{11}^2\Omega^{(2,2)*}\bar{V}_1 + 2X_1X_2\sigma_{12}^2\Omega^{(2,2)*}\bar{V}_{12} + X_2^2\sigma_{22}^2\Omega^{(2,2)*}\bar{V}_2}{\sigma_{12}^2\Omega^{(1,1)*}[X_1\bar{V}_1 + X_2\bar{V}_2]}. \tag{5}$$

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