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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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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:

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

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

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

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

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

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

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

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Here the subscripts 1 and 2 relate to the monomers and dimers of the gas, respectively; α_{ef_1} α_{ef_2}, β_1, and α_{mix} are the coefficients of accommodation of the energy and of the composition of the gas components and the mixture as a whole; $\gamma = C_p/C_v$; $Q_p(T)$ is the dissociation energy; ξ is a correction factor which depends on the flow regime of the gas. In the general case of an arbitrary chemically reactive mixture of gases, the coefficient of accommodation of the energy of the mixture, α_{mix}, is a complicated function of the composition and the molecular specific heats of the components. However, in the case of a dissociating gas, as was shown in [3], the equation $\alpha_{mix} = \alpha_{ef_1} = \alpha_{ef_2}$ holds; we shall make use of this equation later. In [3] it was also shown that in the measurement of the thermal conductivity of a gas in the temperature-jump regime the correction factor ξ tends to its limiting value $\xi_0 \approx 1$.

If we consider that the effective thermal conductivity of a dissociating gas under the above-described conditions of local thermochemical equilibrium is given by the relation

$$\lambda_{ef} = \lambda_{tr} = \lambda_{mix} + \frac{PD_{12}(T)}{T}\left[\frac{Q_p(T)}{RT}\right]^2 \frac{\alpha(1-\alpha)}{2}, \tag{6}$$

where λ_{mix} is the thermal conductivity of the "frozen" mixture and $D_{12}(T)$ is the binary coefficient of diffusion of the monomer–dimer system, then it follows from Eq. (1) that all its terms are dependent to an equal degree on the gas composition and the reaction energy. This means that under these conditions our approach to the organization of an experiment to measure the thermal conductivity of a dissociating gas and to the analysis of the results obtained should take account of the possible significant effect of the dissociation reaction not only in the volume of the gas but also at the boundary between the gas and the surface of the measuring cell. When an experimenter investigates the thermal conductivity of a dissociating gas, he is naturally interested not only in the actual value of λ_{tr} but also in calculating from this value the components of the effective thermal conductivity. Consequently, in solving the problem formulated, it is necessary to investigate first of all what effect the specific interaction of the dissociating gas with the surface of the measuring cell has on the determination of the components of λ_{tr}.

In the generally accepted written form of Eq. (1) this connection is unclear, and therefore the equation must be transformed. This question is dealt with in detail in [2, 4], and the results of the discussion reduce to the following. Since the only quantities measured in the experiment, except for λ_{exp}, are the reference parameters P and T, Eq. (1) can be represented as a series expansion in powers of the pressure on an isotherm, in the form

$$\lambda_{exp}(P)_T = \lambda_{exp}(0) + \lambda'_{exp}(0)P + \lambda''_{exp}(0)P^2/2 + \ldots \tag{7}$$

or

$$(P/\lambda_{exp})_T = AB_* + (1/\lambda_*)P + A_*P^2 + C_*P^3 + \ldots \tag{8}$$

The coefficients of expansions (7) and (8) are the algebraic sums of the corresponding coefficients of the series expansions in powers of the pressure for λ_{tr} and AB_{ef}. In particular, AB_*, $1/\lambda_*$, $\lambda_{exp}(0)$, $\lambda'_{exp}(0)$, and $\lambda''_{exp}(0)$ are equal to:

$$AB_* = 8\left(\frac{2-\xi_0\alpha_{ef1}}{2\alpha_{ef1}}\right)\left(\frac{\gamma_1-1}{\gamma_1+1}\right)\frac{T}{\overline{V}_1(T)}A; \tag{9}$$

$$\frac{1}{\lambda_*} = \frac{1}{\lambda_1} + \frac{AB_*}{K_p(T)}\left\{1 - \frac{B_1}{B_2} - \frac{2B_1}{B_{chem}}\Psi(0)\right\}; \tag{10}$$

$$\Psi(0) = \sigma_{11}^2\Omega^{(2,2)*}/\sigma_{12}^2\Omega^{(1,1)*}; \tag{11}$$

$$\lambda_{exp}(0) \equiv 0; \tag{12}$$

$$\lambda_{exp}(0) = 1/AB_*;\ \lambda''_{exp}(0) = -2/\lambda_*(AB_*)^2. \tag{13}$$

Here λ_1 is the thermal conductivity of the monomer of the dissociating gas.

From (9) and (13) it follows that the coefficients AB_* and $\lambda'_{exp}(0)$ of the expansions (7) and (8) characterize the interaction of the monomer of the dissociating gas with the surface of the measuring cell and make it possible to determine from the experimental data the coefficient of accommodation of the energy of the monomer, α_{ef_1}. From (10) and (13) it follows that the coefficients $1/\lambda_*$ and $\lambda''_{\exp}(0)$ are a combination of λ_1 and a complex characterizing the transfer of energy from the dissociating gas to the surface of the cell. Since (10) and (13) involve the value of the geometric factor A, the value of λ_* determined from the experimental data is an individual value for each measuring cell, and consequently it is not a physical parameter of the dissociating gas. This conclusion can be carried over to all the leading coefficients of the expansions (7) and (8). Thus, we have shown that in the case of a dissociating gas, the special nature of the interaction between the molecules and the cell surface leads to a variation of the calculated components of the effective thermal conductivity as a function of the geometry of the measuring system. In the case of a pure gas or a nonreactive gas mixture of constant composition, Eq. (8) has the form

$$P/\lambda_{\exp} = AB_* + P/\lambda_{\text{tr}} \ ; \ P/\lambda_{\exp} = AB_{\text{mix}} + P/\lambda_{\text{mix}}, \tag{14}$$

from which we can determine directly the thermal conductivities λ_{tr} for the pure gas and λ_{mix} for the nonreactive gas mixture. Consequently, comparing (7), (8), and (14), we can see that the above reasoning embodies the basic difference between a dissociating gas and nonreactive gas systems from the viewpoint of investigating its thermal conductivity in the low-pressure range.

From (9)-(13) it follows (this is also true for the leading coefficients of the expansions (7) and (8)) that a decisive role in the corrections for the interaction between the gas and the surface is played by the constant of dissociation equilibrium $K_p(T)$ and the reaction energy $Q_p(T)$. For example, in [2] it was shown that in alkali-metal vapors, which are also dissociating gases, the aforementioned corrections are significant only for lithium and sodium, which have low $K_p(T)$ values in the investigated temperature range, while they are negligible for potassium, rubidium, and cesium.

The temperature-jump correction AB_{ef}/P or its components in the coefficients of the expansions (7) and (8) can be determined by calculation, but this requires knowing the exact values of the quantities appearing in it. An analysis of the literature data on $Q_p(T)$, for example, for the vapors of alkali metals showed that today this value is known to within no better than ±5%. Hence $K_p(T)$, and consequently the composition of the alkali-metal vapors, especially at low temperatures, is determined with a substantial error. It must be borne in mind that the coefficient of accommodation of the composition is an individual characteristic of the system formed by the gas and the specific surface of the cell and is evidently unpredictable in a number of cases.

In our opinion, there are two possible ways of determining the correction for the temperature jump. The first is based on the harmonization of the experimental data on the viscosity of the dissociating gas, where the effect of the mixture in the correction for slippage is negligibly small [6], and the thermal conductivity when the two quantities are processed simultaneously. The basic ideas of such an approach are discussed in [4]. However, it should be noted that the effectiveness of the simultaneous analysis of the viscosity and the thermal conductivity of the dissociating gas is limited by the low accuracy, and in a number of cases also by the lack of information on the Maxwell parameter and the specific heat of the monomer and the dimer.

The second way is based on conducting special experiments to investigate the thermal conductivity and the temperature jump in the dissociating gas at low pressures. Let us consider Eq. (1). It can be written in a different form as

$$\frac{P}{\lambda_{\exp}} = \frac{P}{\lambda_{\text{tr}}} + AB_* F(P,\ T), \tag{15}$$

where

$$F(P,\ T) = \left\{X_1 + X_2\left(\frac{\gamma_1 - 1}{\gamma_1 + 1}\right)\left(\frac{\gamma_2 + 1}{\gamma_2 - 1}\right)\frac{\overline{V}_2}{\overline{V}_1} + \alpha(1-\alpha)\left(\frac{\gamma_1 - 1}{\gamma_1 + 1}\right)\left[\frac{2Q_p}{RT} - 1\right]\left[\frac{Q_p}{RT}\right]\beta_1\Psi(\sigma)\right\}^{-1}, \tag{16}$$

and from this it follows that the correction for the temperature jump in the dissociating gas is proportional to AB_*. The complex AB_*, in turn, according to Eq. (8), can be determined for the measuring cell directly from the experimental data without any further calculations. Con-

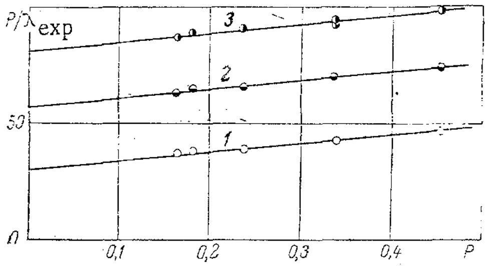

Fig. 1. Results of the investigation of the thermal conductivity of air at low pressures and a temperature of T = 305°K: 1) cell 1, λ_{tr_1} = 0.0267 W/m·°K; 2) cell 2, λ_{tr_2} = 0.0270 W/m·°K; 3) cell 3, λ_{tr_3} = 0.0270 W/m·°K. P/λ_{exp} in mm Hg·°K/W; P, in mm Hg.

sequently, if we measure λ_{exp} for a dissociating gas on the isotherm as a function of the pressure with the aid of two or more measuring cells with different values of A and the same surface characteristics (β_1 = idem), carry out the processing of the results in the coordinates P/λ_{exp} and P for determining the AB_* of each cell, and then in the coordinates P/λ_{exp} and AB_*, then we can obtain both the values of λ_{tr} and the values of the function F(P, T). The advantages of this approach are obvious, since here we use only the experimentally determinable values λ_{exp}, P, and T.

The first investigations of this nature consisted in the measurement of the thermal conductivity and the temperature jump in sodium vapors [3], carried out with two cells operating by the hot-filament method with a null segment [7]. It should be noted that in [3] all the theoretical conclusions were confirmed.

From Eqs. (2)-(5) it follows that the formation of the temperature jump in dissociating gases is influenced by the value of the reaction energy and the composition independently of the causes of the dimerization. In order to verify this and accumulate information, in the present study we chose a number of carbonaceous acids as the substances to be investigated. In the vapors of carbonaceous acids there is a dimerization-dissociation reaction on the basis of an unsaturated hydrogen bond with an energy value $Q_p \approx$ 14-15 kcal/mole. The dissociation constant $K_p(T)$ of this reaction is relatively small, which makes the composition of the vapor vary over a wide range at low pressures in the experiment. The reaction rate in the vapors of carbonaceous acids is fairly high and enables us to assume that in the dissociating gas we have local thermochemical equilibrium. Consequently, the results of the measurements can be processed according to the scheme described. Another advantage of carbonaceous acids is their relatively low aggressiveness and the possibility of conducting the investigations in the "room" temperature range (up to 400°K). It should also be noted that the accuracy of the recommended values [8] of the reaction energy $Q_p(T)$ of carbonaceous acids is low, and our arguments about the difficulty of introducing corrections for the temperature jump by a calculation method are valid for these acids.

For an experimental investigation of the thermal conductivity and the temperature jump in carbonaceous-acid vapors (propionic acid, C_2H_5COOH) we set up an apparatus consisting of three measuring cells, a thermostating vessel, a vaporizing tank, a vacuum system, and a gas system. The measuring cells were prepared by the hot-filament method and consisted of tungsten wires with diameters of 0.098, 0.050, and 0.028 mm, arranged axially in molybdenum tubes with diameters of 7.00 and 6.80 mm. The working length of the filaments averaged 185 mm, and that of the tubes 205 mm. The geometric factors of the temperature jump (for the cells) were equal: A_1 = 4.81 mm^{-1}, A_2 = 8.20 mm^{-1}, and A_3 = 13.06 mm^{-1}. The choice of tungsten and molybdenum as the materials for the measuring cells was made on the basis of the fact that these metals have high thermal resistance coefficients and weak catalytic properties, which is important in the investigation of polyatomic chemically reactive gases. The other elements of the apparatus were made of 1Kh18N9T steel and Teflon.

The vaporizing tank with a cryothermostating system enabled us to realize a saturation-temperature range from −20°C to +100°C. The vapor pressure in the apparatus was determined from the P_s—T_s relation $\lg P_s = 8.902 - 2473/T_s$ [9] (P in mm Hg, T in °K).

TABLE 1. Experimental Values λ_{exp} Found on Three Measuring Cells

P, mm Hg	λ exp W/m·°K	λ exp W/m·°K	λ exp W/m·°K
1	2	3	4
306°K Isotherm			
0,146	0,01554	0,01086	0,00820
0,154	0,01791	0,01229	0,00925
0,155	0,01784	0,01173	0,00888
0,204	0,02377	0,01738	0,01271
0,205	0,02377	0,01742	0,01254
0,273	0,02961	0,02328	0,01862
0,274	0,02975	0,02338	0,01862
0,395	0,03945	0,03209	0,02710
0,397	0,03922	0,03300	0,02747
0,462	0,04562	0,03631	0,03105
0,559	0,05087	0,04078	0,03539
0,826	0,05802	0,04924	0,04466
1,057	0,05912	0,05296	0,04944
1,423	0,06082	0,05502	0,05230
2,166	0,06071	0,05476	0,05315
326°K Isotherm			
0,135	0,00959	0,00622	0,00461
0,138	0,00961	0,00616	0,00457
0,141	0,00949	0,00602	0,00443
0,180	0,01202	0,00801	0,00626
0,191	0,01292	0,00887	0,00677
0,206	0,01337	0,00901	0,00687
0,207	0,01383	0,00927	0,00716
0,244	0,01687	0,01156	0,00897
0,273	0,01762	0,01236	0,00971
0,280	0,01789	0,01268	0,00979
0,285	0,01803	0,01265	0,00988
0,333	0,02149	0,01600	0,01302
0,397	0,02558	0,01915	0,01552
0,399	0,02422	0,01885	0,01549
0,442	0,02623	0,02137	0,01781
0,449	0,02709	0,02152	0,01790
0,529	0,03110	0,02716	0,02045
0,568	0,03195	0,02762	0,02289
0,773	0,04010	0,03492	0,02917
1,071	0,04669	0,04219	0,03874
1,587	0,05445	0,05078	0,04803
2,370	0,05912	0,05592	0,05337
3,217	0,06135	0,05792	0,05625
4,022	0,06173	0,05983	0,05786
5,082	0,06149	0,05847	0,05733
6,279	0,06125	0,05888	0,05679
344°K Isotherm			
0,155	0,01098	0,00772	0,00600
0,155	0,01113	0,00787	0,00604
0,203	0,01328	0,00991	0,00782
0,217	0,01392	0,01085	0,00863
0,248	0,01631	0,01174	0,00986
0,363	0,01710	0,01375	0,01131
0,479	0,02017	0,01663	0,01442
0,489	0,01977	0,01646	0,01404
0,802	0,02535	0,02258	0,02033
1,024	0,02926	0,02671	0,02460
1,138	0,03026	0,02769	0,02544
1,643	0,03562	0,03372	0,03173
2,683	0,04594	0,04406	0,04244
5,343	0,05476	0,05316	0,05231
5,507	0,05490	0,05383	0,05268
6,269	0,05643	0,05540	0,05495
11,221	0,06102	0,05991	0,05949
16,972	0,06051	0,05966	0,05932
26,935	0,05793	0,05698	0,05648
364°K Isotherm			
0,129	0,00742	0,00546	0,00360
0,151	0,00969	0,00682	0,00522
0,164	0,00867	0,00594	0,00443
0,231	0,01089	0,00781	0,00600
0,274	0,01229	0,00917	0,00727
0,278	0,01224	0,00897	0,00702
0,373	0,01470	0,01154	0,00947
0,464	0,01499	0,01187	0,00983
0,565	0,01668	0,01390	0,01171
0,616	0,01768	0,01501	0,01287
0,634	0,01709	0,01455	0,01266
0,901	0,01934	0,01695	0,01532
4,220	0,03453	0,03356	0,03323
7,243	0,04276	0,04222	0,04203
10,943	0,05030	0,05007	0,04953
19,567	0,05686	0,05681	0,05705
26,198	0,05899	0,05869	0,05934
38,351	0,05985	0,05944	0,06005
67,886	0,05834	0,05819	0,05855
392°K Isotherm			
0,143	0,00773	0,00472	0,00379
0,152	0,00754	0,00471	0,00362
0,231	0,01078	0,00737	0,00565
0,231	0,01086	0,00736	0,00575
0,237	0,01241	0,00863	0,00692
0,322	0,01369	0,00995	0,00813
0,334	0,01312	0,00945	0,00769
0,461	0,01525	0,01140	0,00948
0,465	0,01587	0,01213	0,01016
0,900	0,01874	0,01582	0,01445
1,065	0,01912	0,01664	0,01554
2,440	0,02360	0,02190	0,02157
3,515	0,02575	0,02489	0,02442
5,250	0,02792	0,02748	0,02687
9,757	0,03139	0,03117	0,03093
16,846	0,03760	0,03754	0,03720
28,354	0,04536	0,04468	0,04475
39,183	0,05079	0,05057	0,05070
55,920	0,05537	0,05516	0,05554
59,722	0,05733	0,05738	0,05740
78,981	0,05912	0,05864	0,05838
116,12	0,06137	0,06153	0,06185
148,17	0,06247	0,06185	0,06303

Before investigating the thermal conductivity and the temperature jump in the propionic acid vapors on the apparatus, we carried out analogous measurements for argon and air. According to Eq. (14), the results of the measurement of the thermal conductivity of the pure gas at low pressures, obtained on several cells with different values of A, should be mapped in the coordinates P/λ_{exp} and P by parallel lines. The inclination of the lines determines the value of $1/\lambda_{tr}$, and their intersection with the ordinate axis determines AB_*. As can be seen from Fig. 1, the experiment confirmed the conclusions drawn from Eq. (14). The thermal conductivities obtained for argon and air agree well with the literature data [10]. From the AB_* values obtained, we calculated the coefficients of accommodation of the energy, α_{ef_1}, for argon and air on the assumption that $\xi_0 \approx 1$. To within the limits of experimental error, the values of α_{ef} both for air and for argon were the same on all the cells, which indicates that the state of the surface of the working filaments of the cells was identical.

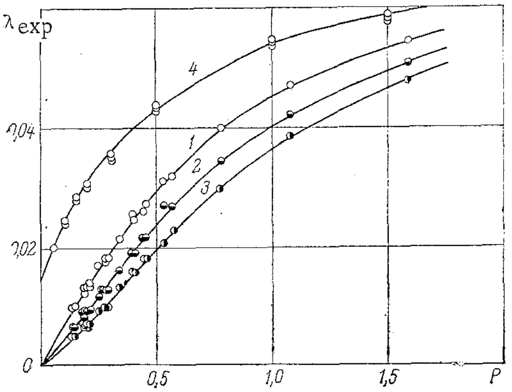

Fig. 2

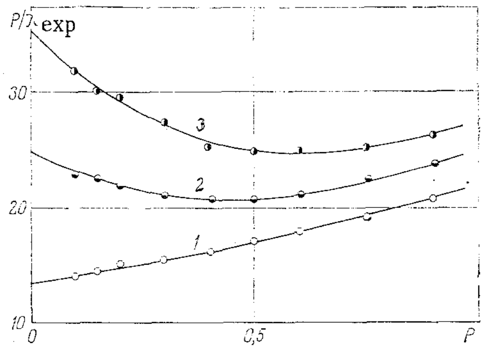

Fig. 3

Fig. 2. Experimental and true values of the thermal conductivity of propionic acid vapor on the 326°K isotherm: 1) cell 1; 2) cell 2; 3) cell 3; 4) λ_{tr}. λ_{exp} in W/m·°K.

Fig. 3. Experimental data on the thermal conductivity of propionic acid vapor on the 326°K isotherm in the coordinates P/λ_{exp} and P: 1-3) curves for cells 1-3.

The thermal conductivity of the propionic acid vapors was measured on the 306, 326, 344, 364, and 392°K isotherms as a function of the pressure. The measurement results are shown in Table 1. In the calculation of λ_{exp} we introduced a correction for the radiant transfer of heat from the filament and for the heat losses from the ends of the filament. These corrections are customary for the hot-filament method and are discussed in detail in the literature [11].

To illustrate the characteristic behavior of λ_{exp} for the dissociating gas in the low-pressure range, we selected the 326°K isotherm, the data for which are shown in Figs. 2 and 3 in the coordinates λ_{exp} and P and the coordinates P/λ_{exp} and P, respectively. Now we consider Eqs. (7)-(13). As can be seen, as $P \to 0$, λ_{exp} also approaches zero. The first derivative of the function $\lambda_{exp}(P)$ at the point $P = 0$ is determined by the value of AB_* for a specific measuring cell. It follows from Fig. 2 that the absolute value of $\lambda'_{exp}(0)$ decreases as A, the geometric factor for the temperature jump, increases, which corresponds to Eq. (12). According to (13), the sign of the second derivative of $\lambda_{exp}(P)$ at the point $P = 0$ may be either positive or negative and is determined by the sign of $1/\lambda_*$. As was noted above, $1/\lambda_*$ has an individual value for each cell, and its sign is determined by the relation between the positive term $1/\lambda_1$ and the negative term $AB_*\{1 - B_1/B_2 - 2B_1\psi(0)/B_{chem}\}/K_p(T)$, which depends on AB_*, B_{chem}, and $K_p(T)$ (see Eq. (10)). The total influence of the geometry of the measuring cells, the reaction energy, and the constant of dissociation equilibrium specifically on the 326°K isotherm was put together in such a way that for a cell with filament diameter 0.098 the value of $\lambda''_{exp}(0) < 0$, for a cell with filament diameter 0.050 $\lambda''_{exp}(0) \approx 0$, and for a cell with filament diameter 0.028 $\lambda''_{exp}(0) > 0$. In the coordinates of Fig. 3 this influence was reflected in the sign of the first derivative at the point $P = 0$. Thus, the behavior of the experimental data on the 326°K isotherm in the coordinates λ_{exp} and P and the coordinates P/λ_{exp} and P is completely explained by the structure of the coefficients of the expansions (7) and (8).

In conclusion, we must point out one curious conclusion which follows from the form in which Eq. (10) is written. Since the value of the complex $AB_*\{1 - B_1/B_2 - 2B_1\Psi(0)/B_{chem}\}/K_p(T)$ is always negative and varies as a function of T from 0 to $-\infty$, the parameter $1/\lambda_*$ obviously can vary from $1/\lambda_1$ to $-\infty$, passing through zero. This means that for a specific measuring cell there exists a temperature $T_c(\alpha_{ef1}; A)$ such that when it is approached "from above," the value of λ_* goes off to $+\infty$, while when it is approached "from below," the value goes off to $-\infty$. This temperature, which naturally depends on the geometric factor A of the cell and the accommodation of the energy of the monomer on the surface, may be regarded as a characteristic for the system consisting of the dissociating gas and the measuring cell. It can serve as a criterion of the influence of the temperature jump on the measurement and the calculation of the effective thermal conductivity of the dissociating gas in the low-pressure region. Thus, when $T_c(\alpha_{ef1}; A)/T \gg 1$, the role of the reaction effect in the temperature jump is neg-

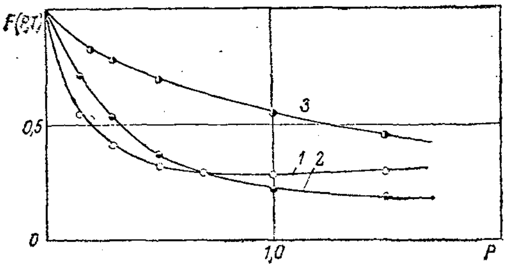

Fig. 4. F(P, T) plotted against pressure for different temperatures: 1) 306°K; 2) 326°K; 3) 392°K. F(P, T) is a dimensionless quantity.

TABLE 2. Effective Thermal Conductivity of Propionic Acid Vapor as a Function of Temperature and Pressure

P, mm Hg	λ_{ef}, W/m·K				
	306 K	326 K	344 K	364 K	392 K
0,1	0,0272	0,0236	0,0182	0,0194	0,0216
0,2	0,0404	0,0304	0,0206	0,0204	0,0217
0,3	0,0502	0,0354	0,0225	0,0216	0,0218
0,4	0,0570	0,0398	0,0242	0,0222	0,0219
0,5	0,0618	0,0432	0,0258	0,0226	0,0220
1,0	0,0685	0,0540	0,0328	0,0247	0,0220
1,5	0,0680	0,0582	0,0372	0,0267	0,0223
2,0	0,0666	0,0608	0,0402	0,0284	0,0238
3,0		0,0644	0,0496	0,0318	0,0258
4,0		0,0650	0,0529	0,0350	0,0271
5,0		0,0648	0,0553	0,0379	0,0282
6,0		0,0644	0,0570	0,0405	0,0289
7,0			0,0585	0,0435	0,0297
8,0			0,0597	0,0455	0,0304
9,0			0,0607	0,0477	0,0311
10,0			0,0613	0,0504	0,0319
20,0			0,0604	0,0572	0,0404
30,0			0,0575	0,0597	0,0464
40,0				0,0599	0,0513
50,0				0,0597	0,0544
60,0				0,0592	0,0568
70,0				0,0582	0,0583
80,0					0,0592
90,C					0,0598
100,0					0,0605
120,0					0,0615
140,0					0,0623
160,0					0,0627

TABLE 3. Thermal Conductivity of the Monomer of Propionic Acid, Determined Experimentally (λ_1) and by Calculation from Viscosity Data ($\lambda(\eta)_1$)

T, K	306	326	344	364	392
λ_1, W/m·K	0,0116	0,0138	0,0159	0,0182	0,0213
$\lambda(\eta)_1$, W/m·K	0,0129	0,0140	0,0152	0,0163	0,0182

ligibly small; it obviously can be dealt with according to the nonreactive-gas scheme, and the measurement can be carried out in one cell. In our experiments the existence of T_c (α_{ef_1}; A) becomes evident for a cell with filament diameter 0.028. From the constructions in the coordinates P/λ_{exp} and P it follows (see Fig. 3) that for this cell on the 392°K and 364°K isotherms $1/\lambda_* > 0$, on the 344°K isotherm $1/\lambda_* \approx 0$ to within the accuracy of the processing of the experimental data, and on the 326°K and 306°K isotherms $1/\lambda_* < 0$. According to our estimates, for the aforementioned cell T_c (α_{ef_1}; A) = 344°K. It should be noted that on the 326°K isotherm, for a cell with filament diameter 0.050 the value of $1/\lambda_* < 0$. Consequently, for this cell the value of T_c (α_{ef_1}; A) lies in the 326-344°K interval.

In the analysis of the experimental data on the temperature jump in dissociating gases the determination of the complex AB_* is of great importance. From Fig. 3 it follows (and this is also true of the other isotherms in this study) that in the coordinates P/λ_{exp} and P the value of AB_* for each cell, when we select the appropriate minimum pressures for the experiment, can be determined with fairly high accuracy.

The subsequent procedure in the processing of the experimental data consisted in plotting the measurement results in the coordinates P/λ_{exp} and AB_* and determining the value of the function F(P, T) on an isotherm as a function of pressure. It should be noted that in the coordinates adopted here, the data for all the cells usually fall along the same straight line. In our opinion, this indicates that the value of β_1, the coefficient of accommodation of the composition, is the same for all the cells in the specific conditions of our experiment. The results obtained by calculating the function F(P, T) are shown in Fig. 4, where the minimum on the 306°K isotherm corresponds to the composition of a gas with a degree of dissociation about $\alpha = 0.5$.

The direct determination of the function F(P, T) from experimental data on the thermal conductivity of a dissociating gas is naturally restricted to low pressures, where the error in the value determined is acceptable. In our case this region is limited to pressures no higher than $P \approx 2$ mm Hg. The correction for the temperature jump must be introduced over the entire interval of pressures used. Therefore it is important to consider the question of extrapolating F(P, T) to the region $P > 2$ mm Hg. For this purpose, we ascertained the variation of F(P, T) with the composition of the vapors on an isotherm in the pressure range 0-2 mm Hg, and we extended the function so determined to higher pressures. It should be noted that the deterioration in the accuracy of F(P, T) as a result of the extrapolation is compensated by decrease in the actual correction for the temperature jump, $AB_*F(P, T)/P$, as the pressure increases. The composition of the propionic acid vapors was calculated by using the values of $K_p(T)$ determined from the equation $\lg K_p(T) = 10.834 - 3316/T$ [8].

Analysis of the experimental data of the present study showed that the results for the three cells agree only when we introduce a temperature-jump correction according to Eq. (15). In Fig. 2 this is shown for the 326°K isotherm. If we try to introduce a correction according to the scheme for a monomer or a binary nonreactive mixture, we find that, first of all, the results for the cells will not agree, and, secondly, the values of the thermal conductivity will turn out not to be real. For example, if we apply to the data for the 326°K isotherm a temperature-jump correction according to the monomer scheme, we find that at a pressure of 0.1 mm Hg for a cell with filament diameter 0.098 the value of $\lambda_{dist} = 0.067$ W/m·°K, and for a cell with filament diameter 0.028, $\lambda_{dist} = -0.027$ W/m·°K.

The values of the effective thermal conductivity for propionic acid vapors as a function of pressure on the 306°K, 326°K, 344°K, 364°K, and 392°K isotherms, averaged over all the cells, are shown in Table 2. Carrying out the experiments at low pressures enabled us to determine with sufficient accuracy the values of the thermal conductivity of the monomer, λ_1, which are shown in Table 3. In this table, for comparison, we show the data for the thermal conductivity of the monomer $\lambda(\eta)_1$, calculated by the formula

$$\lambda_1 = f\eta_1\hat{C}_{v1}, \tag{17}$$

where η_1 is the viscosity of the monomer and $\hat{C}_{v_1}$ is its specific heat at constant volume. The data on the viscosity of the monomer are taken from [12], and the data on the specific heat from [9]. The Maxwell parameter was calculated by Aiken's formula: $f = (9\gamma - 5)/4$, where $\gamma = C_p/C_v$. From Table 3 it follows that the function $\lambda_1(T)$ obtained in the present study is steeper than the function calculated by Eq. (17). This difference is probably attributable to the fact that the Aiken calculation of f for polyatomic gases yields, as a rule, a lower variation of $\lambda(\eta)$ with temperature than in the experimental method. This question is discussed in detail in [13].

Thus, it follows from the foregoing that the correction for the temperature jump in a dissociating gas, AB_{ef}/P, unlike the analogous correction in a pure gas, is also a function of the gas composition and the energy of the dissociation reaction. The influence of the interaction of the dissociating gas with the surface of the measuring cell on the experimental investigation of its thermal conductivity at low pressures is such that from the processing of the experimental data obtained in one cell it is possible to find only the values λ_*, A_*, etc., which are a combination of the components of the effective thermal conductivity and the temperature-jump factor B_{ef}. The values of the components can be determined only by the further introduction of corrections into the calculation, taking account of the constant of the dissociation equilibrium $K_p(T)$, the dissociation-reaction energy $Q_p(T)$, and the geometric factor A for the cell. Moreover, in a number of cases the errors in the values of $Q_p(T)$ and $K_p(T)$ are so large that the calculation of the corrections cannot be effective. It is also shown that the effective thermal conductivity of a dissociating gas can be determined directly without using any information on the nature of the interaction of this gas with the surface, by carrying out special experiments on two or more measuring cells with different values of the geometric factor. In such experiments we can determine not only λ_{tr} but also the structure of $B_{ef}(P, T)$.

NOTATION

λ_{exp}, λ_{tr}, λ_{ef}, λ_{mix}, λ_1, thermal conductivities (experimental, true, effective, mixture, and monomer); A, geometric factor for the measuring cell; r_1, r_2, radii of the filament and the inner surface of the tube of the measuring cell; B_{ef}, temperature-jump factor; B_*, temperature-jump factor for the monomer; P, pressure; $\overline{V}(T)$, thermal velocities of the molecules; α_{ef_1}, α_{ef_2}, β, α_{mix}, coefficients of accommodation of the monomer, dimer, composition, and mixture; X_1, X_2, mole fractions of the monomer and the dimer, α, degree of dissociation; ξ, correction multiplier; γ, ratio of specific heat at constant pressure to specific heat at constant volume; C_p, C_v, specific heat values at constant pressure and constant volume; $\sigma^2\Omega^{(2.2)*}$, $\sigma^2\Omega^{(1.1)*}$, viscosity and diffusion cross sections of interaction; $D_{12}(T)$, binary coefficient of diffusion; $Q_p(T)$, reaction energy; R, gas constant; T, temperature; λ_*, A_*, C_*, expansion coefficients; f, Maxwell parameter; η, viscosity; $K_p(T)$, dissociation equilibrium constant.

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