EXPERIMENTAL INVESTIGATION OF THE THERMAL CONDUCTIVITY OF TOLUENE, BIPHENYL, AND CARBON TETRACHLORIDE VAPOR

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New experimental data have been obtained on the thermal conductivity of toluene, biphenyl, and carbon tetrachloride vapor. The data obtained are compared with formulas proposed for the thermal conductivity of polyatomic gases and also with the data of recent NBS tables.

Modern technology and standardization require the systematic investigation of the thermophysical properties, in particular, the thermal conductivity of gases. In previous articles, the results of such investigations have been presented for argon [1], hydrogen [2], and helium [3]. This article presents the results of an experimental investigation of the thermal conductivity of three substances in the gaseous state: toluene, carbon tetrachloride, and biphenyl.

Measurements. The thermal conductivity of the vapor was investigated by the hot-wire method. The thermal conductivity of the test substance was determined on the basis of the measurements using the formula

$$\lambda = A\,\frac{W - W_{\text{rad}}}{\Delta t_g}, \qquad \text{(I)}$$

where $A = \ln(D/d)/2\pi l$ is the instrument constant; W is the power released over the measurement range; W_r is the radiative component of the heater power; and Δt_g is the temperature difference in the gas layer.

In conducting the experiments, we took the following corrections into account: 1) radiative heat transfer; 2) the temperature drop in the wall of the measuring tube; 3) heat losses from the ends of the heater [4].

The elimination of convection was ensured by a suitable choice of the geometry of the measuring tube and the temperature gradient in the gas layer. In all the experiments, $\mathrm{Gr}\cdot\mathrm{Pr} < 1000$.

The characteristics of the measuring tube were: length of measuring interval l = 155.5 mm; inside diameter of tube D = 3.98 mm; outside diameter of tube D_e = 5.98 mm; diameter of measuring wire d = 0.100 mm; resistance of measuring wire at t = 0° C, R_0 = = 1.6570 ohms; and resistance of external resistance thermometer, R_0 = 11.138 ohms.

The experimental apparatus is shown schematically in Fig. 1.

To take the effect of the temperature jump into account, measurements must be made at various vapor pressures. Therefore, we used glass U-manometer 1, one arm of which contained liquid source 2 of the test vapor above the mercury. Electric heater 3 enclosed the manometer in the region of the liquid, so that the necessary pressure could be created in the apparatus.

Before beginning the experiments, to check the operation of the platinum resistance thermometers, we compared the temperature readings of the measuring wire and a resistance thermometer wound around the walls of the tube at "nonheating" currents ($I_{\text{wire}} \approx I_{\text{wall}} \approx 0.01$ A). The deviations δt of the resistance thermometer readings did not exceed ±0.02° C. Similar measurements were also made after the experiments at various temperatures, and the δt did not exceed ±0.03. This shows that the apparatus was satisfactorily assembled so that the spring centered the wire in the tube without bending it. The operation of the apparatus was checked on a well-studied substance—air. The data obtained proved to be in good agreement with the most reliable published data [5]. The maximum discrepancy was 1%.

The results of experiments on toluene vapor at t = = 430° C showed that a change in vapor pressure from

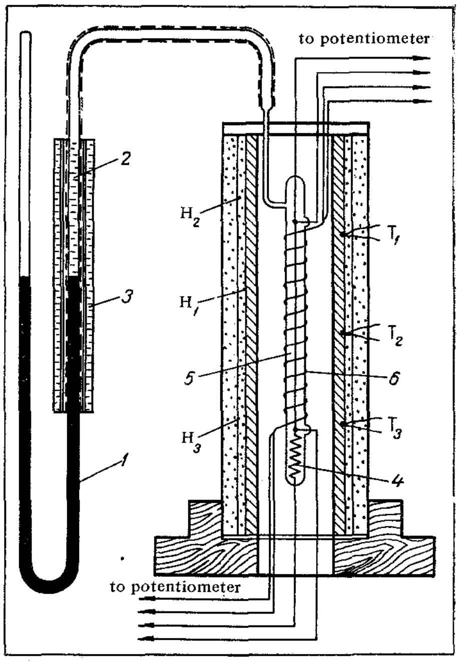

Fig. 1. Diagram of the experimental apparatus: 1) mercury manometer; 2) test liquid; 3) electric heater; 4) spring; 5) platinum electric heater; 6) platinum resistance thermometer at the surface of the measuring tube; T_1, T_2, and T_3—thermocouples; H_1—main heater; H_2 and H_3—screening heaters.

Table 1

Experimental Data

t_w, °C	t_{tw}, °C	Δt, °C	Δt_{tw}, °C	Δt_g, °C	W_{meas}, mW	W_{rad}, mW	λ', mW/ /m·deg	$\delta\lambda_c$, %	λ, mW/ /m·deg	$\bar{t}$, °C
Toluene (C_7H_8)										
47.35	24.63	22.72	0.03	22.69	77.1	0.69	12.55	4.6	11.89	36.0
120.33	101.53	19.11	0.03	18.77	95.2	1.01	18.56	3.76	17.68	110.9
146.98	128.84	18.14	0.03	18.11	103.1	1.28	21.05	3.56	20.06	137.9
147.44	129.57	17.87	0.03	17.84	103.1	1.22	21.28	3.54	20.42	138.5
171.50	154.05	17.50	0.04	17.46	107.0	1.47	22.68	3.4	21.86	162.8
242.57	227.78	14.79	0.04	14.75	117.9	2.15	29.03	3.02	28.14	235.2
243.44	228.57	14.87	0.04	14.83	118.0	2.19	28.89	3.03	28.03	236.0
260.55	246.58	13.97	0.04	13.93	116.7	2.33	30.94	2.95	29.54	253.6
378.46	363.64	14.82	0.05	14.77	169.8	5.12	42.33	2.53	40.24	371.0
398.01	383.87	14.14	0.05	14.09	172.2	5.47	45.04	2.46	42.72	390.9
398.22	384.15	14.07	0.05	14.02	172.1	5.47	45.23	2.45	42.94	391.2
435.70	421.92	13.79	0.05	13.74	176.6	6.63	47.45	2.4	44.72	428.9
435.36	421.74	13.62	0.05	13.57	176.5	6.51	47.92	2.4	45.24	428.5
Carbon tetrachloride (CCl_4)										
46.58	24.83	21.75	0.02	21.73	44.7	0.58	7.50	5.9	7.08	35.7
56.77	25.54	31.23	0.02	31.21	66.7	0.81	7.79	5.8	7.33	41.2
78.66	58.43	20.23	0.02	20.21	48.9	0.70	8.96	5.5	8.34	68.5
96.43	77.09	19.34	0.02	19.32	51.0	0.81	9.63	5.25	8.96	86.8
134.59	116.0	18.59	0.02	18.57	55.7	1.28	10.82	4.9	10.23	125.3
140.45	121.45	19.00	0.02	18.95	56.2	1.16	10.93	4.85	10.35	130.9
159.22	140.67	18.55	0.02	18.52	58.2	1.40	11.35	4.8	10.82	150.0
180.34	162.32	18.02	0.02	18.00	60.5	1.63	12.10	4.7	11.51	171.3
207.94	190.10	17.84	0.02	17.82	63.4	1.98	12.68	4.55	12.15	199.0
254.44	237.36	17.08	0.02	17.06	67.9	2.9	14.12	4.3	13.52	245.9
355.40	318.80	16.60	0.03	16.58	75.2	4.18	15.82	2.6	15.53	326.6
Biphenyl ($C_{12}H_{10}$)										
198.36	163.82	34.54	0.04	34.50	178.4	3.4	18.84	3.3	18.25	181.1
250.33	221.03	29.30	0.04	29.26	194.0	4.3	23.96	3.18	23.14	235.6
285.83	255.17	30.66	0.05	30.62	211.2	5.8	24.89	3.18	24.07	270.5
311.67	279.41	32.26	0.05	32.21	257.5	7.2	28.61	3.03	27.56	295
230.68	291.52	39.16	0.06	39.1	306.6	9.8	28.14	3.06	27.33	311.1
332.54	292.42	40.12	0.06	40.06	318.3	10	28.49	3.04	27.56	312.5
375.0	340.99	34.01	0.06	33.95	310.1	11.1	32.68	2.85	31.75	358

180 to 450 mm had practically no effect on the thermal conductivity. Moreover, we calculated the correction for the temperature jump from the relation presented in [1] at an accommodation coefficient $a = 0.93$ [6]. At 100–400 mm Hg and a temperature of T = 702° K, the correction was less than 0.1%.

Results of the investigation. 1. Toluene (C_7H_8) (Fig. 2). The thermal conductivity of toluene vapor was measured in the temperature range from 309 to T ≅ ≅ 702° K. In the experiments, we used chemically pure toluene: $n_D^{20} = 1.497$, $t_{b.p} = 110–111°$ C, $\rho^{20} = 0.867$ g/cm^3.

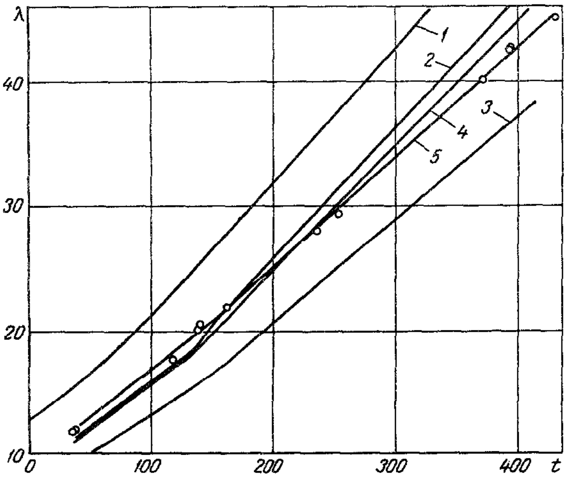

Fig. 2. Thermal conductivity of toluene vapor: 1) NBS tables; 2) modified Eucken correction; 3) simple Eucken correction; 4) Bromley method; 5) curve based on our experimental points.

The results of the experiments are presented in Table 1.

2. Carbon tetrachloride (CCl_4). In the experiments, we used pure carbon tetrachloride: $n_D^{20} = 1.4602$, $t_{b.p} = 76.7°$ C, $d_4^{20} = 1.594$.

The thermal conductivity of CCl_4 vapor was measured on the temperature interval 309–608° K at corresponding pressures of 100–500 mm Hg.

Since, in the experiments with toluene vapor at the same pressures and temperatures, the temperature jump was negligibly small, it can be even more readily disregarded in the experiments with carbon tetrachloride and biphenyl vapor, since the molecular weights of these two substances are 1.5 times as great as that of toluene.

The results of the experiments are given in Table 1.

3. Biphenyl ($C_{12}H_{10}$). The experiments were conducted with pure biphenyl: $n_D^{77.1} = 1.5882$, $d_4^{73} = 0.992$, $t_{m.p} = 70.5°$ C, $t_{b.p} = 256°$ C.

The thermal conductivity of the biphenyl vapor was measured on the temperature interval 454–631° K at corresponding pressure p = 100–780 mm Hg.

An experiment at constant vapor temperature ≅295° C showed that a change of pressure from 100 to 780 mm Hg had no effect (to within 0.3%) on the value of λ; this shows that, in practice, it is possible to disregard the temperature jump. Table 2 presents the smoothed λ of all the test substances in the gaseous state for the same temperature.

Table 2

Smoothed Data on the Thermal Conductivity λ (mW/m • deg)

T, °K	Toluene	Carbon tetrachloride	Biphenyl
300	11.2	6.9	—
325	13.0	7.7	—
350	14.9	8.5	—
375	16.8	9.3	—
400	18.8	10.1	—
425	20.8	10.9	—
450	22.9	11.6	18.4
475	25.0	12.3	19.8
500	27.2	13.0	21.4
525	29.4	13.7	23.2
550	31.6	14.4	25.2
575	34.00	15.1	27.2
600	36.2	15.8	29.4
625	38.4	—	31.8
650	40.6	—	34.6
675	43.0	—	—
700	45.4	—	—

Comparison of the experimental results with data obtained by other authors. The only published experimental data on the thermal conductivity of toluene vapor are those obtained by Abas-Zade at temperatures of 273–574° K [7]. But the Abas-Zade graph only gives the data for the saturated vapor. For benzene, however, data are presented for both the saturated vapor and for a pressure $p \leq 1$ atm. Naturally, the values of the thermal conductivity of the superheated vapor lie below the values of λ for the saturated vapor. It should be noted that, for benzene vapor, Abas-Zade's low-pressure data are also in good agreement with Moser's data at $p \leq 1$ atm. For benzene, the values of λ for the saturated vapor differ from the λ at low pressures according to Abas-Zade's experiments by not more than 12% at $t = 100°$ C and 23% at $t = 280°$ C. If we introduce the same correction into the values of λ for saturated toluene vapor and determine the thermal conductivity at $p = 1$ atm, we find that the Abas-Zade data differ from ours on the average by 2%. This calculation is to a certain extent conditional. But at the same time it shows that the Abas-Zade data on toluene vapor at $p \leq$ ≤ 1 atm are in perfectly satisfactory agreement with our own experimental data.

We note that in the NBS tables [8] the Abas-Zade data relating to the saturation line are erroneously taken as the values of λ at $p \leq 1$ atm.

Experimental data on the thermal conductivity of carbon tetrachloride vapor are given by Moser [9] and Masia [10], the maximum descrepancy between their results being 7%. Moser used the hot-wire method as a relative method. The standard was air with a thermal conductivity at 0° C, $\lambda_0 = 5.66 \cdot 10^{-5}$ cal/cm • sec • °C.

On the basis of numerous studies, it is now accepted that for air at 0° C, $\lambda_0 = 5.83 \cdot 10^{-5}$ cal/cm • sec • °C; consequently, Moser obtained values of the thermal conductivity of CCl_4 vapor that were too low by about 3%. If we correct Moser's values of λ for CCl_4 using more accurate values for the λ of air, the discrepancy between Moser's data and those of Masia amounts to 4%.

The results of our measurements are compared with the data of Masia and Moser in the graph shown in Fig. 3. It is clear from the graph that our results are in better agreement with the data of Masia, the discrepancy being about 2%, whereas the discrepancy with Moser's data is 5.4%. Moser's low data may have been obtained because in his experiments the wall temperature of the measuring tube was not measured directly but taken equal to the temperature of the thermostated chamber containing the saturated vapor of various liquids. The thermal conductivity of biphenyl vapor was investigated in 1966 by Reiter [11] up to 600° K. The discrepancies between our results and Reiter's data do not exceed 3% (see Fig. 4).

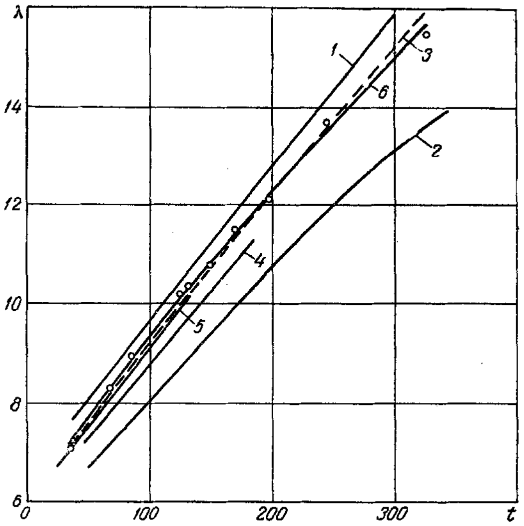

Fig. 3. Thermal conductivity of carbon tetrachloride vapor: 1) modified Eucken correction; 2) simple Eucken correction; 3) Bromley method; 4) Moser's data; 5) Masia's data; 6) curve based on our experimental points.

However, Reiter's extrapolated values at higher temperatures are much too high; thus, at $T = 700°$ K they are 15% too high.

Other data on $C_{12}H_{10}$ are included in a book published by the National Bureau of Standards [8]. Un-

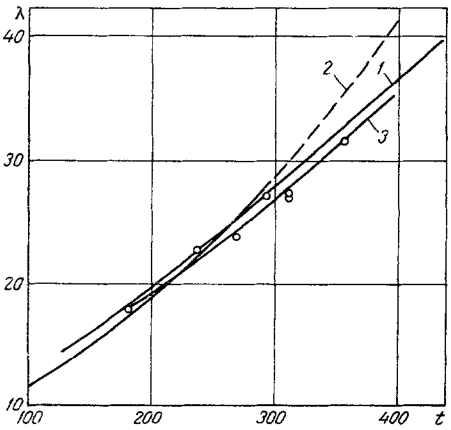

Fig. 4. Thermal conductivity of biphenyl vapor: 1) NBS tables; 2) Reiter's data (experiment and extrapolation–dashed line); 3) curve based on our experimental points.

fortunately, it is not stated whether these data were obtained experimentally or by calculation. It is clear from the graph (Fig. 4) that they differ from our data by about 3%.

Comparison of experimental data with data calculated on the basis of the kinetic theory of gases. We compared the experimental data on the thermal conductivity of toluene and CCl_4 vapor with the theoretical formulas of Eucken [12], Mason and Monchick [13], and Bromley [14] for polyatomic gases.

Eucken proposed that the translational, rotational, and vibrational energy components be taken separately into account:

$$\frac{\lambda M}{\eta} = 2.5\, C_{\text{trans}} + f_{\text{int}}\, C_{\text{int}}. \tag{1}$$

Setting $f_{\text{trans}} = 2.5$, $C_{v\,\text{trans}} = 3R/2$, $f_{\text{int}} = 1$, $C_{v\,\text{int.}} = C_v - 3R/2$ [14], we obtain

$$\frac{\lambda M}{\eta} = \frac{15}{4} R \left(\frac{4}{15} \frac{C_v}{R} + \frac{3}{5} \right). \tag{2}$$

As a rule, Eq. (2) gives values of λ that are too low in comparison with the experimental values. Monchick and Mason [13] proposed a more accurately derived modified Eucken correction [15]

$$\frac{\lambda M}{\eta} = \frac{15}{4} R + \left(C_v - \frac{3}{2} R \right) \frac{\rho D_{11}}{\eta}, \tag{3}$$

where

$$f_{\text{int}} = \frac{\rho D_{11}}{\eta} = \frac{5}{6} \frac{\Omega^{(2.2)*}}{\Omega^{(1.1)*}}. \tag{4}$$

Here, $\Omega^{(1.1)*}$ and $\Omega^{(2.2)*}$ are collision integrals.

Expression (3) usually gives values of λ that are somewhat too high. For complex polyatomic gas molecules, Bromley proposed taking the Eucken correction into account with allowance for the molecular structure [14]:

$$\frac{\lambda M}{\eta} = (2{,}5 - \alpha) C_{\text{disp}} + \beta C_{\text{vib}} + \psi C_{\text{rot}} + C_{\text{int. rot}}, \tag{5}$$

C_{disp}, C_{rot}, C_{vib} are the group components of displacement, rotation, and vibration; α is a coefficient characterizing the interaction of the colliding molecules.

Equations (2), (3), and (5) were used to compute the thermal conductivity of toluene vapor. The quantity $\Omega^{(2.2)*}/\Omega^{(1.1)*}$ was determined from tables presented in [16] for the Lennard-Jones potential. The value of ε, needed to calculate the reduced temperature ($T^* = (k/\varepsilon)T$), was determined from data on the viscosity η [16]. At the same time, from the data on η we also determined the constant σ [17, 18]. The values of ε and σ proved to be as follows: for toluene $\varepsilon/k = 380.2°$ K; $\sigma = 5.907$ Å; for carbon tetrachloride $\varepsilon/k = 322.7$; $\sigma = 5.947$ Å. Calculations were not made for biphenyl vapor, since we were unable to find viscosity data.

Our experimental data are compared with the values calculated from the above equations in Figs. 2 and 3.

a) Toluene. From the graph (Fig. 2), it is clear that the simple Eucken correction gives values that are too low; Eqs. (3) and (5) (modified Eucken correction and Bromley method) both give values of λ that are in satisfactory agreement with our experimental data, the discrepancy being between 3 and 7%.

b) Carbon tetrachloride (Fig. 3). The simple Eucken correction gives excessively low values of λ; the modified correction gives values that are too high. Good agreement, within 2%, with our experimental data is given by the Bromley calculation.

Estimates of experimental accuracy. The maximum relative error of the experimental data is composed of the maximum errors of the quantities entering into the formula from which λ was determined:

$$\lambda = A \frac{Q}{\Delta t_g}, \tag{6}$$

where $A = \ln(D/d)/2\pi l$ is the instrument constant.

The relative measuring error

$$\delta\lambda = \frac{\Delta\lambda}{\lambda} + \frac{\Delta A}{A} + \frac{\Delta Q}{Q} + \frac{\Delta(\Delta t_g)}{\Delta t_g}.$$

The maximum error $\delta\lambda = 1.5\%$. In this case, the radiation error $\delta W_{\text{rad}} = 0.2\%$; the error in determining the temperature drop in the gas layer $\delta(\Delta t_g) = 0.2\%$; the error in determining the correction for the heat losses from the ends of the measuring wire $\delta\lambda_e = 0.3\%$; and the relative error of the quantity A $\delta A = 0.8\%$.

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