EXPERIMENTAL DETERMINATION OF THE THERMAL CONDUCTIVITY OF BINARY GAS MIXTURES

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A test apparatus is described for determining the thermal conductivity of gases and gas mixtures by the hot filament method. Values have been obtained for helium and argon as well as for their mixtures within the 293-394°K temperature range under a pressure of P = 1 atm.

More attention is being paid now to experimental studies concerning the thermal conductivity of gas mixtures, inasmuch as exact values of the thermal conductivity are needed for the design of heat exchangers and also for the correct interpretation of many physical and physicochemical phenomena related to molecular transport in gas mixtures.

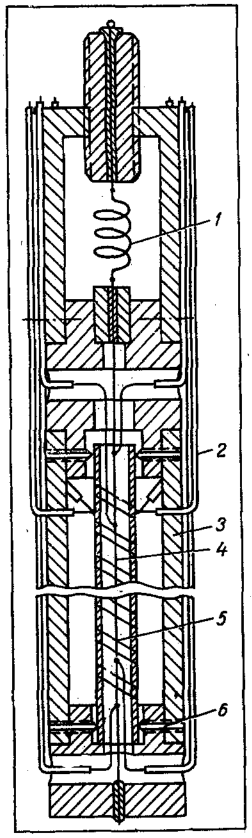

Fig. 1. Construction of the measuring cell: 1) tungsten spring; 2) insulating capillaries; 3) cell housing; 4) inner thermometer; 5) outer thermometer; 6) centering screws.

Among the most widely used methods of determining the thermal conductivity of gases and gas mixtures today is the hot filament method, which operates on the principle of heat transfer in a gas contained between two coaxial cylinders. The inner cylinder comprises a plantinum filament serving as both a heater and a resistance thermometer. The outer cylinder comprises a capillary glass tube on which another platinum resistance thermometer is wound bifilarly. After stabilization, a steady thermal flux flows radially from the heater through the test layer of gas to the wall of the capillary.

In this case the thermal conductivity can be defined by the expression

$$\lambda = \frac{AQ_T}{\Delta t_{meas} - BQ_T \pm \Delta t_{deg}}, \qquad (1)$$

where

$$A = \frac{\ln d_2/d_1}{2\pi l}, \qquad B = \frac{\ln d_3/d_2}{2\pi l \lambda_w}.$$

The quantities in this formula are the instrument constant A which depends on the geometrical dimensions of the measuring cell (the diameter of the platinum heater is d_1 mm, the inside diameter of the capillary is d_2 mm, the length of the test segment is l m) and the constant B defined not only by the geometrical dimensions but also by the thermal conductivity of the capillary material (the outside diameter of the capillary is d_3 mm, the thermal conductivity of the capillary material is λ_w W/m · deg), the quantity of heat transmitted through the layer of test material by conduction only Q_T (W), the temperature difference between the inner and the outer resistance

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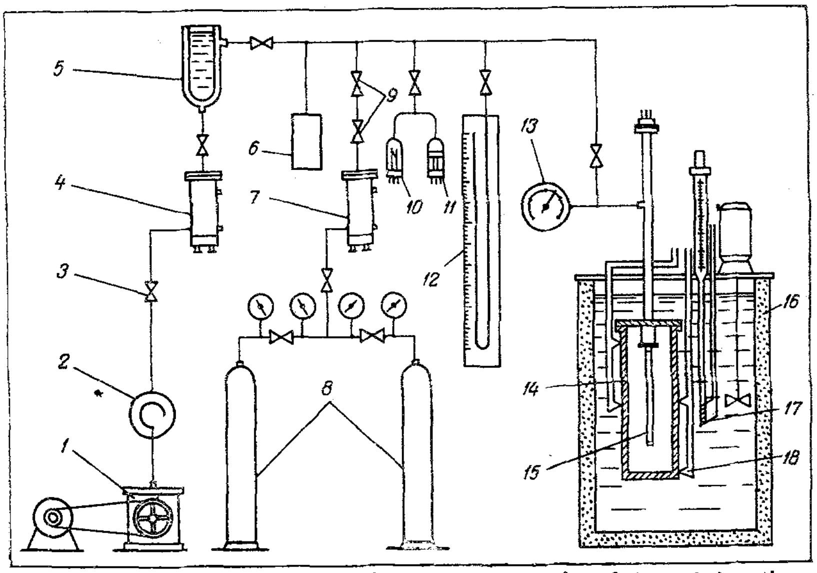

Fig. 2. Schematic diagram of the apparatus for determining the thermal conductivity of gas mixtures: 1) prevacuum pump; 2) oil trap; 3) vacuum valve; 4) diffusion pump; 5) nitrogen trap; 6) bottle for preparing the mixture; 7) gas drying system; 8) gas tanks; 9) metering valves; 10 and 11) manometric lamps; 12) mercury manometer; 13) sampling vacuumeter; 14) working chamber; 15) measuring cell; 16 thermostat; 17) temperature regulating system; 18) temperature control system.

thermometer $\Delta t_{meas} = t_1 - t_2$ (°C), and the correction to the readings of the inner thermometer calibrated against the outer thermometer Δt_{cal}.

The measuring cell shown schematically in Fig. 1 was constructed on the hot filament principle for studying the thermal conductivity of gases and gas mixtures within the 293-393°K temperature range. The inner platinum resistance thermometer 4 was fastened rigidly to the lower part of the metallic housing 3 and was welded to spring 1 of grade A-1 tungsten wire 150 μ in diameter. The glass capillary was centered relative to the inner resistance thermometer 4 by means of eight adjusting screws 6, which made it possible to reduce the eccentricity between filament and capillary to a negligible amount.

The inner and the outer resistance thermometer were both built to specifications for platinum resistance thermometers [1] and were then calibrated against two reference points (triple point of water [2] and boiling point of water [3]). This calibration yielded

$$\frac{R_{100}}{R_0} = 1.3816.$$

Above 100°C, the resistance thermometers were calibrated in a thermostat against laboratory mercury thermometers within an accuracy of ±0.01°C.

The capillary was calibrated and the filament eccentricity was established by means of a model MIR-12$^\times$ microscope with a model MOV-1-15$^\times$ ocular micrometer screw. The length of the test segment was measured with a model IZA-2 comparator.

The geometrical dimensions of the measuring cell and the parameters of the resistance thermometers were as follows: inside diameter of capillary 3.935 mm, outside diameter of capillary 5.965 mm, wire diameter of inner resistance thermometer 0.071 mm, length of test segment 98.13 mm, wire diameter of outer resistance thermometer 0.071 mm, thickness of tested gas layer 1.932 mm, resistance of inner thermometer 2.5726 Ω at 0°C, resistance of outer thermometer 12.175 Ω at 0°C, value of constant A calculated from the geometrical dimensions 6.511, value of constant B calculated from the geometrical dimensions 0.963, eccentricity between filament axis and capillary axis 0.067 mm, and the correction for eccentricity 0.05%.

TABLE 1. Test Data for Determining the Thermal Conductivity of the Helium–Argon System

t_1, °C	t_2, °C	$Q\cdot10^4$, W	$Q_r\cdot10^4$, W	$Q_c\cdot10^4$, W	$\frac{Q_c}{Q}$, %	$Q_T\cdot10^4$, W	$\lambda\cdot10^3$, W/m·deg	t_G, °C	Δt, °C
				Ar					
37,48	27,11	289,8	1,1	5,8	2,03	282,8	17,82	32,29	10,34
45,93	30,63	432,4	1,2	8,6	1,99	422,6	18,04	38,28	15,26
48,77	32,04	482,5	2,0	9,5	1,97	470,9	18,36	40,40	16,71
56,19	38,27	523,6	2,2	9,9	1,91	511,4	18,64	47,23	17,87
64,09	42,11	654,1	3,1	12,2	1,87	638,7	18,97	53,10	21,92
67,07	51,77	462,9	2,1	8,7	1,89	451,9	19,30	59,42	15,26
86,91	64,31	716,6	3,8	12,2	1,70	700,4	20,22	75,61	22,53
114,28	69,69	1463,1	8,8	17,9	1,70	1436,3	21,00	91,98	44,45
127,50	80,02	1598,7	10,4	27,7	1,70	1560,5	21,40	103,73	47,33
139,80	89,59	1718,1	12,2	29,1	1,69	1676,6	21,80	114,69	50,05
				75% Ar — 25% He					
43,49	31,92	578,1	1,3	7,6	1,33	569,1	32,18	37,70	11,52
55,74	42,03	708,7	1,7	9,1	1,28	697,8	33,31	48,88	13,64
66,88	52,85	761,0	2,0	9,4	1,24	749,5	34,96	59,86	13,96
80,65	65,21	856,0	2,5	10,2	1,19	843,1	35,75	72,93	15,36
87,92	72,59	865,8	2,7	10,1	1,17	852,9	36,43	80,25	15,25
97,94	82,08	921,9	3,1	10,5	1,14	908,3	37,50	90,01	15,77
108,68	93,07	935,0	3,3	10,3	1,11	921,3	38,65	100,87	15,52
121,20	105,11	1011,0	3,9	10,8	1,07	996,3	40,56	113,15	16,00
127,60	109,38	1124,5	4,6	11,8	1,05	1108,0	39,84	118,49	18,12
				50% Ar — 50% He					
36,05	27,87	656,1	0,8	6,6	1,02	648,5	52,02	31,96	8,12
44,69	35,34	770,5	1,1	7,6	0,99	761,7	53,47	40,01	9,28
58,57	48,75	863,4	1,3	8,2	0,95	853,8	57,09	53,66	9,74
66,13	55,78	927,4	1,5	8,6	0,93	917,2	58,20	60,95	10,26
75,54	64,44	1002,7	1,7	9,0	0,91	991,8	58,69	69,99	11,01
86,80	75,37	1062,5	2,0	9,3	0,88	1051,1	60,42	81,08	11,33
97,66	84,90	1214,3	2,5	10,3	0,85	1201,4	61,87	91,28	12,65
109,30	96,07	1300,6	2,9	10,7	0,83	1286,9	63,94	102,68	13,11
119,66	104,97	1478,4	3,5	11,9	0,81	1463,0	65,47	112,31	14,55
125,90	109,72	1655,4	4,0	13,2	0,79	1638,1	66,58	117,81	16,02
				25% Ar — 75% He					
40,07	31,38	1151,1	0,9	9,7	0,85	1140,4	86,55	35,72	8,58
47,97	38,28	1312,1	1,1	10,8	0,83	1300,1	88,51	43,12	9,57
64,07	54,03	1420,3	1,4	11,1	0,78	1407,7	92,55	59,05	9,91
75,39	64,89	1549,8	1,6	11,7	0,76	1536,3	96,64	70,14	10,35
87,24	76,49	1630,0	1,9	11,9	0,73	1616,0	99,33	81,86	10,60
95,96	85,19	1687,1	2,1	12,1	0,72	1672,9	102,68	90,57	10,61
107,92	96,09	1910,1	2,5	13,2	0,69	1894,2	105,91	102,00	11,65
122,10	109,33	2161,2	3,1	14,5	0,67	2143,5	111,00	115,71	12,57
127,85	113,43	2417,1	3,7	16,0	0,66	2397,3	110,03	120,64	14,18
				He					
36,44	31,37	1136,8	0,5	7,5	0,66	1128,7	148,14	33,90	4,96
40,04	34,99	1149,3	0,5	7,5	0,65	1141,2	150,43	37,51	4,94
53,02	47,43	1317,1	0,7	8,2	0,63	1308,1	155,90	50,22	5,46
56,40	50,08	1507,2	0,8	9,3	0,62	1496,9	157,83	53,24	6,18
66,55	61,23	1302,3	0,8	7,8	0,60	1293,7	162,15	63,89	5,20
80,16	67,62	3200,2	2,1	18,8	0,59	3179,3	169,22	73,89	15,24
88,31	77,07	2918,5	2,0	16,6	0,57	2899,7	172,28	82,69	10,96
98,39	86,99	3037,2	2,2	16,9	0,56	3018,0	176,90	92,69	11,10
108,14	96,25	3206,4	2,6	17,3	0,54	3186,4	179,13	102,19	11,58
117,44	105,48	3291,0	2,8	17,3	0,53	3270,8	182,90	111,46	11,65

Note: t_1, t_2) readings of inner and outer resistance thermometers, respectively; Q) total heat generated by heater; Q_r) heated transmitted from heater to capillary by radiation; Q_c) heat dissipated along electric current and potential leads; λ) thermal conductivity of test gas; t_G) gas temperature; Δt) temperature drop across layer of test gas.

An overall view of the test apparatus for determining the thermal conductivity of gases and gas mixtures is shown in Fig. 2. In order to eliminate the thermodiffusion effect in gas mixtures [4-7], the measuring cell 15 was placed inside a working chamber 14 having a volume of 1400 cm^3 and a hermetic plug

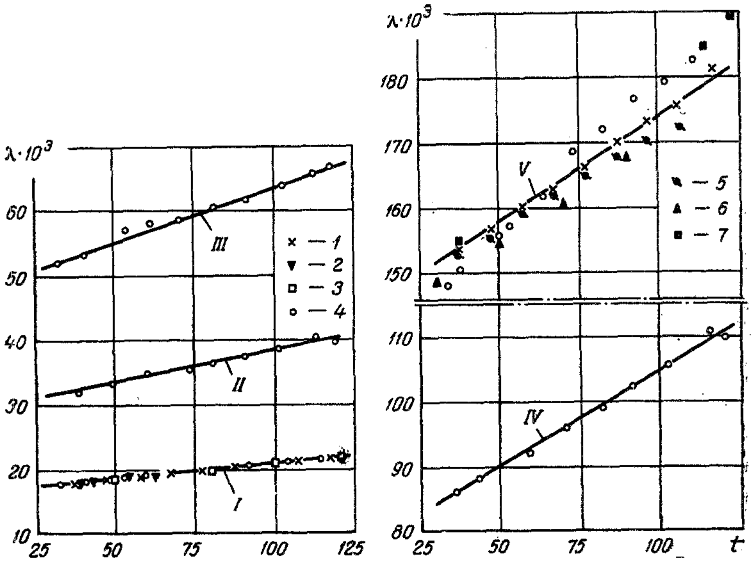

Fig. 3. Thermal conductivity of the helium–argon system as a function of the temperature, at the following molal concentrations of the heavier component: I) $x_2 = 1.0$; II) 0.75; III) 0.50; IV) 0.25; V) 0.0; 1) adjusted values according to [11, 12]; 2) test data in [13]; 3) test data in [14]; 4) our test data; 5) test data in [15]; 6) test data in [17]; 7) test data in [16]. Thermal conductivity λ (W/m · deg), temperature t (°C).

through which all leads from the measuring cell were brought out to the instrument panel. In order to maintain a constant temperature at the outside wall of the capillary, the cell together with the working chamber was placed in a thermostat 16 filled with grade VKZh-94 silicon-organic fluid. The thermostat precision was improved by means of a temperature regulator operating in conjunction with a wide-pulse Guy modulator [8]. This stabilization system made it feasible to maintain the temperature inside the thermostat constant within ±0.01°C. The use of a massive cylindrical $V = 1400$ cm^3 working chamber made of brass with a $\delta = 7$ mm wall thickness ensured a uniform temperature field within 0.005°C along the test segment.

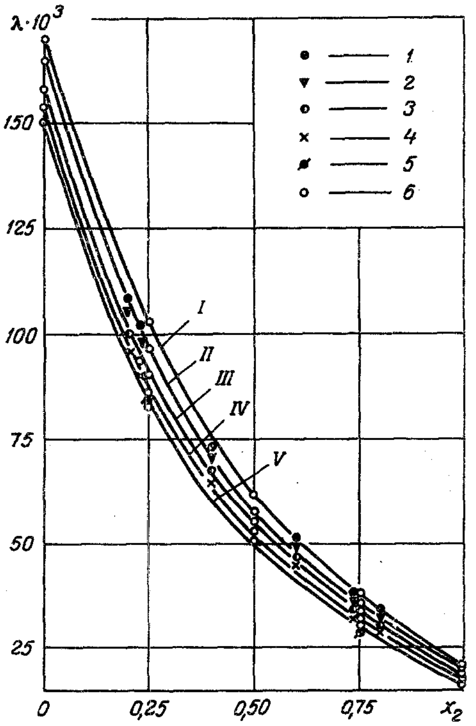

Fig. 4. Thermal conductivity of the helium–argon system as a function of the concentration, at t = const: I) 90°C [(1) test data in [17, 19]]; II) 70°C [(2) test data in [17, 19]]; III) 50°C [(3) test data in [17, 19]]; IV) 35°C [(4) test data in [17, 19]]; V) 23.8°C [(5) test data in [20]]; 6) our test data. Thermal conductivity λ (W/m · deg).

The uniformity of the temperature field during the experiment was checked by means of two differential thermocouples 18. The longest time to stabilize a uniform temperature field in the test cell was approximately 4 h.

The performance of the apparatus was first checked on a well known substance, namely on air. The thermal conductivity data agreed closely with the most reliable published data on air [9, 10].

With this apparatus was then measured the thermal conductivity of helium–argon mixtures within the 293-393°K temperature range.

The results of measurements are shown in Table 1 together with corrections for radiation, for heat dissipation from the filament along electric current and potential leads, and for the temperature drop across the capillary wall – all accounted for in the design. In Fig.3 our test data are compared with those obtained by other authors. According to the graphs, our values agree closely with those in [11-17]; they differ from values suggested in [11, 12] for argon by ±0.3% and for helium by ±1.7%.

Because of the large differences between the thermal conductivity of argon and helium, the gas temperature t_G and the temperature drop across the gas layer Δt are quite different at the same electric heating current and at a constant temperature at the outside surface of the capillary. For this reason, we have plotted the thermal conductivity of the system as a function of the temperature at a constant concentration. On the basis of these data, one can determine the thermal conductivity as a function of the concentration at any temperature up to 394°K.

The thermal conductivity of the helium–argon system as a function of the concentration at 23.8, 35, 50, 70, and 90°C is shown in Fig.4 for the following molal concentrations of the heavier component: 0, 0.25, 0.50, 0.75, and 1.0. Our data agree closely with the data in [17-22], with the maximum difference not exceeding 1.5%.

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