THERMAL CONDUCTIVITY OF THE HYDROGEN – HELIUM MIXTURE

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Test data are presented pertaining to the thermal conductivity of the hydrogen–helium mixture over the 0-150°C temperature range. Discussed is also the existence of a minimum in the composition characteristic of thermal conductivity within a wide temperature range.

A study of the thermal conductivity of the hydrogen–helium mixture is very worthwhile from the standpoint of revealing why the thermal conductivity becomes minimum at a certain ratio of polyatomic and monoatomic gas in the mixture.

The existence of a minimum in the composition characteristic of thermal conductivity, at a certain hydrogen concentration in the hydrogen–helium mixture, was noted by Madison [1] as well as by Schmauch and Dinerstein [2]. They have found that the thermal conductivity is minimum at an ~8% hydrogen content. Hansen, Frost, and Murphy [3] measured the thermal conductivity of this mixture by means of a chromatographic heat-conduction cell and detected a minimum at an ~13% hydrogen content.

At this hydrogen content the thermal conductivity of the mixture was 0.5% lower than that of pure helium. Van Ee [4] noted a similar trend in his experiment with thermal diffusion. Neal, Greenway, and Coutts [5] have confirmed the existence of such a minimum at a 17% hydrogen content when the temperature is 312°K, the thermal conductivity being then 5 ± 2% lower than that of pure helium. Barua alone [6] and with Mukhopadhyay [7] also measured the thermal conductivity of the hydrogen–helium mixture. In [6] are given data obtained at 303 and 318°K, in [7] are given data covering the 90-473°K temperature range. Mukhopadhyay and Barua obtained data indicating a minimum thermal conductivity at a 14.5% hydrogen content, with the thermal conductivity of the mixture being 8% lower than that of pure helium. The data obtained by Tondon, Gandhi, and Saxena [8] indicate that the thermal conductivity of the mixture with a hydrogen content from 0 to 25% is 1% lower than that of pure helium.

The existence of a minimum in the composition characteristic of thermal conductivity at $T = 273°K$ has been confirmed experimentally by Minter [9], at an 8% hydrogen content. Biolsi and Mason [10] have shown that, as the temperature rises, the minimum thermal conductivity shifts toward pure helium. Cauwenbergh and Van Dael [11] measured the thermal conductivity of this mixture at 296.8°K. Their measurements have revealed the existence of a smooth minimum within the 8-14% range of hydrogen content, with $\lambda_{mix}/\lambda_{He} = 0.995$.

Golubev [12] measured the thermal conductivity of the hydrogen–helium mixture under various pressures, beginning at a temperature of 77.96°K. Under a pressure $p = 1$ MN/m^2 the composition characteristic of the thermal conductivity has a soft minimum at an ~60% hydrogen content, i.e., the minimum of this characteristic has shifted toward pure hydrogen.

We will not discuss here the accuracy of the test data obtained by the various authors; this could be a subject for another separate study. We will only note that the test data of all authors indicate the existence of a minimum in the thermal conductivity as a function of the hydrogen content, although Barua's data in [7] are not considered accurate enough at low hydrogen contents.

The test data of the various authors plotted in Fig. 1 pertain to the thermal conductivity of this mixture as a function of the concentration of the lighter component and, according to the graph, there is a

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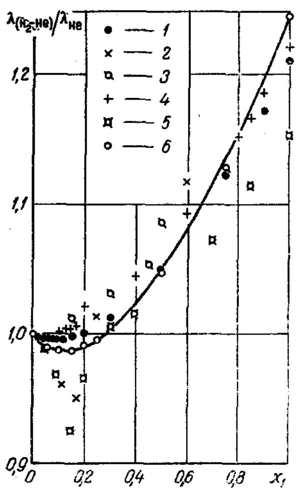

Fig. 1

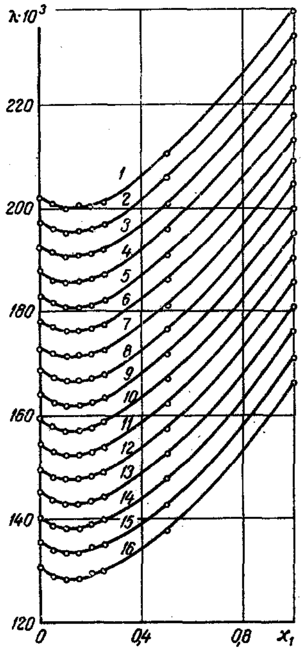

Fig. 2

Fig. 1. Test data pertaining to the thermal conductivity of the hydrogen–helium mixture: 1) data in [11] at 23.8°C; 2) data in [5] at 39°C; 3) data in [6] at 30°C; 4) data in [8] at 50°C; 5) data in [7] at 20.1°C; 6) our data at 23.8°C.

Fig. 2. Thermal conductivity λ (W/m·deg) of the hydrogen–helium mixture, as a function of the hydrogen concentration, based on tests: 1) T = 150°C; 2) 140; 3) 130; 4) 120; 5) 110; 6) 100; 7) 90; 8) 80; 9) 70; 10) 60; 11) 50; 12) 40; 13) 30; 14) 20; 15) 10; 16) 0.

certain discrepancy between the concentration at which the thermal conductivity of the mixture is minimum and the concentration at which it becomes equal to that of pure helium.

This discrepancy calls for a careful study of the thermal conductivity of the hydrogen–helium mixture, especially since the sharp minimum noted in [5] is attributable to the failure there to consider convective heat losses (as suggested in [8]) and since the results in [7] can be explained on the basis of measurement errors (as suggested in [10]).

The test data in [11] obtained by the relative method with very sensitive measuring devices (thermistors) are, in our opinion, the most reliable ones. Their accuracy, which has been checked against already well-known values for pure gases, lies within ±1% [13].

We measured the thermal conductivity of the hydrogen–helium mixture by the absolute method with a hot filament, which had been described earlier in [14] together with its sources of error. The temperature characteristics of thermal conductivity at concentrations $x_1 = 0.0$, 0.05, 0.10, 0.15, 0.20, 0.25, 0.50, and 1.00 were found linear over the 0-150°C range. It was possible, therefore, to represent them in the form of equations derived by the method of least squares and then used for obtaining the composition characteristics of thermal conductivity at any temperature within the test range. In Fig. 1 are also shown our test data obtained by this method at 23.8°C and sufficiently close to the data in [8-11], our values deviating not more than by 1.3%.

The composition characteristics of thermal conductivity in Fig. 2 were obtained by the said method over the 0-150°C temperature range. Within this range the curves have a minimum at 13% hydrogen content in the mixture, while at a 26% hydrogen content the thermal conductivity of the mixture becomes equal to that of pure helium and then increases monotonically with a still higher hydrogen (lighter component of

TABLE 1. Coefficients A_{12} and A_{21} for Determining the Thermal Conductivity of the Hydrogen–Helium Mixture [15]

T, °K	A_{12}	A_{21}	T, °K	A_{12}	A_{21}
90,2	1,361	0,8566	328,2	1,178	1,034
258,3	1,217	1,010	353,4	1,183	1,047
273,3	1,214	1,030	378,3	1,166	1,030
293,3	1,195	1,006	393,3	1,296	1,108
303,2	1,127	0,980	298,2	1,192	1,056
303,3	1,196	1,049	474,3	1,238	1,053
318,2	1,146	1,000			

TABLE 2. Temperature Characteristic of the $\lambda_{H_2}/\lambda_{He}$ Hydrogen and Helium Thermal Conductivity Ratio

T, °K	$\lambda_{H_2}/\lambda_{He}$	T, °K	$\lambda_{H_2}/\lambda_{He}$	T, °K	$\lambda_{H_2}/\lambda_{He}$	T, °K	$\lambda_{H_2}/\lambda_{He}$
50	0,5	200	1,1391	330	1,2250	900	1,2485
80	0,8418	210	1,1417	340	1,2270	950	1,2573
90	0,8891	220	1,1452	350	1,2289	1000	1,2656
100	0,9306	230	1,1575	400	1,2283	1100	1,2876
110	0,9725	240	1,1692	450	1,2289	1200	1,3037
120	0,9988	250	1,1716	500	1,2202	1300	1,3209
130	1,0209	260	1,1739	550	1,2128	1400	1,3407
140	1,0453	270	1,1761	600	1,2200	1500	1,3674
150	1,0688	280	1,1862	650	1,2235	1600	1,3884
160	1,0831	290	1,2027	700	1,2302	1700	1,4187
170	1,0971	300	1,2119	750	1,2371	1800	1,4475
180	1,1122	310	1,2143	800	1,2434	1900	1,4858
190	1.1261	320	1,2166	850	1,2461	2000	1,5164

the mixture) content. The relative magnitude of this minimum $(\lambda_{mix}-\lambda_{He})/\lambda_{He}$ decreases from 1.8 to 1.15% with rising temperature, although the absolute difference $\lambda_{mix}-\lambda_{He}$ remains constant and approximately equal to $2.35 \cdot 10^{-3}$ W/m·deg at all temperatures.

The existence of a minimum thermal conductivity of the hydrogen–helium mixture can be explained in two ways [15]:

1. From the point of view that one kind of molecules resists the transport of heat by another kind of molecules. Indeed, the coefficients A_{12} and A_{21} in the Vasil'eva formula for the thermal conductivity of a mixture each characterizes such a resistance and their product is $A_{12}A_{21} > 1$ for the hydrogen–helium mixture (Table 1). According to this table, hydrogen molecules resist the transport of heat by heavier helium molecules more than helium molecules resist the transport of heat by lighter hydrogen molecules.

2. Inasmuch as hydrogen molecules are diatomic, it becomes necessary to consider also their angular degrees of freedom with respect to the transport of heat in the gas mixture. The mechanism by which the angular degrees of freedom are excited depends on the frequency of intermolecular collisions and on the relative velocity of colliding molecules. In a mixture of light and heavy molecules (the latter having a lower velocity) angular degrees of freedom are excited with greater difficulty.

Since most of the heat in the mixture is transported by hydrogen molecules, hence the thermal conductivity of the mixture will decrease most when the hydrogen concentration is low. This statement applies to the temperature range where quantum effects are negligible.

We will now consider the low-temperature range. Inasmuch as no test data are available pertaining to the thermal conductivity of the hydrogen–helium mixture within the 10-70°K temperature range, it is difficult to assess the trend of the thermal conductivity as a function of the hydrogen concentration. Apparently, however, this function has no minimum within that temperature range. We assert so on the basis of having analyzed the temperature characteristic of the coefficient $f = \lambda M/\eta C_V$ (Fig. 3). At very low-temperatures hydrogen behaves like a monoatomic gas, it seems, with $f \approx 2.5$. As the temperature rises, angular degrees of freedom are excited and coefficient f decreases below 2.5. Beginning at 60-70°K, the composition characteristic of thermal conductivity will have a minimum at a sufficiently high hydrogen concentration – as has been confirmed also by Golubev's data [12].

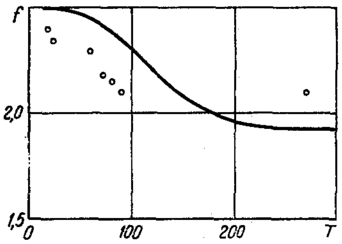

Fig. 3. Coefficient f as a function of the hydrogen temperature T (°K) [17].

It is worthwhile to examine the temperature characteristic of the ratio λ_1/λ_2 (Table 2). This ratio accounts for the effect of both mass and diameter of molecules on the transport of heat. An analysis of test data pertaining to the thermal conductivity as a function of the hydrogen concentration indicates a minimum when $A_{12}A_{21} > 1$ and λ_1/λ_2 is sufficiently close to unity.

According to Table 2, $\lambda_1/\lambda_2 > 0.8$ within the 50-100°K range, remains constant and approximately equal to 1.22 within the 300-650°K range, and approaches 1.516 at 2000°K. The composition characteristic of thermal conductivity ceases to have a minimum at temperatures ~600°K. It is to be noted that at temperatures close to 5000°K the mixture becomes one of monoatomic gases, inasmuch as at these temperatures hydrogen ceases to dissociate and its f coefficient becomes equal to 2.5 [16].

Further experimental study of the hydrogen–helium mixture is required for a more complete explanation of its thermal conductivity versus hydrogen concentration characteristics.

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