RADIATION EFFECT IN MEASURING THE THERMAL
CONDUCTIVITY OF SATURATED HYDROCARBONS

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The results of an experimental estimate of the radiation effect in measuring the thermal
conductivity of saturated hydrocarbons at high temperatures and pressures by means of the
hot-wire method are given.

Saturated hydrocarbons, which are characterized by considerable transmission in the infrared region, belong to semitransparent media, where energy transfer is effected by several mechanisms simultaneously, for instance, molecular heat conduction and radiation if the medium is stationary. Therefore, the radiative component of the measured thermal–conductivity coefficient must be estimated in experimental investigations of the thermal conductivity of these substances.

The method of estimating the effect of radiation has been sufficiently well developed for plane-parallel layers of semitransparent liquids. In particular, it has been demonstrated theoretically and experimentally [1-5] that this effect can be considerable even at room temperature.

The case of a cylindrical layer, which corresponds to the experimental conditions in the coaxial-cylinder and the hot-wire methods, is especially important in investigating the thermal conductivity of liquids. The above problem for a cylindrical layer has been analyzed in very few papers [6-9], while the data supplied by individual authors are sometimes contradictory. This called for an experimental investigation of the radiation effect in measuring the value of λ of liquid organic compounds by means of the hot-wire method.

It is known that the radiative component of the thermal–conductivity coefficient of liquids can be estimated by measuring the coefficient for different optical thicknesses $\tau = kH$ of the layer. Considerable difficulties stemming from the design features of the measuring tube are encountered in changing the value of τ by varying H, as was done in using the hot-wire method for a plane-parallel layer. Therefore, we decided to vary the value of k of saturated hydrocarbons by mixing them with small amounts of liquids characterized by high absorption of infrared radiation. For this purpose, we prepared mixtures of heptane and dodecane with 7% isobutyl and isoheptyl alcohols, respectively. Our measurements of the thermal-conductivity coefficients of these alcohols, the results of which are given in Table 1, yielded virtually equal values of λ and roughly equal values of the derivatives $(d\lambda/dT)_p$ and $(d\lambda/\partial p)_T$ with heptane and dodecane [11]. However, alcohols are characterized by strong absorption in the infrared region where saturated hydrocarbons are transparent. Mixtures prepared in this way alter the absorption factors of heptane and dodecane, while leaving virtually unchanged the other properties affecting thermal conductivity.

Figure 1 shows, in particular, the infrared absorption spectra of dodecane and of a mixture of dodecane and 7% isoheptyl alcohol. It is evident from the figure that, in the wavelength range 7.5-10 μ corresponding to maximum radiation at 300-400°K (the bottom scale in Fig. 1 illustrates Planck's law [16]), i.e., in the range where dodecane (as well as all other saturated hydrocarbons) is virtually transparent, addition of isoheptyl alcohol produces a strong absorption peak, which increases the absorptivity of dodecane.

In order to determine how this change in the absorptivity of saturated hydrocarbons affects the radiant flux, we investigated the temperature field in plane-parallel layers of the above liquids and mixtures. The

TABLE 1. Measured Thermal-Conductivity Coefficients of Liquid Organic Compounds

Pressure P, bar	Temperature T, °C	Temperature drop in the layer ΔT	Thermal-conductivity coefficient λ	Pressure P, bar	Temperature T, °C	Temperature drop in the layer ΔT	Thermal-conductivity coefficient λ
	Isobutyl alcohol				93% heptane + 7% isobutyl alcohol		
0,98	29,84	6,18	0,1348	0,98	22,00	7,39	0,1250
0,98	32,16	8,27	0,1351	0,98	25,80	10,31	0,1238
245	29,89	5,73	0,1448	245	21,99	6,86	0,1370
245	32,09	7,80	0,1434	245	25,78	9,37	0,1359
245	33,60	6,33	0,1430	245	113,22	7,90	0,1128
490	29,80	5,41	0,1538	245	117,11	10,41	0,1117
490	31,88	7,26	0,1528	490	22,02	6,40	0,1461
735	29,68	5,15	0,1612	490	25,82	8,76	0,1451
735	31,88	6,91	0,1610	490	113,20	5,94	0,1240
980	29,57	4,91	0,1687	490	117,10	9,36	0,1232
980	31,62	6,60	0,1677	735	21,98	6,04	0,1552
1225	31,57	6,37	0,1741	735	25,84	8,21	0,1544
1225	36,20	9,14	0,1736	735	113,20	5,62	0,1338
1470	31,66	6,19	0,1795	735	117,09	8,64	0,1333
1470	35,16	8,92	0,1780	980	21,96	5,76	0,1629
1715	31,58	6,00	0,1846	980	25,79	7,86	0,1618
1715	34,96	8,57	0,1859	980	113,18	5,42	0,1423
1960	31,52	5,80	0,1903	980	117,08	8,12	0,1417
1960	35,04	8,33	0,1900				
2205	31,44	5,59	0,1965				
2205	34,56	7,99	0,1950				
	Isoheptyl alcohol				93% dodecane + 7% isoheptyl alcohol		
0,98	29,64	6,50	0,1388	0,98	23,38	5,68	0,1397
0,98	32,07	8,69	0,1380	0,98	25,30	7,00	0,1390
245	29,63	4,90	0,1478	0,98	77,20	7,31	0,1265
245	32,03	5,60	0,1469	0,98	79,12	8,67	0,1269
245	33,44	6,18	0,1467	0,98	132,57	8,60	0,1130
490	28,32	4,61	0,1455	0,98	133,84	10,78	0,1125
490	29,46	5,71	0,1450	245	23,36	5,31	0,1492
735	29,36	6,73	0,1627	245	25,27	6,55	0,1482
735	31,52	7,34	0,1620	245	77,18	6,77	0,1374
980	29,32	5,26	0,1695	245	79,13	7,97	0,1376
980	31,30	7,03	0,1685	245	132,58	7,92	0,1236
1225	29,20	5,09	0,1750	245	133,87	9,90	0,1232
1225	31,15	6,68	0,1746	490	23,35	5,02	0,1578
1470	29,10	5,02	0,1803	490	25,25	6,20	0,1568
1470	31,10	6,34	0,1800	490	77,20	6,30	0,1472
1715	30,05	4,90	0,1852	490	79,11	7,45	0,1470
1715	32,14	6,80	0,1846	490	132,58	7,30	0,1346
1960	29,81	4,76	0,1890	490	133,87	9,11	0,1340
1960	31,70	6,48	0,1887	735	23,41	4,78	0,1659
				735	25,28	5,88	0,1648
				735	79,10	5,90	0,1557
				735	80,02	7,06	0,1557
				735	132,60	6,90	0,1430
				735	133,87	8,59	0,1435
				980	23,39	4,62	0,1715
				980	25,30	5,67	0,1712
				980	78,70	5,69	0,1622
				980	80,18	6,76	0,1620
				980	132,61	6,40	0,1514
				980	133,88	8,00	0,1512

layer thickness was varied in the range from 1.2 to 4.5 mm. The investigations were performed in the range of room temperatures by using the interferometric method and the device which has been described in detail in [4, 5]. It should only be mentioned here that the temperature difference at the boundaries of the liquid layer, as well as between any two isotherms in the layer, was calculated with respect to the number of interference bands by means of the relationship

$$\Delta T = \frac{m\Lambda}{l\dfrac{dn}{dT}}.$$

The interference pattern was photographed on a film, from which microphotograms were obtained by means of an IFO-451 microphotometer. The use of a microphotometer considerably simplifies the interpretation of interferograms, as images of the interference pattern on a scale of up to 100:1 can be obtained. This, of course, makes it possible to determine with a high degree of accuracy the distribution of interference bands along the layer thickness (and, thus, the temperature).
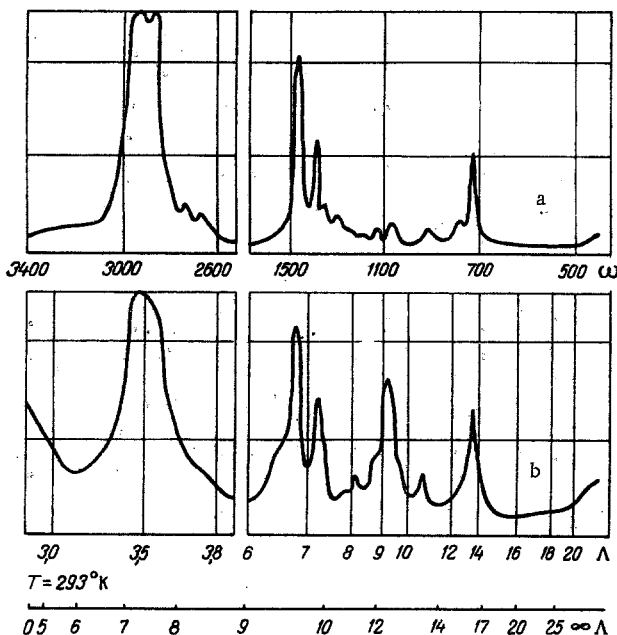
Fig. 1

Fig. 2

Fig. 1. Infrared absorption spectra. a) Dodecane, H = 0.025 mm; b) mixture of dodecane and 7% iso-heptyl alcohol, H = 0.025 mm; (ω, cm^{-1}; Λ, μ).
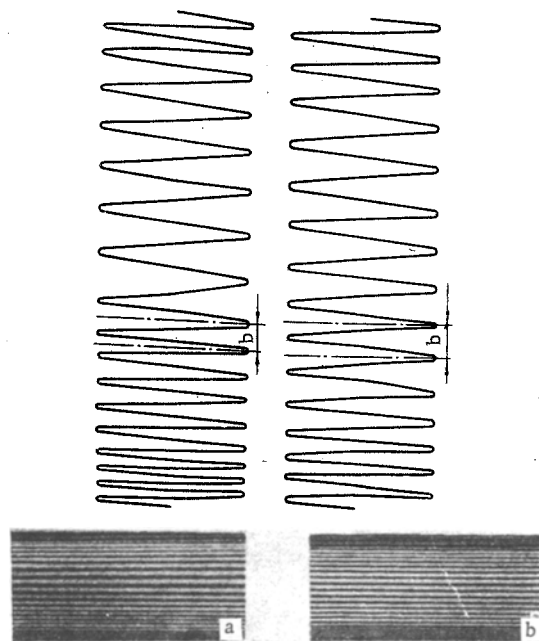
Fig. 2. Interference pattern in liquid layers with a thickness of 4.5 mm. a) Dodecane, ΔT = 5.8°C; b) mixture of dodecane and 7% isoheptyl alcohol, ΔT = 5.76°C.

As an example, Fig. 2 shows the interference patterns and the microphotograms for dodecane and the mixture of dodecane and isoheptyl alcohol, obtained under identical conditions: H = 4.5 mm; ΔT = 5.8°C; T_{me} = 20°C; the same compensating wedge was used for observing the interference pattern. It is obvious from the figure that the distance b between the interference bands, which are identified with isotherms, varies along the layer thickness. Since the local temperature gradient dT/dx is proportional to the density of interference bands 1/b, it is not a constant quantity, which agrees with the nonlinear temperature distribution in the layer.

Figure 3 shows the distribution of interference bands along the layer thickness without an allowance for the effect of the compensating wedge. It is evident from the figure that the distribution of interference bands along the layer thickness deviates much less from a linear behavior for the investigated mixture than for the pure liquid. This indicates that the radiation effect was reduced considerably in the dodecane layer after alcohol was added to it.

According to [10], in order to estimate the effect of radiation on the value of λ_{eff}, it is necessary to compare ΔT_{eff} with the temperature drop ΔT that would occur in the same liquid layer and for the same thermal flux, but with the heat transfer effected only through thermal conduction. We determine the value of ΔT on the basis of the consideration that the temperature distribution in the layer must be linear and the thermal flux proportional to the local temperature gradient dT/dx, which is constant and equal to its value near the wall. Such a comparison shows that the radiation effect in the investigated mixtures has been reduced by approximately one half in comparison with heptane and dodecane, for which it amounts to 7 and 4%, respectively [4].

Measurements performed on 1.2-mm layers have shown that, while the radiative component of thermal conductivity lies within 2-3% for pure liquids, the temperature distribution in mixtures hardly differs from a linear distribution, i.e., the radiation effect in this case lies within the limits of experimental error.

In order to estimate the effect of radiation in a cylindrical layer, we measured the thermal conductivity coefficients of the above mixtures by means of the hot-wire method and compared the results with the earlier data on λ for pure liquids [11].
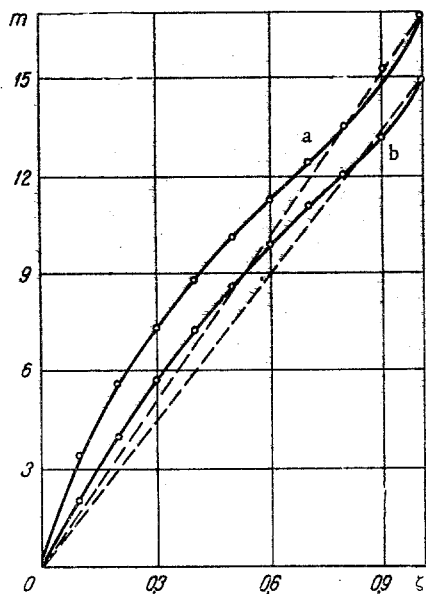
Fig. 3

Fig. 4

Fig. 3. Distribution of interference bands along the layer thickness (H = 4.5 mm; ΔT = 5.8°C). a) Dodecane; b) mixture of dodecane and isobutyl alcohol; $\zeta = x/H$.
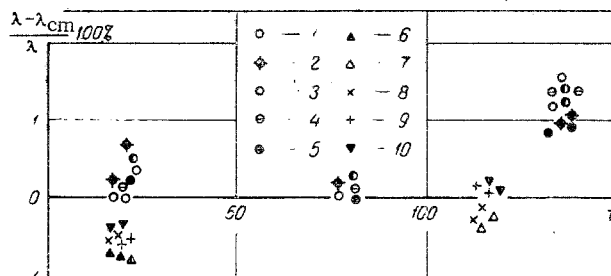
Fig. 4. Comparison between experimental data on the thermal–conductivity coefficients of semitransparent organic liquids and their mixtures. Mixture of 93% dodecane and 7% isoheptyl alcohol. 1) p = 0.98 bar; 2) 245; 3) 490; 4) 735; 5) 980; mixture of 93% heptane and 7% isobutyl alcohol: 6) p = 0.98 bar; 7) 245; 8) 490; 9) 735; 10) 980 (t, °C).

The thermal–conductivity coefficients were investigated by using the absolute hot-wire method. The measuring tube was made of quartz and had the following characteristics: inside diameter of the capillary, 0.749 mm; outside diameter, 1.63 mm; length of measuring section, 99.3 mm; thickness of the investigated liquid layer, 0.326 mm; the diameter of the platinum wire of the external and internal resistance thermometers was equal to 0.097 mm. The measuring cell was placed in a high-pressure autoclave, which, in turn, was placed in a 40-liter oil-filled cylindrical vessel. Oil circulation was ensured by means of two U-10 ultrathermostats. The considerable thermal inertia of the system virtually eliminated temperature fluctuations in the investigated medium. The pressure in the system was created by means of the hydraulic press of a class 0.05 MP-2500 piston–weight pressure gauge.

The electric resistance was measured by means of an ordinary potentiometric circuit, using an R-309 semiautomatic high-resistance potentiometer. An R-348 semiautomatic potentiometer was used for calibrating the resistance thermometers. Both potentiometers belong to class 0.005 instruments.

In order to improve the accuracy in determining λ, we introduced corrections to account for the secondary phenomena arising in the use of this method: end effects, the temperature drop in the liquid layer, eccentricity, changes in the dimensions of the measuring tube with temperature and pressure variations, and the effect of pressure and temperature on the readings of the resistance thermometers.

A more detailed description of the experimental device is given in [12-15]. The theoretical maximum experimental error amounts to less than 2%. The thermal conductivity was investigated with respect to isotherms at 245-bar intervals. The results obtained in measuring the thermal–conductivity coefficients of the mixtures are given in Table 1.

For estimating the effect of the radiative component, points corresponding to values of $(\lambda - \lambda_{mi})/\lambda$ · 100% at different temperatures and pressures are plotted in Fig. 4. It is evident that there is virtually no deviation of λ for the investigated mixtures from the thermal–conductivity coefficients of heptane and dodecane. The maximum discrepancy is observed for dodecane at p = 0.98 bar and T = 407°K. It amounts to 1.6%. The share of the radiative component tends to decrease with an increase in pressure throughout the investigated temperature range.

Thus, we conclude on the basis of these experiments that in thin cylindrical layers (H $\approx$ 0.3 mm) of liquid organic compounds which are semitransparent in the infrared region, the share of the radiative

component of thermal conductivity is small and lies within the limits of experimental error in the temperature range from 290 to 410°K.

NOTATION

λ_{eff}, ΔT_{eff}	are the thermal-conductivity coefficient and the temperature difference at the layer boundaries for radiative–conductive heat exchange, respectively;
λ, ΔT	are the thermal-conductivity coefficient and the temperature difference for conductive heat-exchange, respectively;
τ	is the optical thickness;
k	is the absorption factor;
H	is the thickness of the liquid layer;
m	is the number of interference bands;
Λ	is the wavelength of the light used;
l	is the extent of the liquid layer along the beam;
dn/dT	is the temperature coefficient of the refractive index of the liquid;
b	is the distance between two interference bands.

LITERATURE CITED

1. H. Poltz, Int. J. Heat and Mass Transfer, 8, 515 (1965).
2. H. Poltz, Int. J. Heat and Mass Transfer, 10, 1075 (1967).
3. G. Schödel and U. Grigull, Int. Konf. Wärmeübertragung, Versailles, 4 (1970).
4. T. V. Gurenkova, P. A. Norden, and A. G. Usmanov, Inzh.-Fiz. Zh., 21, No. 2 (1971).
5. T. V. Gurenkova, P. A. Norden, and A. G. Usmanov, Inzh.-Fiz. Zh., 24, No. 5 (1973).
6. L. A. Pigal'skaya, Inzh.-Fiz. Zh., 18, No. 1 (1970).
7. V. Z. Geller, I. A. Poramonov, and G. D. Tatevosov, in: Thermophysical Characteristics of Liquids [in Russian], Nauka (1973).
8. A. A. Men', Inzh.-Fiz. Zh., 25, No. 1 (1973).
9. A. A. Men', Teplofiz. Vys. Temp., 11, No. 4 (1973).
10. A. A. Men' and O. A. Sergeev, Inzh.-Fiz. Zh., 22, No. 1 (1972).
11. G. Kh. Mukhamedzyanov and A. G. Usmanov, Thermal Conductivity of Organic Liquids [in Russian], Khimiya (1969).
12. I. Kh. Mukhametzyanov, G. Kh. Mukhamedzyanov, and A. G. Usmanov, Tr. Kazan. Khim.-Tekhnol. Inst., 43 (1969).
13. I. Kh. Mukhametzyanov, G. Kh. Mukhamedzyanov, and A. G. Usmanov, Tr. Kazan. Khim.-Tekhnol. Inst., 44 (1971).
14. I. Kh. Mukhametzyanov, G. Kh. Mukhamedzyanov, and A. G. Usmanov, Tr. Kazan. Khim.-Tekhnol. Inst., 47 (1971).
15. I. Kh. Mukhametzyanov, G. Kh. Mukhamedzyanov, and A. G. Usmanov, in: Heat and Mass Transport [in Russian], Vol. 7 (1972).
16. M. Z. Czerny, Z. Phys., 139, 302 (1954).