11. A. A. Galkin, V. I. Kurochkin, A. G. Demishev, et al., "Investigation of heat exchange and the creation of cryostats with a long operating time," Dokl. Akad. Nauk Ukr. SSR, Ser. A. Fiz.-Mat. Tekh. Nauki, No. 8, 55-58 (1982).

EXPERIMENTAL STUDY OF THE THERMAL CONDUCTIVITY OF LITHIUM VAPOR

N. B. Vargaftik, V. M. Kapitonov,
and A. A. Voshchinin

UDC 546.34:536.212.2

The thermal conductivity of lithium vapor is measured. Equations are derived for calculation of the effective thermal conductivity and its components over a wide range of temperature and pressure.

In recent years lithium has become an important material in a number of technological fields. It is used in atomic energy devices and in space vehicle construction. This has stimulated interest in the thermophysical properties of lithium vapor.

In the case of alkali metal vapors, divergence has been found between experimental and calculated data (increasing from cesium to sodium) for both the atomic component of thermal conductivity and the effect of the dimerization reaction.

Until the present, experimental data on the thermal conductivity of lithium vapor has been absent from the literature, because experiments with lithium involve serious technological problems, due to the element's high boiling point and reactivity.

The thermal conductivity of lithium vapor was studied by the coaxial cylinder method, used previously for other alkali metals. However, because of the unique features of lithium and the higher temperature interval involved, the construction of the apparatus was changed. The measurement cell was connected to an evaporator. All of its components were formed of niobium alloys with high corrosion resistance to alkali metal vapors. Measurements were performed with two different gaps between the cylinders – 0.20 and 0.66 mm (Table 1).

Vapor was supplied to the intercylinder gap by two tubes from the evaporator.

The vapor pressure was determined from the saturated vapor elasticity curve [1] with thermocouples installed in the evaporator:

$$\lg P_s = 1{,}01325\cdot 10^5 \left[8.5088 - \frac{8363}{T} - 1{,}02573 \lg T - 1.3091\cdot 10^{-4} T + 1{,}08872 \exp\left(-\frac{2940}{T}\right)\right]. \quad (1)$$

The measurement cell was placed within a thermostatic chamber. The internal volume of the thermostat was filled with high purity argon at a pressure of about $1\cdot 10^5$ Pa to prevent oxidation of the niobium components. The argon also served as a heat-transport medium, decreasing the contact thermal resistance of the thermocouples. A detailed diagram of the apparatus and description of the construction were presented previously in [2].

To monitor the operation of the device the thermal conductivities of inert gases were measured. Thermal conductivity values for argon and neon, measured before and after experiments with lithium, agreed well with each other. This indicated normal operation of the equipment.

Using data from the inert gas experiments, the contact thermal resistance ΔT_C was determined as a function of thermal flux liberated by the internal heater, and corrections were determined for the temperature head at the point of thermocouple attachment to the cylinder

---

Sergo Ordzhonikidze Aviation Institute, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 49, No. 4, pp. 634-640, October, 1985. Original article submitted September 21, 1984.

0022-0841/85/4904-1208$09.50

TABLE 1. Geometric Dimensions of Measurement Cylinders

Quantity measured, mm	Device		
	I	II	III
Inner diam. of outer cylinder	12,10	13,07	13,06
Outer diam. of inner cylinder	11,70	11,75	11,74
Intercylinder gap	0,20	0,66	0,66
Length of active section	83,0	59,3	60,0
Cylinder length	200	200	200
Cylinder wall thickness	1,0	1,0	1,0

walls, which were then considered in calculating the thermal conductivity coefficient of the lithium vapor.

In measurements of the thermal conductivity of lithium vapor the indications of three external and three internal thermocouples located at various heights differed by no more than 0.1-0.2°K. Lithium vapor thermal conductivity was measured along isotherms at various pressures. Temperature heads from 12 to 26°K were used.

Preliminary experiments were performed at temperatures to 1340°K (series I) with an intercylinder gap of 0.20 mm. These experiments confirmed the possibility of measuring lithium vapor thermal conductivity with the equipment used. However, the correction ΔT_c for lithium vapor is significantly larger than it is for vapors of the other alkali metals in measurements with the same gap. Therefore, to produce a significant reduction in this correction the gap was increased to 0.66 mm, which decreased the correction for contact temperature shift ΔT_c to 12-16%.

The lithium used in the experiments was type LÉ-1, which, according to GOST 8774-75, has the following composition (mass %): Li > 99.5, Na < 0.06, K < 0.05, Ca < 0.03, Mg < 0.02, Mn < 0.001, Fe < 0.005, Al < 0.003, silicon oxides <0.01, nitrides <0.05. Filtering of the experimental material in a barochamber with metalloceramic filters produced the following gaseous impurity content (mass %): O_2, 0.01; N_2, 0.006-0.02; C, 0.001-0.003; H_2, 0.001.

Thermal conductivity of lithium vapor was studied over the temperature interval 1200-1450 °K at pressures from $4 \cdot 10^2$ to $80 \cdot 10^2$ Pa. Values of the thermal conductivity coefficient were calculated with the expression

$$\lambda = A\,\frac{W - W_{\mathrm{rad}}}{\Delta T - \Delta T_c}\,B, \qquad (2)$$

where $A = (\ln D/d)/2\pi l$ is the equipment geometric factor, $B = 1 + \delta T_{sh}$ is the correction for temperature shift. The quantity of heat transferred by radiation was determined from the Stefan—Boltzmann expression.

The literature offers a large number of reliable experimental studies of the emissivity ε of niobium alloys [3]. The good agreement (within 1-2%) of inert gas thermal conductivity coefficients measured before and after lithium experiments with the different devices indicated that the emissivity of the cylinder materials did not change. The fraction of radiation in the total heat flux in series I (preliminary) experiments comprised from 8 to 15%, and 20-30% in series II-III.

The correction for temperature shift was calculated from the well-known expression [4]

$$\delta T_{\mathrm{sh}} = \frac{2\lambda\sqrt{2\pi\mu/R}\,(2-\alpha)\sqrt{T}}{Ph\alpha 2\left(\dfrac{C_V}{R}+\dfrac{1}{2}\right)}. \qquad (3)$$

It has been established in studies of the thermal conductivity of sodium, potassium, and cesium vapor that the accommodation coefficient for the system alkali metal—nickel is equal to unity independent of the temperature [5, 6]. On the basis of experimental data, Makhrov [7] demonstrated that the accommodation coefficient for alkali metal vapors on tungsten is equal to unity. This allows us to take $\alpha = 1$ in calculating the correction for temperature shift.

In the case of lithium vapor, the expression used to calculate the temperature shift δT_{sh} appearing in the correction to B of Eq. (2) has the form

TABLE 2. Experimental Data on Thermal Conductivity of Lithium Vapor

T, K	P, Pa	$\lambda\cdot10^4$ W/m·K
Series I (Preliminary exptl. data)		
1229,4	412	780
1230,8	618	810
1231,0	1370	872
1231,0	1370	886
1335,0	585	803
1335,5	585	810
1339,5	1317	836
Series II		
1303,6	400	820
1307,6	686	832
1308,1	693	830
1308,1	707	826
1311,4	1400	866
1311,5	1400	846
1317,0	2666	912
1318,0	2706	897
1319,1	2779	919
1316,7	600	815
1300,2	1347	873
1301,4	1346	860
1306,5	1346	843
1317,9	2067	879
1318,4	2053	872
1319,0	2066	889
1337,6	2840	908
1393,6	1387	863
1423,2	6533	902
1415,7	8000	983
1415,8	8000	959
Series III		
1226,5	660	832
1227,3	667	829
1227,0	667	838
1231,5	1200	898
1234,1	1200	886
1297,3	587	801
1297,1	600	797
1298,9	1253	835
1290,6	1946	874
1329,1	660	833
1329,5	667	825
1327,7	1246	837
1327,5	1200	840
1327,4	1180	855
1327,4	1160	849
1328,6	2639	928
1328,9	2639	893
1330,5	2706	925
1331,3	2733	924
1331,8	2746	902

$$\delta T_{sh} = \frac{3.62\cdot10^{-2}\lambda_1\sqrt{T}}{Ph}. \tag{4}$$

The values of λ_1 were found for each isotherm by extrapolating the function $\lambda = f(x_2)$ to $x_2 = 0$. In the current experiments the correction for temperature shift varied from 2 to 20%.

The maximum error in determination of lithium vapor thermal conductivity coefficient was 6.7%, with the uncertainty in referring λ to P and T not exceeding 0.9%. Results of the measurements are presented in Table 2. Detailed tables of experimental data with all corrections can be found in [8, 9].

Over the temperature and pressure ranges considered the thermal conductivity of lithium vapor can be considered as a process of energy transfer in a two-component gas mixture with consideration of occurrence of the dimerization reaction

$$\lambda = \lambda_f + \lambda_r. \tag{5}$$

In extrapolating the experimental data to $x_2 = 0$, the thermal conductivity of the monatomic component λ_1 was determined. The molecular concentration of lithium was determined from the data of [10].

For the temperature dependence of λ_1 the following equation was obtained:

$$\lambda_1(T)\cdot10^4 = 179 + 0.46T. \tag{6}$$

The experimental data for various pressures (various contents of biatomic molecules) permit determination of the effect of the dimerization reaction, characterizable by the relative section for atom—molecule collisions: $\beta_{12}^2 = \sigma_{12}^2\Omega^{(2,2)*}/\sigma_{11}^2\Omega^{(2,2)*}$.

After finding β_{12}^2, the ratio $(\lambda - \lambda_1)/\lambda_1$ was calculated for each experimental point, while for isotherms it was approximated by a polynomial function of x_2, similar to Eq. (7). For the desired value β_{12}^2, that value which produced agreement with the experimental data was chosen. Thus, β_{12}^2 was found for each isotherm, and then averaged. The value found proved to equal 3.6 ± 0.2.

The values of $\beta^2{}_{12}$ are quite large. Therefore, for transport processes in lithium vapor the contribution of energy transfer of dimerization by the diffusion flow to the total thermal flux is somewhat less than in the case of other alkali metal vapors.

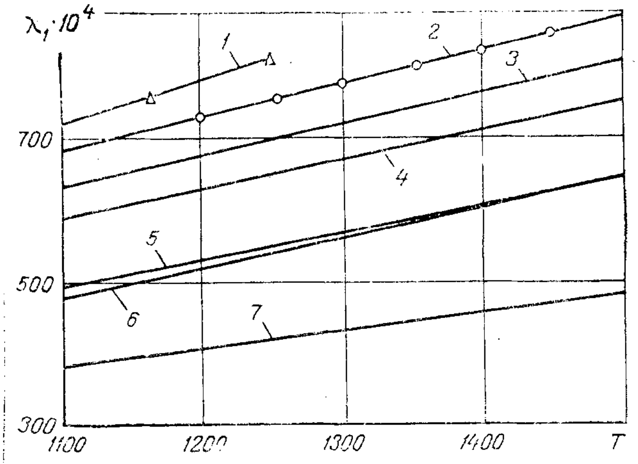

Fig. 1. Comparison of calculated and experimental values of thermal conductivity coefficient of monatomic lithium vapor $\lambda_1 \cdot 10^4$ W/m·K: 1) data of [17]; 2) present study; 3) [16]; 4) [15]; 5) [14]; 6) [13]; 7) [12]; T, °K.

The dependence of thermal conductivity of monatomic lithium vapor λ_1 on temperature and the quantity $\beta^2{}_{12}$ were used to create a thermal conductivity equation for lithium vapor at temperatures of 1000-1600°K and pressures from 0.1 kPa to the saturation line. The system of successive approximations presented in [11] was used:

$$\lambda(x_2, T) = \lambda_1(T)\left[1 - 3{,}980x_2 + 14{,}68x_2^2 - 53{,}36x_2^3 + 0{,}09236\left(\frac{T_r}{T}\right)^2 \frac{x_2(1-x_2)}{(1+x_2)^2}\right], \tag{7}$$

where $T_r = D_0(T)/R$ is the "reaction temperature." Values of T_r for lithium vapor were calculated with the equation

$$T_r = 13583 + 0{,}297(T - 1000) + 0{.}043 \cdot 10^{-3}(T - 1000)^2. \tag{8}$$

Neglect of terms in the series for x_2 beginning with the fourth leads to an uncertainty of less than 0.5% at x_2 = 7%.

In addition to the total thermal conductivity, its components were also calculated: frozen thermal conductivity

$$\lambda_f(x_2, T) = \lambda_1(T)[1 - 3.980x_2 + 14.68x_2^2 - 53{,}36x_2^3] \tag{9}$$

and the thermal conductivity produced by energy transfer due to the dimerization reaction:

$$\lambda_r(x_2, T) = \lambda_1(T)\, 0.09236\left(\frac{T_r}{T}\right)^2 \frac{x_2(1-x_2)}{(1+x_2)^2}. \tag{10}$$

It is appropriate to compare the values of λ_1 and β_{12}^2 with theoretically computed results.

Results for λ_1 diverge more (although within the limits of computation uncertainty) from experiment when approximate semiempirical methods [12-14] are used. The superior agreement with λ_1 data calculated in [15] can be explained by the fact that that study used experimental results for the transport coefficients of other alkali metals. The results of the quantum-mechanical calculations of [16] deviate less from the experimental data (Fig. 1).

The value $\beta_{12}^2 \approx 1$ obtained in [12, 13] led to a severely elevated effect of the dimerization reaction on the thermal conductivity of lithium vapor. In [15] it was assumed that $\beta_{12}^2 = 2.5$. The value of β_{12}^2 presented in [16] was 3.36 ± 0.5. Within the limits of experimental error this agrees with the currently obtained value of 3.6.

Very recently experimental data have been published on the thermal conductivity of lithium vapor in the temperature range 1020-1255°K at pressures of $0.23 \cdot 10^2$-$18.46 \cdot 10^2$ Pa [17] (i.e., in the range where the correction for temperature shift is significant). The results presented for the thermal conductivity coefficient of the monomer λ_1 of lithium vapor agrees within the uncertainty indicated in [17] (±10%) with the results of the present study.

NOTATION

T, ΔT, temperature and temperature change between cylinders; ΔT_c, ΔT_{sh}, corrections for contact temperature change at point of thermocouple attachment and for temperature shift; D, d, inner diameter of outer cylinder and outer diameter of inner cylinder; l, length of active section of measurement cylinder; W, W_{rad}, total thermal flux and fraction of heat transferred by radiation from inner to outer cylinder; P, pressure; P_s, saturated vapor pressure; x_2, molecular concentration; λ, effective thermal conductivity coefficient; λ_1, thermal conductivity coefficient of monatomic component; λ_f, thermal conductivity of "frozen" mixture of components; λ_r, thermal conductivity due to energy transfer of dimerization reaction; D_0, dissociation energy at temperature T, °K; α, accommodation coefficient; μ, molecular weight; C_V, molar heat capacity at constant volume; R, universal gas constant; h, intercylinder gap; β_{12}^2, relative atom–molecule collision section; $\sigma_{11}^2\Omega^{(2,2)*}$, $\sigma_{12}^2\Omega^{(2,2)*}$, effective atom–atom and atom–molecule collision sections.

LITERATURE CITED

1. V. S. Yargin, N. I. Sidorov, E. L. Studnikov, and Yu. K. Vinogradov, "Transport properties of saturated lithium vapor," Inzh.-Fiz. Zh., 43, No. 3, 494 (1982).
2. A. A. Voshchinin and V. M. Kapitonov, "Apparatus for experimental study of thermal conductivity of alkali metal vapors at high temperatures," Zavod. Lab., No. 3, 837-838 (1980).
3. L. N. Latyev, V. A. Petrov, V. Ya. Chekhovskii, and E. N. Shestakov, Radiative Properties of Solids (Handbook) [in Russian], A. E. Sheindlin (ed.), Énergiya, Moscow (1974).
4. H. S. Gregory, "The determination of the coefficient of accommodation from aspect of temperature drop effect," Philos. Mag., 22, No. 146, 256-267 (1936).
5. N. B. Vargaftik and A. A. Voshchinin, "Experimental study of thermal conductivity of sodium and potassium vapors," Teplofiz. Vys. Temp., 5, No. 5, 802-811 (1967).
6. N. B. Vargaftik and V. V. Kerzhentsev, "Experimental study of the thermal conductivity coefficient of cesium vapor," Teplofiz. Vys. Temp., 10, No. 1, 59-66 (1972).
7. V. V. Makhrov, "Thermal accommodation of alkali metal vapor on tungsten at high temperatures," Teplofiz. Vys. Temp., 16, No. 4, 737-743 (1978).
8. A. A. Voshchinin and V. M. Kapitonov, "Experimental determination of thermal conductivity of monatomic lithium vapor at high temperatures," in: Physical Processes in Neutral and Ionized Gases [in Russian], Moscow Aviation Inst. (1981), pp. 60-63.
9. A. A. Voshchinin and V. M. Kapitonov, Measurement of Lithium Thermal Conductivity in the Gaseous Phase at High Temperatures [in Russian], Moscow (1982); manuscript deposited at VINITI by Moscow Aviation Institute, July 5, 1982, No. 3476-82.
10. N. B. Vargaftic (Vargaftik), Thermophysical Properties of Gases and Liquids, Wiley, New York (1975).
11. V. S. Yargin, N. I. Sidorov, and E. L. Studnikov, "Viscosity and thermal conductivity of alkali metals in the gaseous phase," in: Reviews of Thermophysical Properties of Materials, No. 5 [in Russian], IVTAN (1978).
12. C. F. Bonilla and C. S. Lee, "Thermal conductivity of alkali metal vapors and argon," in: Proceedings of the 7th Conference on Thermal Conductivity, Nat. Bur. Stand. (1967), pp. 561-578.
13. É. É. Shpil'rain, K. A. Yakimovich, E. E. Totskii, et al., Thermophysical Properties of Alkali Metals [in Russian], Standartov, Moscow (1970).
14. B. M. Smirnov and M. I. Chibisov, "Kinetic coefficients for monatomic alkali metal vapors," Teplofiz. Vys. Temp., 9, No. 3, 513-516 (1971).
15. A. Ya. Polishchuk, É. É. Shpil'rain, and I. T. Yakubov, "Thermal conductivity and viscosity of lithium vapor," Inzh.-Fiz. Zh., 38, No. 3, 429-433 (1980).
16. V. S. Yargin, "Viscosity and thermal conductivity of lithium in the gaseous phase," in: Proceedings of the 8th Symposium on Thermophysical Properties, Nat. Bur. Stand., Gaithersburg, Md., Vol. 2 (1982), pp. 179-184.
17. D. L. Timrot, V. V. Makhrov, and F. I. Pil'nen'skii, "Experimental study of thermal conductivity of lithium vapor," Teplofiz. Vys. Temp., 22, No. 1, 40-47 (1984).