EXPERIMENTAL STUDY OF THERMAL CONDUCTIVITY IN LITHIUM IN THE GASEOUS PHASE AT HIGH TEMPERATURES

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Thermal conductivity of lithium vapor is measured over the temperature range of 1400-1800 K at pressures of 10-80 kPa. The temperature dependence of thermal conductivity of the monatomic vapor is obtained and the effect of molecular components on thermal conductivity is studied.

The experimental study of thermal conductivity of lithium vapor was carried out by the nonsteady-state monotonic heating method. The basic relationships for the monotonic thermal regime were presented in [1-3].

A diagram of the experimental apparatus is shown in Fig. 1. The measurement cell was constructed of niobium and located within heater chamber 1. The central element of the measurement cell was a bar 2 with diameter $2R_0 = 9.548$ mm and length $l = 60.124$ mm, located coaxially within a cylindrical cavity in block 3. The gap between the bar and block was filled with the material to be studied. Gap size was 0.575 mm. During experiment the time dependence of bar temperature $T_0(\tau)$ and the temperature differential across the gap were measured. Knowledge of the function $T_0(\tau)$ permits determination of the bar heating rate $b_0 = dT_0(\tau)/d\tau$ and then, from the known heat capacity of the bar, the thermal flux passing through the material under study. The thermal flux and temperature differential are related to the thermal conductivity of the material in the gap and permit calculation of the latter. A number of corrections must be introduced in this calculation to consider radiant heat exchange, heat loss through bar mounting points, contact thermal resistance at the points of thermocouple attachment, and temperature discontinuity at the gas–solid boundary. Corrections characteristic of the nonsteady state regime must also be considered (for nonlinearity of heating and the temperature dependence of thermophysical properties of the specimen material), as well as corrections related to inhomogeneity of the block and bar temperature fields.

The size of the gap between block and bar is used in the thermal conductivity calculation and must be maintained to a high accuracy. For this purpose the cylindrical surfaces of the block and bar were fitted so that deviations from cylindrical measured in various sections did not exceed 2-3 μm. The surface finish produced by this was class 12, which also helped reduce radiant heat transfer. The mounting details joining the bar and block were made as thin as possible (without degrading strength of the construction) to reduce heat leakage. To equalize the temperature field the measurement cell was placed in a massive molybdenum cylinder 4. Temperature was measured by four VR 5/20 thermocouples (8-11), connected to an R-348 potentiometer.

The alkali metal was introduced with filling device 7, from which the metal was driven in a melted state by argon pressure into the measurement cell, which was preheated to a temperature somewhat exceeding the lithium saturation temperature at the chosen experimental pressure P. The argon pressure on the metal surface in the filler P_{Ar} was measured by a reference manometer 6 and maintained constant throughout an individual experiment. The vapor pressure in the cell was determined as the difference $P = P_{Ar} - P_h$, where $P_h = \rho gh$ (ρ is the density of the liquid metal, h is the difference between metal levels in the measurement cell and filler).

A monotonic heating regime was insured by a KPZ-L programmable controller and a regulator system. The latter included a KSP-1 potentiometer connected to a control thermocouple 5 and R-111 recording unit, driven by signals from a clock and the potentiometer. In accordance with the specified regulation law the R-111 transforms the unbalance signal into a unified dc signal which is then fed to a thyristor heater power controller.

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TABLE 1. Thermal Conductivity of Gaseous Lithium $\lambda \cdot 10^4$, W/(m•K)

T, K	λ_1	P, kPa							On saturation line
		1	5	10	30	50	80	100	
1000	576								694
1150	642	798							811
1200	664	758							847
1250	685	744							881
1300	707	744	868						912
1350	729	753	837	923					940
1400	751	766	824	886					966
1450	772	783	823	867					990
1500	794	802	829	861	963				1011
1550	816	821	841	864	941	1000			1030
1600	838	842	856	872	930	977	1031		1046
1650	860	863	873	885	928	965	1009	1033	1061
1700	882	884	891	900	932	961	997	1017	1073
1750	904	905	910	917	941	963	992	1008	1084
1800	925	927	930	935	954	970	993	1006	1094
1850	947	949	951	955	968	981	998	1009	1102
1900	969	971	972	975	985	995	1008	1016	1108
1950	991	992	993	995	1003	1010	1020	1028	1114
2000	1013	1014	1015	1016	1022	1027	1035	1040	1118

The problem of best description of the heating curve and precise definition of the heating rate required a large number of temperature measurements over a limited experimental time. A time interval measurement system was created for this purpose, consisting of two electronic timers operating in a time measurement mode, and a clock generator used to trigger and halt the timers. When a specified emf level occurred across the potentiometer (potentiometer indicator passing the zero graduation) one timer was switched on and the other off. Thus the time delay of the thermocouples relative to each other was measured. Use of this method made it possible to separate the processes of measurement and recording readouts, significantly increasing the volume of information obtained.

The thermal conductivity coefficient was calculated with the expression

$$\lambda = \frac{R_0 \ln (R_1/R_0)}{\bar{S}_s (1 + A_1) + 2\bar{S}_f (1 + A_2)} \; \frac{Q - Q_\varepsilon - Q_{\text{K}}}{\vartheta_0} (1 + \Delta\sigma_g), \tag{1}$$

where $Q = Cb_0$ is the total thermal flux supplied to the bar and $C = cM$ is the heat capacity of the bar.

The specific heat of the niobium c was taken from [14], while the thermal conductivity coefficient was referred to the mean temperature of the gas interlayer.

Corrections for axial inhomogeneity of the cell temperature field, and thermal fluxes supplied to the bar by radiation and the mounting details were calculated with the expressions

$$A_1 = \left(1 + \frac{m}{\mu^2 \vartheta_0}\right) \left(\frac{\exp(\mu l/2) - \exp(-\mu l/2)}{\mu l} - 1\right); \tag{2}$$

$$A_2 = \left(1 + \frac{m}{\mu^2 \vartheta_0}\right) \left(\frac{\exp(\mu l/2) + \exp(-\mu l/2)}{2} - 1\right), \tag{3}$$

where

$$m = -\frac{b_0}{a_{\text{M}}} + \frac{4(\Delta T_1 + \Delta T_2)}{l^2};$$

$$\mu^2 = \frac{2}{\lambda_{\text{M}} R_0} \left(\frac{\lambda}{R_1 - R_0} + H\right); \quad H = 4\varepsilon_n \sigma T_0^3, \tag{4}$$

$$Q_\varepsilon = \bar{H} [S_s (1 + A_1) + 2S_f (1 + A_2)] \vartheta_0,$$

$$\tilde{H} = \varepsilon_n \sigma T_0^3 \left[2 + \frac{\vartheta_0 (1 + A_1)}{T_0} + \left(1 + \frac{\vartheta_0 (1 + A_1)}{T_0} \right)^2 + \left(1 + \frac{\vartheta_0 (1 + A_1)}{T_0} \right)^3 \right],$$

$$Q_{\text{к}} = 2\lambda_{\text{м}} \frac{S_{\text{к}}}{\delta_{\text{к}}} (1 + A_2) \vartheta_0. \quad (5)$$

Thermal expansion of the cell material was considered in the calculations. The coefficient of linear expansion for niobium was taken from [5].

To a great extent the accuracy of determination of the thermal conductivity coefficient depends on the accuracy with which the bar heating rate b_0 is determined. This quantity is found by differentiating the time dependence of bar temperature $T_0(\tau)$. For a system with high thermal inertia such as the measurement cell under consideration, the problem of smoothing and differentiating a stepped function T_i, specified at points $a = \tau_0 < \tau_1 < \tau_2 \ldots < \tau_n = b$ with some uncertainty can best be solved using cubic spline functions [6]. Smoothing consists of minimizing the functional

$$\Phi(u) = \int_a^b [u'']^2 d\tau + \sum_{i=0}^{n} P_i [u(\tau_i) - T_i]^2, \quad (6)$$

where the conditions of best passage of the curve near the experimental T_i values and minimum "bending" of the function $u(\tau)$ are combined. A program for spline approximation of the measurement cell heating curve was composed in accordance with [6]. The weight matrix P_i was chosen such that deviations of the measured temperature values T_i from the smoothed $u(\tau_i)$ did not exceed the uncertainty of the temperature measurements.

Since the correction for radiation at high temperature proves significant, before and after each series of experiments with lithium the emissivity of the measurement cell material was checked. To do this a vacuum of 10^{-2} Pa was maintained in the cell. Under such conditions heat transport by thermal conductivity through the residual gas did not exceed 0.1%. Experiments at low temperatures where the fraction of radiation comprised less than 2% were used to determine the complex S_k/δ_k required for calculating heat loss through the mounting details. Then, with consideration of the S_k/δ_k value, the integral emissivity of the material was determined over the entire temperature range. Comparison of the vacuum experiment results showed that the quantity ε remained constant within the limits of experimental uncertainty, and thus the action of the lithium vapor on the niobium surface produced no noticeable changes in its structure. The function $\varepsilon(T)$ thus obtained was used to introduce corrections for radiation in the main experiments with the metal.

The correction for contact thermal resistance of the thermocouples and the temperature difference between the point of thermocouple attachment and the edge of the measurement gap was obtained experimentally using high purity inert gases.

The correction for temperature discontinuity on the gas—solid boundary was introduced by considering the dissociation reaction using the technique recommended in [7]. The value of this correction did not exceed 5%.

The thermal conductivity of the lithium vapor was studied on 10, 30, 50, and 80 kPa isobars at temperatures in the range 1400-1800 K. Several series of experiments were performed on each isobar. In total 223 experimental points were obtained. We estimate the uncertainty of the data to be 5%.

The theory of transport processes in alkali metal vapors considers such vapor to be an ideal reacting mixture of atomic and molecular components. Estimates show that the effect of the real nature of the vapor on its thermal conductivity in this parameter range can be neglected with an error less than 1%. According to the theory of Hirshfelder and Brokaw [8-10] the thermal conductivity of such a mixture is defined by the expression:

$$\lambda(P, T) = \lambda_1(T) \left[\frac{1 + A_1 x_2 + A_2 x_2^2}{1 + A_3 x_2 + A_4 x_2^2} + \frac{A_5 x_2}{1 + A_6 x_2} + A_7 \left(\frac{D_0(T)}{RT} \right)^2 \frac{x_2 (1 - x_2)}{(1 + x_2)^2} \right], \quad (7)$$

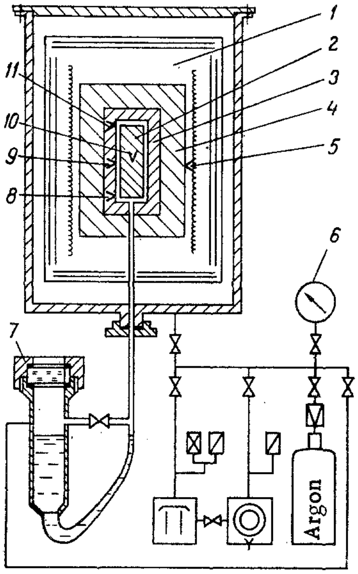

Fig. 1. Diagram of experimental apparatus.

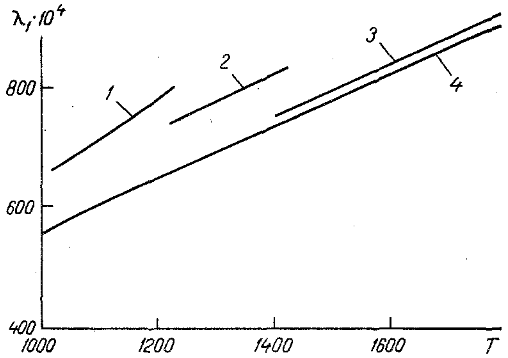

Fig. 2. Thermal conductivity of monatomic lithium vapor $\lambda_1 \cdot 10^4$ W/(m•K): 1) data of [14]; 2) [15]; 3) present study; 4) [16, 17]. T, K.

where the expression in square brackets characterizes the effect of vapor composition on thermal conductivity. All the coefficients A_i in this expression depend only on the ratio β_{12}^2 of the effective atom–molecule collision section to the effective atom–atom collision section; x_2 is the concentration of the molecular component; $D_0(T)$ is the dissociation energy at temperature T.

It follows from Eq. (7) that the vapor thermal conductivity at fixed T and P is uniquely related to $\lambda_1(T)$ and β_{12}^2, so the goal of processing the experimental data was determination of the temperature dependence $\lambda_1(T)$ and the quantity β_{12}^2. The values obtained for $\lambda_1(T)$ and β_{12}^2 allow use of the theoretically well justified Eq. (7) to extrapolate to parameter ranges not covered by experiment.

An important step in developing a method for generalizing the experimental data was choosing a hypothesis as to the form of the temperature dependence of λ_1 and β_{12}^2. Results of theoretical and experimental studies of alkali metal vapor thermal conductivity indicate that the temperature dependence of thermal conductivity of a monatomic vapor in the temperature range considered is practically linear. Therefore, it is natural to assume

$$\lambda_1(T) = A + BT. \tag{8}$$

The quantity β_{12}^2 depends very slightly on temperature. No available study of lithium transport coefficients in the gaseous phase was succeeded in describing this dependence, so that we take as a second hypothesis

$$\beta_{12}^2 = \text{const}. \tag{9}$$

With the aid of Eqs. (8), (9) we write Eq. (7) in the form

$$\lambda = f(A, B, \beta_{12}^2, x_2, T), \tag{10}$$

where A, B, and β_{12}^2 are unknown parameters. These can be found by approximating the experimental data with a surface of the form of Eq. (7) by the method of least squares. An optimization program was written for this purpose. The dissociation energy D_0^0 at T = 0 was taken equal to 101,900 J/mole based on [11, 12]. The remaining data required for the calculation were taken from handbook [13]. The following parameter values were obtained by the processing: $A = 14.11 \cdot 10^{-3}$ W/(m•K), $B = 43.54 \cdot 10^{-6}$ W/(m•K^2), $\beta_{12}^2 = 3.05$.

Figure 2 compares values of the lithium vapor thermal conductivity obtained in the present study with results of the experiments of [14, 15] and the theoretical calculations of [16, 17] performed with potential curves obtained in [18, 19] by a quantum mechanical variation method. As is evident from Fig. 2, the λ_1 values obtained above agree with the theoretical calculations within the accuracy of the latter. At a temperature of 1400 K, where our data overlap the results of [15], the divergence in λ_1 comprises 9%, which is within the limits of the total experimental uncertainty.

With the λ_1 and β_{12}^2 values found Eq. (7) was used to calculate lithium thermal conductivity in the gaseous phase for temperatures of 1000-2000 K and pressures of 1-100 kPa. The calculation results are presented in Table 1.

NOTATION

R_0, bar radius; l, bar length; T_0, bar temperature; b_0, bar heating rate; P, vapor pressure in measurement cell; g, acceleration of gravity; R_1, radius of block internal cylindrical surface; ϑ_0, temperature differential between block and bar at midsection over height; $\bar{S}_s$, $\bar{S}_f$, areas of side and face surfaces in midsection between bar and block; Q_ε, Q_k, thermal fluxes to bar via radiation and mounting details; A_1, A_2, corrections for axial inhomogeneity of measurement cell temperature field; $\Delta\sigma_g$, correction for nonlinearity of heating rate and temperature dependence of vapor thermophysical properties; M, bar mass; λ_m, a_m, thermal conductivity and thermal diffusivity of bar material; ΔT_1, ΔT_2, temperature difference between ends of bar and midsection; ε_r, reduced emissivity of cell material; S_s, S_f, areas of bar side and face surfaces; S_k, δ_k, area and length of the details connecting the bar with the block; ϑ_c, correction for contact thermal resistance between thermocouples and wall; λ, lithium vapor thermal conductivity; λ_1, monatomic vapor thermal conductivity; β_{12}^2, relative atom-molecule collision section.

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GENERALIZATION AND ANALYTIC DESCRIPTION OF THERMAL CONDUCTIVITY OF PARAFFIN AND AROMATIC HYDROCARBONS AND THEIR MIXTURES

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Experimental data on thermal conductivity of liquid binary mixtures of aromatic hydrocarbons with n-hexane are generalized.

At present unified theoretical expressions satisfactorily describing the thermal conductivity λ of liquids and gases as a function of temperature and pressure do not exist. Therefore the authors employed the cylindrical tricalorimeter method of [1, 2] to measure λ of aromatic hydrocarbons and their liquid binary mixtures with n-hexane. It was possible to generalize the measurement results by quite reliable equations.

The simplest sufficiently accurate expression was the Tait isotherm equation [3]. The authors of [4, 5] changed the form of the Tait equation and used it to describe thermal conductivity of liquids.

Since the analytical solution of the Tait isotherm equation presents definite difficulties, the authors of [6] derived two simple equations to calculate the coefficients of the former. The analytical description of the present data on thermal conductivity of individual hydrocarbons was performed with the first equation

$$\lambda_{p,T} = \lambda_T + \frac{Ap}{1+Bp}, \tag{1}$$

TABLE 1. Values of Quantities Appearing in Eqs. (2) and (3)

Material	Values of A_0, α, T_0			Coeffs. k_i for calc. of A			
	$A_0 \cdot 10^{-6}$	$\alpha \cdot 10^{-6}$	T_0, K	$k_1 \cdot 10^{-6}$	$k_2 \cdot 10^{-6}$	$k_3 \cdot 10^{-6}$	$k_4 \cdot 10^{-6}$
Benzene	468	1,6686	298,15				
Toluene			198,15	1042	—4,373	432,09	—975,867
Orthaxylene			273,15	328	—0,162	77,25	—117,03
Metaxylene	265	2,2	248,15				
Paraxylene	355	1,772	298,15				

Material	Values of A_0, α, T_0			Coeffs. k_i for calc. of B			
	$A_0 \cdot 10^{-6}$	$\alpha \cdot 10^{-6}$	T_0, K	$k_1 \cdot 10^{-6}$	$k_2 \cdot 10^{-6}$	$k_3 \cdot 10^{-6}$	$k_4 \cdot 10^{-6}$
Benzene	468	1,6686	298,15	0	—0,4921	20,932	—28,205
Toluene			198,15	261,6	—1,7786	139,443	—308,6
Orthaxylene			273,15	5,3	—0,9732	45,540	—67,112
Metaxylene	265	2,2	248,15	256,49	—1,852	142,11	—311,56
Paraxylene	355	1,772	298,15	2	—0,1479	11,933	—14,767

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