THERMAL CONDUCTIVITY OF SOME DEUTERATED COMPOUNDS IN THE GASEOUS PHASE

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The results of measurements of the thermal conductivity of CD_4, CH_4, C_2D_4, and C_2H_4 in the temperature range of 300-650°K are presented. The question of the influence of the isotopic effect on the transfer coefficients in gases is discussed.

The results of measurements of the thermal conductivity of D_2O vapors are presented in [1]. The temperature dependence of the ratio $\lambda_{D_2O}/\lambda_{H_2O}$ is determined. It is of interest to obtain experimental data for some other deuterated compounds in a relatively broad temperature range in order to examine the question of the influence of the isotopic effect on the transfer coefficients. For this purpose the thermal conductivity of CD_4 and C_2D_4, as well as of CH_4 and C_2H_4, were measured on the same experimental apparatus in order to obtain sufficiently accurate values for the thermal conductivity ratio of the respective compounds.

The measurements were made by the heated filament method on the experimental apparatus described in [1]. In determining the thermal conductivity from the equation

$$\lambda = \frac{Q \ln \frac{D}{d}}{2\pi l \Delta T_{gas}}$$

the following corrections were taken into account: for radiation from the measuring filament, for heat drain from the ends, and for the temperature drop at the wall of the measuring tube. To eliminate a temperature jump between the material studied and the measuring filament the experiments were conducted at different pressures (P = 100-900 mm Hg). At the maximum pressure in the experiments the correction for the temperature jump did not exceed a few percent.

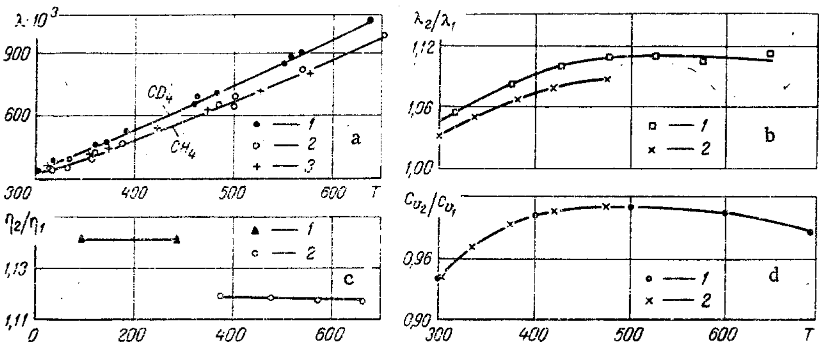

Fig. 1. Experimental data on thermal conductivity: a) CD_4: 1) authors' data; CH_4: 2) authors' data; 3) recommended data [2]; b) $\lambda_2/\lambda_1 = f(T)$: 1) authors' data; 2) [9]; c) $\eta_2/\eta_1 = f(T)$: 1) [15]; 2) [16]; d) $c_{v_2}/c_{v_1} = f(T)$: 1) [12]; 2) [11]. λ, W/m·deg; T, °K.

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TABLE 1. Experimental Data

P, mm Hg	Q, W	$T_{fi}-T_{wa}$, °K	δT_{qu}, °K	δT_{ju}, °K	ΔT_{gas}, °K	λ', W/m·deg	λ_{rad}, W/m·deg	$\delta\lambda_{end}$, W/m·deg	λ, W/m·deg	T_{av}, °K
					For λCD_4					
340	0,0616	5,76	0,02	—	5,74	0,0348	—	0,0005	0,0343	302,33
340	0,2164	18,53	0,06	—	18,47	0,0380	—	0,0005	0,0375	314,06
340	0,0706	4,98	0,02	—	4,96	0,0461	—	0,0006	0,0455	359,12
340	0,2349	15,91	0,07	—	15,84	0,0481	—	0,0006	0,0474	368,27
340	0,7008	42,90	0,19	—	42,71	0,0532	0,0003	0,0006	0,0523	392,38
350	0,1358	6,55	0,04	—	6,51	0,0676	0,0005	0,0007	0,0664	458,67
350	0,2583	12,18	0,07	—	12,11	0,0691	0,0006	0,0007	0,0678	461,06
350	0,7062	32,24	0,19	—	32,05	0,0714	0,0007	0,0008	0,0699	479,22
399	0,1984	7,49	0,05	0,07	7,37	0,0872	0,0010	0,0009	0,0853	551,26
209÷399	0,4200	15,48	0,10	0,15	15,23	0,0894	0,0012	0,0009	0,0873	555,73
209	0,7163	25,96	0,18	0,26	25,52	0,0909	0,0012	0,0009	0,0888	564,88
218÷280	0,7001	22,37	0,16	1,21	21,00	0,1080	0,0020	0,0010	0,1050	643,15
					For λCH_4					
912	0,1054	9,43	0,03	—	9,40	0,0363	—	0,0005	0,0358	316,62
832	0,1549	12,36	0,04	—	12,32	0,0407	—	0,0005	0,0402	351,65
912	0,7033	53,09	0,20	—	52,89	0,0431	—	0,0005	0,0425	355,71
832	0,7079	48,09	0,04	—	48,05	0,0477	0,0001	0,0005	0,0471	333,18
942	0,1392	6,89	0,04	—	6,85	0,0358	0,0006	0,0007	0,0345	432,75
612	0,7137	33,81	0,19	—	33,62	0,0588	0,0003	0,0007	0,0573	502,42
942	0,7160	33,63	0,19	—	33,44	0,0594	0,0003	0,0007	0,0579	502,70
434÷622	0,4183	16,37	0,10	0,13	16,14	0,0340	0,0012	0,0009	0,0319	553,97
182÷442	0,7003	22,87	0,16	0,31	22,40	0,1014	0,0021	0,0010	0,0983	653,55

In the deuterated ethylene the C_2D_4 content was 99.8% and in the deuterated methane the CD_4 content was 98.3% (N_2 and O_2 impurities of ~1.7%). The results of measurements of λ_{CD_4} and λ_{CH_4} are presented in Table 1 and the results of measurements of $\lambda_{C_2D_2}$ and $\lambda_{C_2H_4}$ are presented in Table 2.

The results of the measurements for ordinary methane (CH_4) and deuterated methane (CD_4) are presented in Fig. 1a. The deviations of our data from the values recommended [2] for CH_4 do not exceed 1.5%.

The results of the measurements for ordinary ethylene (C_2H_4) and deuterated ethylene (C_2D_4) are presented in Fig. 2a. The disagreements between our results and the data of other authors [3-8] lie mainly within the limits of 1%.

The values of $\lambda_{CD_4}/\lambda_{CH_4}$ and $\lambda_{C_2D_4}/\lambda_{C_2H_4}$ as a function of the temperature are presented in Fig. 1b and Fig. 2b. The ratio $\lambda_{CD_4}/\lambda_{CH_4}$ obtained by Baker and Brokaw [9] is presented in Fig. 1b for comparison. The disagreement between these and our data does not exceed 2%.

It is helpful to consider the following equation, well known from the molecular-kinetic theory of gases [10]:

$$\lambda = f c_v \eta.$$

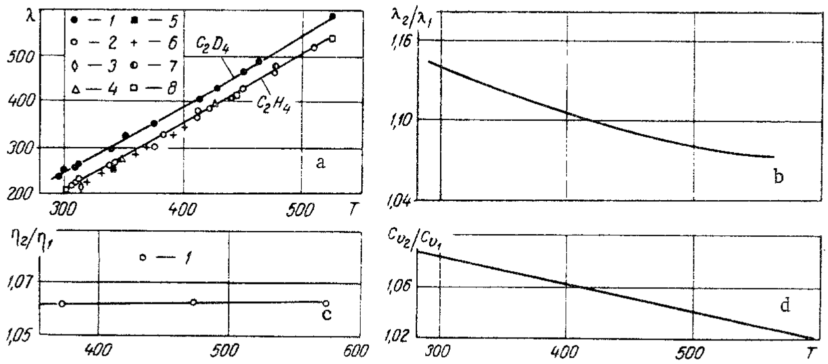

Fig. 2. Experimental data on thermal conductivity: a) C_2D_4: 1) authors' data; C_2H_4: 2) authors' data; 3) [3]; 4) [4]; 5) [5]; 6) [6]; 7) [7]; 8) [8]; b) λ_2/λ_1 = f(T) according to our data; c) η_2/η_1 = f(T): 1) [15]; d) c_{v_2}/c_{v_1} = f(T).

TABLE 2. Experimental Data

P, mm Hg	Q, W	$T_{fl}-T_{wa}$, °K	δT_{qu}, °K	δT_{ju}, °K	ΔT_{gas}, °K	λ, W/m · deg	λ_{rad}, W/m · deg	$\delta\lambda_{end}$, W/m · deg	λ', W/m · deg	T_{av}, °K
					for $\lambda_{C_2D_4}$					
264	0,0588	8,15	0,02	—	8,13	0,0234	—	0,0003	0,0231	295,11
264	0,1009	13,01	0,03	—	12,98	0,0252	—	0,0003	0,0249	299,29
264	0,2059	25,87	0,06	—	25,81	0,0258	—	0,0003	0,0255	310,37
264	0,0559	6,15	0,02	—	6,13	0,0295	—	0,0003	0,0292	340,27
264	0,1967	20,06	0,06	—	20,00	0,0319	—	0,0003	0,0316	351,19
264	0,2973	28,83	0,08	—	28,75	0,0335	—	0,0003	0,0332	358,29
266	0,6253	57,00	0,18	—	56,82	0,0357	0,0003	0,0005	0,0349	375,13
270	0,2339	18,60	0,06	—	18,54	0,0409	0,0004	0,0005	0,0400	409,84
270	0,2347	17,42	0,06	—	17,36	0,0438	0,0004	0,0005	0,0429	426,54
272	0,6689	45,84	0,18	—	45,66	0,0475	0,0005	0,0005	0,0465	448,55
272	0,6115	40,43	0,16	—	40,27	0,0492	0,0005	0,0005	0,0482	459,55
84÷281	0,3468	18,97	0,09	0,07	18,81	0,0597	0,0008	0,0006	0,0583	522,65
					for $\lambda_{C_2H_4}$					
800	0,0747	11,28	0,02	—	11,26	0,0215	—	0,0003	0,0212	304,02
650	0,1434	20,44	0,04	—	20,40	0,0228	—	0,0003	0,0225	311,04
800	0,1533	21,37	0,05	—	21,32	0,0233	—	0,0003	0,0230	312,15
800	0,1138	14,07	0,03	—	14,04	0,0263	—	0,0003	0,0260	339,04
800	0,1135	13,73	0,03	—	13,70	0,0268	—	0,0003	0,0265	342,03
650	0,1587	16,58	0,04	—	16,54	0,0310	0,0002	0,0003	0,0305	375,26
650	0,2339	23,14	0,06	—	23,08	0,0328	0,0002	0,0004	0,0322	380,10
650	0,7047	61,17	0,17	—	61,00	0,0374	0,0003	0,0005	0,0366	411,40
805	0,1241	10,43	0,03	—	10,40	0,0387	0,0003	0,0005	0,0379	413,57
805	0,2476	20,52	0,07	—	20,45	0,0392	0,0003	0,0005	0,0384	422,62
810	0,2545	18,78	0,07	—	18,71	0,0441	0,0005	0,0005	0,0431	450,37
255÷585	0,7054	48,38	0,19	0,47	47,72	0,0479	0,0006	0,0006	0,0467	477,77
55÷255	0,7018	42,94	0,18	0,16	42,60	0,0534	0,0008	0,0006	0,0520	518,15

The ratio of the thermal conductivity of the deuterated compound to that of the hydrogen compound in the gaseous phase can be represented in the form

$$\frac{\lambda_2}{\lambda_1} = \frac{f_2}{f_1}\,\frac{c_{v_2}}{c_{v_1}}\,\frac{\eta_2}{\eta_1},$$

where the index 1 pertains to material containing hydrogen and 2 pertains to the deuterated material.

The value f_2/f_1 was calculated from this equation for ethylene and methane on the basis of our experimental values of λ_2/λ_1. The values c_{v_2}/c_{v_1} are obtained on the basis of heat capacity calculations using spectroscopic data.

Data on c_{v_2}/c_{v_1} from [11, 12] are used for methane. The values of c_v for C_2H_4 are taken from [13] and those for C_2D_4 are based on calculations conducted by V. S. Yungman by methods described in [14]. The values of η_2/η_1 for methane are taken from the experimental data of [15, 16] and for ethylene from [16]. The ratios λ_2/λ_1, η_2/η_1, and c_{v_2}/c_{v_1} as functions of the temperature are presented in Fig. 1b, c, d and in Table 3 for methane and in Fig. 2b, c, d and in Table 3 for ethylene.

It was found that the viscosity ratio η_2/η_1 is equal to the square root of the mass ratio m_2/m_1. This corresponds to the kinetic theory of gases with the condition of the equality of the effective collision cross

TABLE 3

T, °K	λ_2/λ_1	c_{v_2}/c_{v_1}	η_2/η_1	f_2/f_1
		Methane		
400	1,11	1,00	1,12	0,99
500	1,13	1,01	1,12	1,00
600	1,12	1,01	1,12	0,99
		Ethylene		
300	1,14	1,08	1,06	1,00
400	1,11	1,06	1,06	0,99
500	1,10	1,04	1,06	1,00

sections for the viscosity. Here it is characteristic to note that the dependence of λ_2/λ_1 on the temperature is the same as $c_{v_2}/c_{v_1} = f(T)$. Hence it follows that the ratio f_2/f_1 does not depend on the temperature and is equal to unity. The deviation from unity does not exceed 1-2%, which corresponds to the experimental accuracy.

NOTATION

P	is the experimental pressure;
Q	is the heat flux from heated platinum filament;
T_{fi}	is the filament temperature;
T_{wa}	is the wall temperature;
δT_{qu}	is the temperature drop at wall of quartz tube;
δT_{ju}	is the correction for temperature jump;
ΔT_{gas}	is the temperature difference in gas layer;
λ'	is the coefficient of thermal conductivity without allowance for heat drain from the ends and losses to radiation;
λ_{rad}	is the correction for radiation;
$\delta\lambda_{end}$	is the correction for heat drain from ends of measuring tube;
T_{av}	is the average temperature;
λ	is the coefficient of thermal conductivity;
f	is the proportionality coefficient allowing for the degree of exchange between different forms of energy;
c_v	is the specific heat capacity at constant volume;
η	is the viscosity coefficient.

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