High temperature-high pressure thermal conductivities of ethylene and propane

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Thermal conductivities λ of ethylene and propane were measured in the temperature and pressure ranges 400-750 K and 0.1-2.65 MPa (ethylene) and 400-725 K and 0.1 to 0.6 MPa (propane). The data were correlated by expressions of the form $\lambda = \lambda_0(T) \times \lambda_p(P)$, with λ_0 being a second order polynomial in temperature and λ_p a third (ethylene) or a fourth (propane) order polynomial in pressure. The results obtained were compared with previous thermal conductivity measurements.

I. INTRODUCTION

In the previous paper, an apparatus was described for measuring thermal conductivities of gases at high temperatures and at high pressures. In this paper, experimental results are presented for ethylene and propane. In order to prevent the formation of multicellular convection, the temperatures and pressures were kept at values which resulted in Rayleigh numbers less than the critical Rayleigh number of 5×10^4 (see Ref. 1). Thus, the thermal conductivity values of ethylene were measured in the ranges 400 to 750 K and 0.1 to 2.65 MPa. The lowest temperature and pressure used for propane was also 400 K and 0.1 MPa. The highest temperature and pressure reached with propane was 725 K and 0.6 MPa. At high pressures, propane liquified at room temperature.

Laboratory grade test gases of purities 99.5% (ethylene) and 99% (propane) were used in the experiments.

II. RESULTS

The measured heat transfer values are listed in Tables I and II. The thermal conductivities of ethylene and propane were determined by substituting the polynomial

$$\lambda = a + bT + cT^2 \tag{1}$$

into the Fourier equation [Eq. (10) in Ref. 1], and by integrating the resulting equation between d/2 and D/2. By neglecting the corrections for temperature drop across the column λ' , temperature jump at the filament surface λ'' , and thermal expansion of the filament λ''' , the integration gave

$$\frac{Q\lambda}{2\pi}\ln(D/d) = a(T_f - T_b) + \frac{b}{2}(T_f^2 - T_b^2) + \frac{c}{3}(T_f^3 - T_b^3). \tag{2}$$

At each pressure, the values of $Q_{\lambda}(\text{W m}^{-1})$ and $T_f(\text{K})$ given in Tables I and II were used to fit a least squares curve through Eq. (2). With this procedure, the values of the constants a, b, and c were determined at six pressures (Table III). Once a, b, and c were determined, the values of λ (Tables IV and V) and the values of λ' , λ'' , and λ''' were calculated. The total contributions of λ' , λ'' , and λ''' to λ were found to be always less than 0.2%.

Similar to argon, it was found for both ethylene and propane that the thermal conductivity could be expressed as

$$\lambda = \lambda(T, P) = \lambda_T(T) \cdot \lambda_p(P) , \qquad (3)$$

where λ_T (W m⁻¹ K⁻¹) and λ_p (dimensionless) are only functions of temperature and pressure, respectively. By taking λ_T to be the thermal conductivity of the gas at 0.1 MPa and by representing this value by λ_0 , we have

$$\lambda_T = \lambda_0 = a_0 + b_0 T + c_0 T^2 . {4}$$

TABLE I. Tabulation of the ethylene data. Symbols are defined in Ref. 1; $L_S = 34.120$ cm, $L_L = 46.356$ cm.

P (MPa)	T_f (K)	Q_{ms} (W)	\overline{Q}_{mL} (W)	Q _{ms} (W)	\overline{Q}_{mL}^{V} (W)	Q _λ (W m ⁻¹)
0.1	395.0	1.432	2,396	0.0263	0.0459	7.72
	434.8	2.049	3.493	0.0371	0.0698	11,53
	479.7	2.823	4.899	0.0516	0.1059	16.52
	528.9	3,775	6.662	0.0715	0.1549	22,92
	583.6	4.951	8.884	0.0963	0.2229	31.10
	643.0	6.382	11.619	0.1306	0.3192	41.25
	702.8	8,142	14.947	0.1786	0.4505	53.39
	769.7	10,177	18.911	0.2356	0.6314	68.14
0.64	394.4	1.413	2.373	0.0247	0.0442	7.69
	433.2	2.032	3.466	0.0359	0.0683	11.46
	478.4	2.806	4.876	0,0501	0.1031	16.48
	526.8	3.773	6.659	0.0693	0.1514	22,92
	579.3	4.933	8.833	0.0949	0.2183	30.86
	640.1	6.350	11,560	0,1278	0.3116	41.08
	700.5	8.076	14.860	0.1712	0.4405	53.24
	768,2	10.082	18.797	0.2263	0.6163	68.04
1.16	392.5	1,393	2.349	0.0220	0.0405	7,66
	432.2	2.015	3.445	0.0344	0.0661	11.43
	474.9	2.781	4.832	0,0482	0.0994	16.34
	522.7	3,740	6.592	0,0680	0.1466	22,67
	576.4	4.910	8.791	0,0927	0.2137	30.73
	634.2	6.361	11.531	0.1276	0.3059	40.79
	697.4	8.008	14,763	0.1656	0.4268	53,07
	762.0	9.975	18.610	0.2183	0.5931	67.50
1.68	390.7	1.398	2.346	0.0222	0.0327	7.66
	427.6	2.002	3.409	0.0336	0.0640	11, 25
	473.1	2.773	4.819	0.0467	0.0981	16.30
	520.1	3,720	6,557	0.0662	0.1431	22.56
	569,9	4,863	8.686	0.0904	0.2049	30.31
	626.5	6.262	11.345	0.1222	0.2909	40.17
	686.8	7.924	14.545	0.1612	0.4081	52.10
	751.7	9.904	18,398	0.2144	0.5705	66.51
2,17	380.8	1.239	2.088	0.0229	0.0328	6.85
	415.7	1.826	3.103	0.0296	0.0554	10.23
	456.9	2.553	4,391	0.0424	0.0846	14.68
	503,2	3,444	6,028	0.0600	0.1282	20.56
	554.1	4.528	8.066	0.0807	0.1822	28.09
	608.5	5.850	10.556	0.1105	0.2607	37.23
	665.5	7.430	13,583	0.1467	0.3622	48.52
	727.2	9,317	17,220	0.1938	0.5057	62.04
	793.6	11.461	21,490	0.2478	0.6898	78.35
2.65	386.3	1.350	2,283	0.0191	0.0356	7,49
	421.6	1.972	3,357	0.0304	0.0592	11.09
	464.7	2.738	4.740	0.0448	0.0905	15.98
	510.1	3,682	6.460	0.0633	0.1261	22.19
	558.7	4.807	8.541	0.0880	0.1932	29.65
	614.3	6.155	11,114	0.1147	0.2711	39, 25
	674.6	7.820	14,304	0.1548	0.3837	51.12
	734.9	9.698	17.978	0.1974	0.5216	65,02
	803.2	11.99	22,527	0.2562	0.7187	82.34

TABLE II. Tabulation of the propane data. Symbols are defined in Ref. (1); $L_S = 34.230$ cm, $L_L = 46.356$ cm.

P	T_f	\overline{Q}_{ms}	Q_{mL}	\overline{Q}_{ms}^{V}	\overline{Q}_{mL}^{V}	Q_{λ}
(MPa)	(K)	(W)	(W)	(W)	(W)	(W m ⁻¹
0.1	372.9	1.057	1.697	0.0202	0,0279	5.21
	410.4	1.586	2.594	0.0303	0.0476	8.17
	452.7	2.262	3.764	0.0437	0.0760	12, 12
	499.9	3.159	5,317	0.0663	0.1199	17.35
	549.7	4.281	7.284	0.0966	0.1824	24.06
	605.0	5.611	9,671	0.1331	0.2705	32.35
	667.0	7.252	12.672	0.1840	0.3976	42.94
	725.3	9,227	16,213	0,2530	0.5603	55.08
0.2	372.2	1.038	1,667	0.0202	0.0279	5.12
	409.3	1.574	2.574	0.0303	0.0460	8.11
	451.6	2,243	3,732	0.0425	0.0745	12.02
	499.3	3.146	5, 295	0.0663	0,1107	17.36
	549.0	4.237	7,214	0.0945	0.1797	23, 85
	604.6	5,621	9.678	0.1348	0.2721	32.33
	662.7	7.244	12.611	0.1841	0.3911	42,55
	729.8	9.308	16,377	0.2560	0.5714	55.70
0.3	372.2	1.039	1.668	0.0207	0.0279	5.12
	409.5	1,574	2.572	0.0304	0.0471	8.09
	451.0	2.280	3.775	0.0461	0.0770	12.07
	496.8	3.128	5,258	0.0652	0.1186	17.12
	549.7	4.232	7.214	0.0944	0.1797	23.89
	605.8	5.577	9,622	0.1330	0.2691	32.24
	662.5	7.235	12,593	0.1842	0.3912	42.48
	728.4	9, 186	16,203	0.2487	0.5600	55.30
0.4	371.5	1.037	1.664	0.0202	0.0275	5.11
	410.1	1.580	2.583	0.0303	0.0471	8.13
	453.3	2.282	3.791	0.0451	0.0769	12.19
	497,2	3.115	5.245	0.0640	0.1159	17, 14
	548.5	4.247	7,228	0.0951	0.1808	23.88
	605.5	5.596	9,653	0,1330	0.2704	32.33
	663.9	7.215	12.588	0.1818	0.3890	42.60
	727.8	9,205	16, 225	0.2488	0,5599	55.32
0.5	371.5	1.037	1.663	0.0199	0.0275	5.11
	408.1	1.564	2.555	0.0296	0.0460	8,04
	450.7	2,251	3.734	0.0443	0.0754	11.97
	497.6	3.123	5,256	0.0651	0.1169	17, 16
	549.0	4.218	7.194	0.0930	0.1783	23.84
	603.1	5.559	9.593	0.1302	0,2638	32.17
	662.5	7.204	12.557	0.1818	0.3869	42.45
	724.2	9.140	16,094	0.2460	0.5493	54.85
0.6	372.6	1.054	1.695	0.0197	0.0275	5, 22
	409.9	1.594	2.611	0.0296	0.0465	8, 25
	451.4	2.266	3.773	0.0424	0.0738	12.17
	498.0	3, 124	5, 283	0.0611	0.1145	17,36
	548.1	4.224	7.219	0.0900	0, 1743	24.01
	601.2	5.554	9.596	0.1272	0,2585	32.25
	663.1	7.158	12,545	0.1718	0.3777	42.73
	726.8	9.211	16.293	0.2381	0.5440	55.88

A. Ethylene

For ethylene, the thermal conductivity as a function of temperature and pressure was written as $\lambda = (a_0 + b_0 T + c_0 T^2)$

$$\times \left[1 + A\left(\frac{P - P_0}{P_0}\right) + B\left(\frac{P - P_0}{P_0}\right)^2 + C\left(\frac{P - P_0}{P_0}\right)^3\right],\tag{5}$$

where $P_0 = 0.1$ MPa. The constants A, B, and C were determined by employing a least squares fit through Eq. (5) using the experimental values of λ and λ_0 [Eqs. (1) and (4)], and the corresponding values of pressure P. The foregoing procedure yielded the values of the constants A, B, and C given in Table III.

With these constants, Eq. (5) described the data with a standard deviation of 1×10^{-5} . Third, fourth, and fifth order polynomials in temperature and fourth and fifth order polynomials in pressure were also fitted to the data. These polynomials did not improve the correlation significantly.

TABLE III. The constants a, b, c, and A, B, C, D. The units of a, b, c are such as to give λ in W m⁻¹ K⁻¹ when T is in K. A, B, C, and D are dimensionless.

Pressure (MPa)	$a \times 10^{1}$	$b \times 10^3$	$c \times 10^7$	
		Ethylene		
0.1	-0.1768	0.1189	0.2328	
0.64	-0.1749	0.1183	0.2469	
1.16	-0.1791	0.1206	0.2440	
1.68	-0.1862	0.1245	0.2312	
2.17	-0.1874	0.1258	0.2515	
2.65	-0.1897	0.1279	0.2600	
		Propane		
0.1	-0.1595	0.0989	0.4409	
0.2	-0.1595	0.0989	0.4409	
0.3	-0.1639	0.1008	0.4214	
0.4	-0.1623	0.0999	9.4344	
0.5	-0.1640	0.1010	0.4264	
0.6	-0.1635	0.1009	0.4410	
Ethylene		Propane		
A 0.1185×1	.0 ⁻³	0.149	58×10 ⁻³	
3 0.1856×10 ⁻³		0.1205×10 ⁻³		
$C = -0.2493 \times 1$		-0.1846×10^{-3}		
D 0			22×10 ⁻⁴	

A comparison between the heat conduction calculated using λ given by Eq. (5) and the heat conduction measured yields a maximum difference of 0.6% (Fig. 1). Using the analysis given in Ref. 1, the most probable random error in the data was estimated to range from 1.51%-1.78%. The maximum systematic error was estimated to be 0.95%.

The only available information on the thermal conductivity of ethylene is that reported by Vargaftik² and Misic and Thodos.³ Vargaftik's tables give values of λ up to pressures of 150 MPa in the temperature range of 300 to 500 K. Therefore, a direct comparison between the present results and those given by Vargaftik could be made only at 0.1 MPa and at temperatures between 400 and 500 K. The results are presented in Fig. 2. The values given by Vargaftik seem to be 2% to 6% higher than those obtained in the present experiments.

Misic and Thodos developed the following expression for the thermal conductivities of hydrocarbons:

TABLE IV. Thermal conductivity of ethylene calculated using Eq. (1) and the constants a,b, and c given in Table III.

P (MPa)	0.1	0.64	1, 16	1.68	2.17	2.65
T (K)						
400	33.60	33.78	34.21	34.90	35.58	36.36
450	40.54	40.75	41.28	42.11	42.94	43.86
500	47.59	47.82	48.47	49.43	50,42	51,50
550	54.75	55.04	55.78	56.87	58.03	59.26
600	62.04	62.37	63.21	64.43	65.77	67.15
650	69.43	69.83	70.76	72.10	73.62	75.17
700	76.95	77.41	78.43	79.89	81.61	83.32
750	84.58	85,11	86,23	87.79	89.72	91.61

TABLE V. Thermal conductivity of propane calculated using Eq. (1) and the constants a, b, and c given in Table III.

P (MPa)	0.1	0.2	0.3	0.4	0.5	0.6	
T (K)	$\lambda \times 10^3 \text{ (W m}^{-1} \text{ K}^{-1})$						
400	30.67	30.67	30.68	30.68	30.81	31.07	
450	37.49	37.49	37.52	37.52	37.67	37.99	
500	44.53	44.53	44.56	44.58	44.74	45.13	
550	51.79	51.79	51.81	51.85	52.03	52.49	
600	59.27	59.27	59.28	59.34	59.53	60.07	
650	66.98	66.98	66.95	67.05	67.24	67.87	
700	74.90	74.90	74.84	74.98	75.17	75.90	
725	78.94	78.94	78.86	79.03	79.21	79.99	

$$\lambda(T) = \frac{\overline{c}_{p} \times 10^{-4} \left[14.52 (T/T_{c}) - 5.14 \right]^{2/3}}{M^{1/2} (T_{c})^{1/8}} \left(\frac{10P_{c}}{1.0133} \right)^{2/3} ,$$
(6)

where \overline{c}_b is in kJ kmole⁻¹ K⁻¹, M is the molecular weight of the gas, and T_c and P_c are the critical temperature (K) and pressure (MPa), respectively. In principle, this expression [Eq. (6)] is applicable up to 0.5 MPa. In practice, it is difficult to use it beyond 0.1 MPa because the literature does not report accurate specific heat values at higher pressures. Therefore, comparison was made between the present values of λ [Eq. (5)] and those calculated using Eq. (6) at 0.1 MPa only. For this comparison, the values of \overline{c}_b were taken from Ref. 4 and the values of M, T_c , and P_c from Ref. 2. The results given in Fig. 2 show a maximum difference of 0.35% between the present values of λ and those obtained by the Misic—Thodos expression.

B. Propane

The thermal conductivity of propane as a function of temperature and pressure was written as

$$\lambda = (a_0 + b_0 T + c_0 T^2) \left[1 + A \left(\frac{P - P_0}{P_0} \right) + B \left(\frac{P - P_0}{P_0} \right)^2 + C \left(\frac{P - P_0}{P_0} \right)^3 + D \left(\frac{P - P_0}{P_0} \right)^4 \right]. \tag{7}$$

The constants A, B, C, and D were again determined

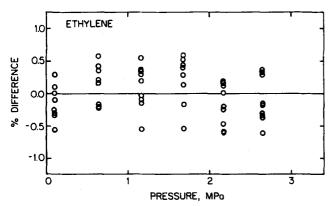


FIG. 1. Percent differences between the measured heat conduction and the heat conduction calculated using the thermal conductivity values given by Eq. (5). The points shown are for temperatures 400-750 K.

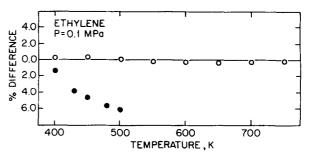


FIG. 2. Percent differences between the thermal conductivity values obtained in the present investigation [Eq. (5)] and the values reported by previous investigators. OMisic and Thodos³ (400-750 K); • Vargaftik² (400-500 K).

by using a least squares fit through Eq. (7) by employing the experimental values of λ and λ_0 [Eqs. (1) and (4)] and the corresponding values of pressure P ($P_0=0.1$ MPa). The constants A, B, C, and D obtained by this procedure are given in Table III. With the constants given in Table III, Eq. (7) described the data with a standard deviation of 1×10^{-5} . Higher-order polynomials in both temperature and pressure (up to fifth order) did not seem to improve the correlation.

A comparison between the values calculated using λ given by Eq. (7) and values of heat conduction measured is shown in Fig. 3. The maximum difference between the calculated and measured values of heat conduction was 0.6%. Using the analysis given in Ref. 1, the most probable random error in the data was estimated to range from 1.51%-1.78%. The maximum systematic error was estimated to be 0.93%.

All values of the thermal conductivity of propane reported in the literature are for a pressure of 0.1 MPa. At this pressure, Ehya, Faubert, and Springer⁵ made measurements of the thermal conductivity of propane in the temperature range of 300 to 1000 K. Vargaftik² reported the values of thermal conductivity for propane between 250 and 825 K. Measurements were performed at 478 K by Mann and Dickens.⁶ Vines and Bennett⁷ measured thermal conductivity values at 399 and 422 K. Values were reported by Leng and Comings⁸ at 413 K

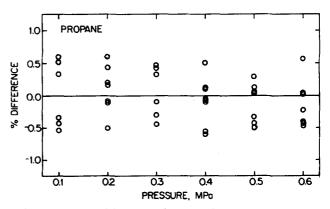


FIG. 3. Percent differences between the measured heat conduction and the heat conduction calculated using the thermal conductivity values given by Eq. (7). The points shown are for temperatures 400-725 K.

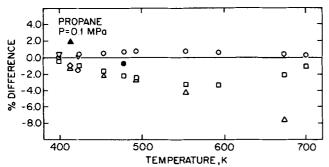


FIG. 4. Percent differences between the thermal conductivity values obtained in the present investigation [Eq. (7)] and the values reported by previous investigators. \circ Ehya, Faubert, and Springer⁵ (399-700 K); \Box Misic and Thodos³ (399-700 K); \triangle Vargaftik² (413-673 K); \triangledown Smith, Durbin, and Kobayashi⁸ (398 and 423 K); \triangledown Vines and Bennett⁷ (413 and 422 K); \blacksquare Mann and Dickens⁶ (478 K); \blacksquare Leng and Comings⁸ (413 K).

while Smith, Durbin, and Kobayashi⁹ measured thermal conductivity values at 398 and 423 K.

Figure 4 compares the present results given by Eq. (7) and those reported previously. Below 450 K, the present data agree with those reported previously to within 2%. In the temperature range of 400 to 700 K, the present results agree with those given by Ehya, Faubert, and Springer to within 0.5%. The Misic-Thodos expression [Eq. (6)] yields thermal conductivity values which are 1%-3% higher than those given by present

experiments. The values given by Vargaftik in the temperature range of 413-673 K seem to be 1%-7.5% higher than those given by present experiments. Convection effects may account for the higher thermal conductivity values reported previously.^{2,3,6,7}

ACKNOWLEDGMENT

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