

Thermal Conductivity of Methane–Ethane Mixtures at Temperatures Between 140 and 330 K and at Pressures up to 70 MPa¹

H. M. Roder² and D. G. Friend²

The paper presents new measurements on the thermal conductivity of three methane–ethane mixtures with methane mole fractions of 0.69, 0.50, and 0.35. The thermal conductivity surface for each mixture is defined by up to 13 isotherms at temperatures between 140 and 330 K with pressures up to 70 MPa and densities up to 25 mol · L⁻¹. The measurements were made with a transient hot-wire apparatus. They cover a wide range of physical states including the dilute gas, the single-phase fluid at temperatures above the maxcondentherm, the compressed liquid states, and the vapor at temperatures below the maxcondentherm. The results show an enhancement in the thermal conductivity in the single-phase fluid down to the maxcondentherm temperature, as well as in the vapor and in the compressed liquid. A curve fit of the thermal conductivity surface is developed separately for each mixture.

KEY WORDS: enhancement; ethane; high pressure; methane; mixtures; thermal conductivity; transient hot-wire apparatus.

1. INTRODUCTION

Experimental measurements of the thermal conductivity of binary mixtures are rare; those that have been published are usually limited to ambient temperature and pressure and apply to either vapor or liquid states, depending on the mixture selected [1]. In contrast, the present measurements on three methane–ethane mixtures cover a large range of both density and temperature. They extend our earlier measurements on the pure components methane [2] and ethane [3] into a new dimen-

¹ Paper presented at the Ninth Symposium on Thermophysical Properties, June 24–27, 1985, Boulder, Colorado, U.S.A.

² Thermophysics Division, National Bureau of Standards, Boulder, Colorado 80303, U.S.A.

sion—composition. The 2476 points reported here for the three mixtures, when added to the 1697 points of the pure components, a total of 4173 points, represent the most comprehensive set of data ever assembled for the thermal conductivity of a binary mixture. This set of data is further unique in that the PVT relation, the equation of state, has been measured for each mixture [4]. This allows us to analyze and correlate the thermal conductivity results in terms of the variables density, temperature, and composition.

In this paper we present the data and, for each mixture, the dependence of thermal conductivity on density and temperature. The analysis of the thermal conductivity of mixtures and pure components to develop a model which includes the dependence on composition also is given in a separate paper [5].

For a given mixture the dilute gas and excess thermal conductivities are quite similar to those of the pure components. In addition, a critical enhancement is found for the mixtures which is very similar to the critical enhancement in the pure components. Our results contradict theory [6, 1], which suggests that an enhancement should not be present in mixtures. A previous light-scattering experiment on a methane–ethane mixture [7] does not exhibit an enhancement [1]. In contrast, our results show an enhancement, as do those obtained by Cohen et al. [8] on He-3–He-4 mixtures for temperatures and densities very close to the liquid–vapor critical point. However, in contrast to Ref. 8, while our results cover a large range of both density and temperature, they do not approach as close to the liquid–vapor critical point.

2. METHOD AND APPARATUS

The measurements were made with a transient hot-wire thermal conductivity apparatus. This instrument has been tested with nitrogen, helium [9], and argon [10, 11]. It has been used to measure the thermal conductivity surfaces of oxygen [12], propane [13], hydrogen [14], methane [2], and ethane [3]. A detailed description of the apparatus and data reduction has been given previously [9].

The apparatus is not specifically designed to measure thermal conductivity in the critical region. Nevertheless, measurements were made as close to the mixture critical temperature and as close to the maxcondentherm as is possible with the present system, bearing in mind that the measurements must be free of convection. Replicate measurements made at the same cell temperature and pressure but with different power levels serve to verify the absence of convection.

The thermal conductivity measurements were made on the same three

Table I. Methane–Ethane Mixture Compositions and Other Mixture Parameters

Mixture No.	Nominal composition (mole %)	Actual composition		Mixture critical parameters ^a			
		Methane (mole fraction)	ethane (mole fraction)	P_c (MPa)	T_c (K)	ρ_c (mol · L ⁻¹)	ρ_{center} (mol · L ⁻¹)
1	70/30	0.68526	0.31474	6.7617	239.779	10.24 ± 0.04	8.75 ± 0.3
2	50/50	0.50217	0.49783	6.7678	262.919	8.96 ± 0.04	8.68 ± 0.3
3	35/65	0.34528	0.65472	6.3449	278.910	8.16 ± 0.04	8.06 ± 0.3

^a P_c and T_c interpolated from Ref. 16; ρ_c calculated from the EOS in Ref. 4.

mixture compositions, which were prepared gravimetrically and used for PVT [4] and viscosity [15] measurements at this laboratory. We refer to the nominal mixture compositions as 70/30, 50/50, and 35/65; actual mixture compositions and other pertinent parameters for the mixtures are given in Table I.

3. BACKGROUND ON MIXTURES

We review here some background on mixtures essential to understanding the measurements reported. A P–T phase diagram for the 70/30 methane–ethane mixture is shown in Fig. 1. The liquid–vapor two-phase region is defined by the bubble- and dew-point lines, which along with the mixture critical point, i.e., the liquid–vapor critical point, were taken from Ref. 16. A second special point along the two-phase boundary is the maximum condensation temperature, the maxcondentherm. The PVT measurements for this mixture, all made in the single-phase regions, are reported in Ref. 4. The PVT surface of the mixture as reported in Ref. 4 is based on an extended BWR equation of state using a “pseudo” pure-fluid, single-component approach.

For mixtures a diffusional contribution to the thermal conductivity is expected. This contribution is predicted to be less than 0.1% at low densities [17] and was shown experimentally to be less than 1% for liquid densities [18]. The thermal conductivity measurements were made along the isotherms shown. For temperatures above the maxcondentherm we have measured complete isotherms covering pressures from near 0 to 70 MPa, i.e., densities up to 25 mol · L⁻¹. However, for temperatures below the maxcondentherm the range of pressure is restricted because we cannot measure thermal conductivities in the liquid–vapor two-phase region. For

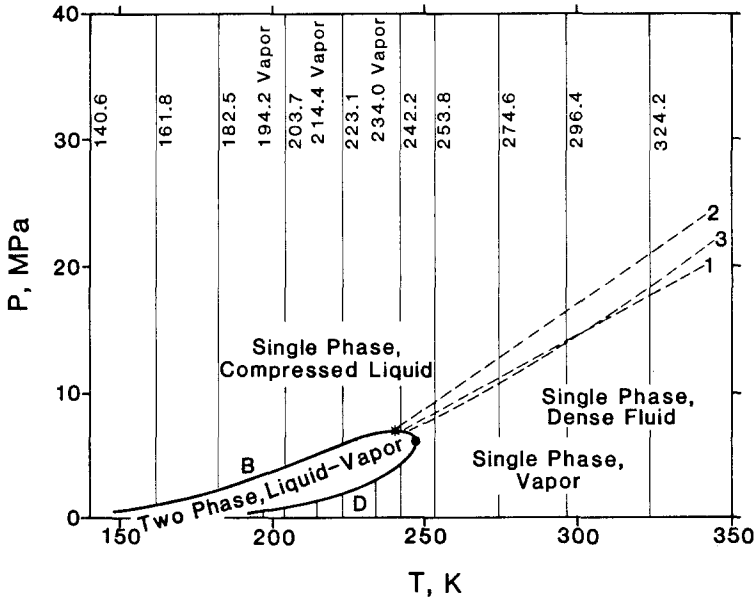


Fig. 1. The P-T phase diagram for the 70/30 methane-ethane mixture. (*) Mixture critical point; (B) bubble-point line; (D) dew-point line [16]; (●) maximum condensation temperature along the two-phase liquid-vapor boundary, the maxcondentherm; (—) isotherms of the thermal conductivity measurements; (---, 1) densities at maximum values of $\Delta\lambda_c$ [this paper]; (---, 2) mixture critical density [4]; (-.-, 3) densities at maximum values of C_p [4].

these temperatures we are restricted to pressures below the dew-point line or above the bubble-point line. Specifically, the approach to the mixture critical point can be carried out only from the compressed liquid side.

4. RESULTS

A total of 899 measurements distributed among 13 isotherms was obtained for the 70/30 mixture, 932 points along 12 isotherms for the 50/50 mixture, and 645 points along 12 isotherms for the 35/65 mixture. On each isotherm measurements were made at a number of different pressures. In the compressed liquid at the lower temperatures, the spacing was about 11 MPa (1600 psia) in pressure. In the single-phase fluid the spacing in pressure was arranged to give a spacing in density of about $0.5 \text{ mol} \cdot \text{L}^{-1}$. At each pressure four different power levels were used, resulting in slightly different experimental temperatures and densities.

An overview of the thermal conductivities is given in Fig. 2, where the lines are isotherms calculated from the correlated surface for each mixture.

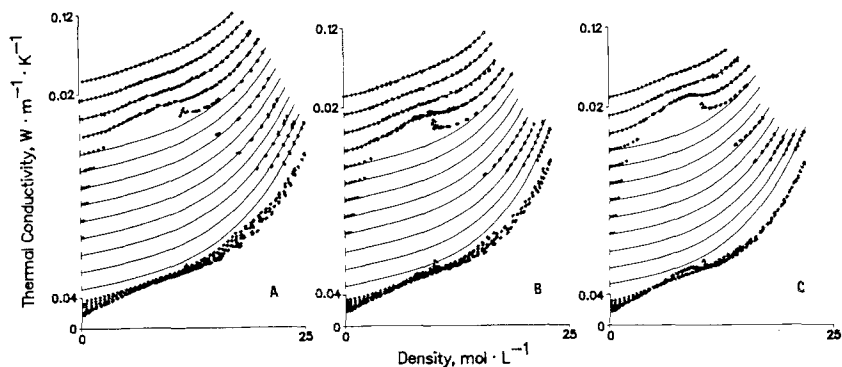


Fig. 2. Overview of the thermal conductivity measurements on methane-ethane mixtures. Bottom part, all measurements on a single scale; top part, individual isotherms separated by $0.02 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. (A) The 70/30 mixture; (B) the 50/50 mixture; (C) the 35/65 mixture.

Complete tables of results for all three mixtures are given in a separate report [19]; similarly the results for the pure components are found in an earlier report [20].

5. CORRELATION OF THE MIXTURE THERMAL CONDUCTIVITY SURFACES

The thermal conductivity surfaces of the mixtures are quite similar to those of the pure components, which are generally correlated in terms of density and temperature [21]:

$$\lambda(\rho, T) = \lambda_0(T) + \lambda_{\text{excess}}(\rho, T) + \Delta\lambda_{\text{critical}}(\rho, T) \quad (1)$$

The first term on the right of Eq. (1) is the dilute gas term, which is independent of density. The second is the excess thermal conductivity. The first two terms taken together are sometimes called the "background" thermal conductivity. The final term is the critical-point enhancement.

A quadratic polynomial in temperature is used to represent the dilute gas values:

$$\lambda_0(T) = A_1 + A_2 T + A_3 T^2 \quad (2)$$

Extrapolations to zero density for the three mixtures are given in Table II.

The excess thermal conductivity is usually represented with a power series in density, where each term in density is slightly dependent on temperature. For the present results a statistical analysis shows the terms in ρ and in ρ^3 to be significant, while the term in ρ^2 is negligible. Continuing in

Table II. Extrapolated Dilute Gas Thermal Conductivities, λ_0 , and Densities at Maximum C_p

Temperature (K)	Extrapolation			Density at maximum C_p (mol · L ⁻¹)
	Maximum density (mol · L ⁻¹)	Dilute gas thermal conductivity		
		W · m ⁻¹ · K ⁻¹	± 2σ	
70/30 mixture				
194.205	0.239	0.01566	0.00000	
203.697	0.394	0.01676	0.00028	
214.446	0.762	0.01856	0.00048	
223.108	0.938	0.01873	0.00018	
234.056	1.563	0.02017	0.00059	
242.269	2.713	0.02186	0.00058	
253.801	2.452	0.02254	0.00027	8.24
274.560	2.579	0.02558	0.00032	8.51
296.388	2.504	0.02878	0.00013	8.74
324.238	2.529	0.03247	0.00027	9.07
50/50 mixture				
231.565	0.672	0.01805	0.00012	
240.324	1.044	0.01939	0.00016	
250.199	1.478	0.02002	0.00026	
260.262	2.260	0.02143	0.00017	
265.141	2.998	0.02211	0.00015	
269.302	2.486	0.02243	0.00022	7.32
290.455	2.366	0.02517	0.00022	7.79
310.922	2.465	0.02803	0.00034	7.97
330.306	2.497	0.03091	0.00019	7.71
35/65 mixture				
227.701	0.544	0.01607	0.00014	
238.942	0.740	0.01729	0.00011	
251.417	0.993	0.01855	0.00014	
259.715	1.373	0.01960	0.00017	
269.358	2.010	0.02080	0.00019	
277.848	2.754	0.02198	0.00014	
283.225	2.517	0.02247	0.00016	7.01
304.469	2.526	0.02550	0.00011	7.41
324.791	2.478	0.02823	0.00010	7.68

odd powers of density we have included a term in ρ^5 . The functional form selected for the excess thermal conductivity is thus

$$\lambda_{\text{excess}}(\rho, T) = (B_1 + B_2 T)\rho + (B_3 + B_4 T)\rho^3 + B_5 \rho^5 \quad (3)$$

Subtracting Eqs. (2) and (3) from the experimental values we obtain remainders, which are plotted in Fig. 3. These remainders are seen to be nearly symmetric about a specific density, which we call ρ_{center} . Our analysis follows that used for the pure components. To represent the mixture enhancements shown in Fig. 3, we use the expression

$$\Delta\lambda_{\text{critical}}(\rho, T) = \text{AMPL} e^{-x^2} \quad (4)$$

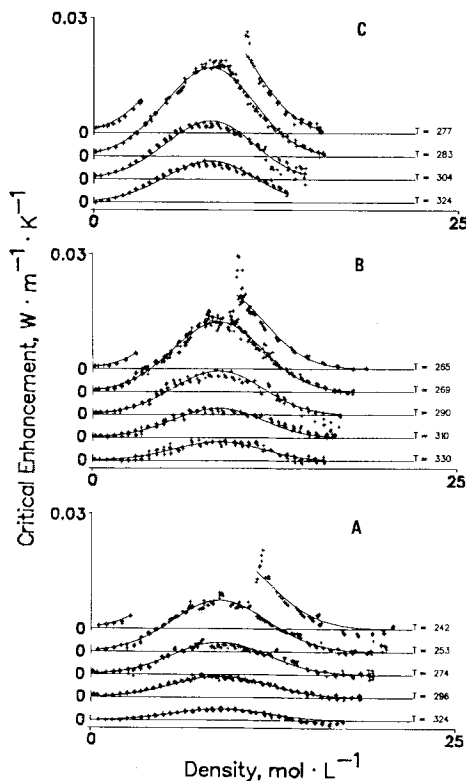


Fig. 3. The critical enhancement for methane-ethane mixtures along isotherms. Isotherms are separated by $0.006 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. (A) The 70/30 mixture; (B) the 50/50 mixture; (C) the 35/65 mixture.

The maximum value of $\Delta\lambda_c$ at $\rho = \rho_{\text{center}}$ is the amplitude (AMPL) of the function for the particular temperature under consideration. The amplitude is chosen to be a simple function of temperature as follows:

$$\text{AMPL} = C_1/(T + C_2) + C_3 + C_4 T$$

The variable x is a simple function of density chosen to be zero at the maximum value of the enhancement, i.e., at the density of ρ_{center} .

$$x = C(\rho - \rho_{\text{center}})$$

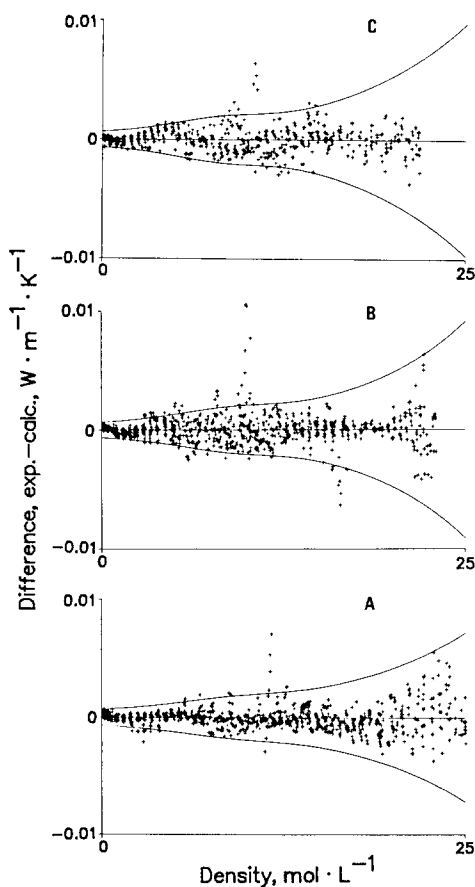


Fig. 4. Deviations of the experimental points from the individual correlations along isotherms. The lines represent deviations equivalent to 3% at the maxcondentherm. (A) The 70/30 mixture; (B) the 50/50 mixture; (C) the 35/65 mixture.

The small asymmetry seen in Fig. 3 is achieved by providing different coefficients above and below the centering density as follows: $x = C_5(\rho - \rho_{\text{center}})$ for $\rho < \rho_{\text{center}}$ and $x = C_6(\rho - \rho_{\text{center}})$ for $\rho > \rho_{\text{center}}$.

Equations (1)–(4) describe the thermal conductivity surfaces of these mixtures in the PVT range of the present measurements. Coefficients for Eqs. (2)–(4) are given in the data report [19].

Deviations between the experimental values and the calculated surfaces are shown for all mixtures in Fig. 4, where the lines represent deviations of 3% calculated for the maxcondentherm. The average percentage deviations for the surfaces are 0.9% for 70/30, 1.1% for 50/50, and 1.1% for 35/65. Systematic deviations for both the vapor and the liquid side of the surfaces at temperatures below the maxcondentherm remain and need to be resolved.

6. DISCUSSION

The precision (2σ) of the measurements has been established as 0.6% [9–11]. For the present results we estimate an overall uncertainty of 1.6%, in keeping with the results for methane [2] and ethane [3]. We are not aware of any other measurements of the thermal conductivity of methane-ethane mixtures. We have compared the present results with an extended corresponding states prediction by Ely and Hanley [1]. The differences between the model and the measurements run up to 20% at the lowest densities, up to 25% at densities of the maximum enhancement, and up to 6% for compressed liquid densities. We suggest that the model could be improved at the lowest densities by using a better correlation for the thermal conductivity of the reference fluid, methane, or by using propane as the reference fluid. The model can be improved further by including an estimated critical enhancement.

Our measurements show a definite enhancement at all temperatures down to the maxcondentherm, as well as in the vapor and compressed liquid at lower temperatures. The enhancement is particularly prominent near the mixture critical temperature. The enhancement in the single-phase fluid is quite similar in magnitude to that of the pure components but differs in the density, ρ_{center} (line 1, Fig. 1), at which the maximum enhancement occurs. It appears that ρ_{center} does not vary appreciably with temperature. We estimate the uncertainty in ρ_{center} to be about $\pm 0.3 \text{ mol} \cdot \text{L}^{-1}$ as shown in Table I. For the pure components the density of maximum enhancement is approximately ρ_c . In the mixtures ρ_{center} is somewhat less than the mixture critical density, shown as line 2 in Fig. 1. It is somewhat larger than the density at which the maximum in C_p occurs, shown as line 3 in Fig. 1.

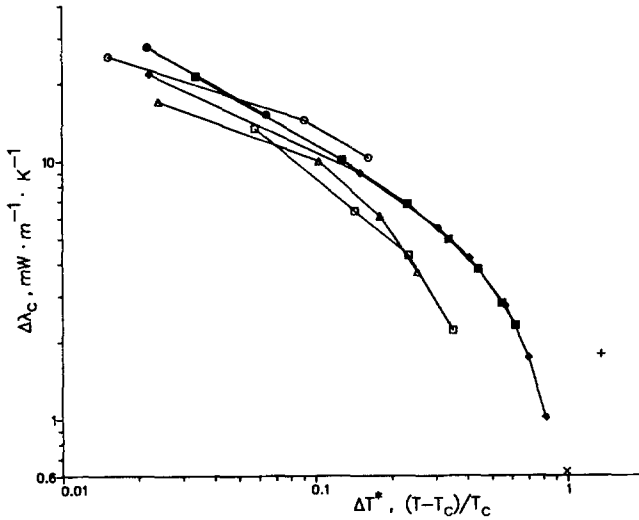


Fig. 5. The maximum enhancement, $\Delta\lambda_c$, at ρ_c for the pure components and at ρ_{center} for the mixtures vs the reduced temperature, ΔT^* .

Pure component	Mixture	Other fluid
(■) Methane [2]	(□) 70/30	(◆) Oxygen [12]
(●) Ethane [3]	(△) 50/50	(×) Argon [10, 11]
	(○) 35/65	(+) <i>n</i> -Hydrogen [14]

For a pure fluid modern theory [22] predicts an infinite thermal conductivity at the critical point and a large enhancement in the immediate vicinity [23]. For a mixture, however, theory suggests that an enhancement will not be present [1, 6]. A light-scattering experiment conducted near the liquid-vapor critical point of a methane-ethane mixture does not show any enhancement [7]. Our results show a definite enhancement [5], contradicting present theory and the light-scattering experiment but in strong agreement with the results on He-3-He-4 mixtures [8].

We plot the maximum $\Delta\lambda_c$ for both pure components and mixtures in Fig. 5. The initial slope for the mixtures in Fig. 5 is very close to a value of 0.56. We interpret Fig. 5 as evidence of a critical enhancement in mixtures.

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