Part I

PHASE EQUILIBRIA
MOLECULAR TRANSPORT
THERMODYNAMICS

Thermal Conductivity of Fluids. Ethane

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Measurements of the thermal conductivity of ethane were carried out at pressures up to 5000 p.s.i.a. in the temperature interval between 40° and 340° F. These measurements were made with a spherical conductivity cell and are only in fair agreement with data of other investigators which were obtained with entirely different types of instruments. The results are presented in tabular and graphical form. It appears that the residual thermal conductivity is a single-valued function of specific weight throughout the range of conditions covered by the investigation.

EXPERIMENTAL information concerning the thermal conductivity of ethane is limited except for data at atmospheric pressure. The measurements of Keyes (*4*), Leng and Comings (*6*), and Lenoir, Junk and Comings (*7*) have established the thermal conductivity at atmospheric pressure and at temperatures up to 160° F. with reasonable accuracy. Only a single provisional measurement reported by Keyes appears to be available at higher temperatures. The measurements of Lenoir, Junk and Comings have determined the effect of pressure upon the thermal conductivity of ethane at pressures up to approximately 2900 p.s.i.a. and at three temperatures between 107.5° and 153° F., Leng and Comings reported data at 154° F. at pressures up to about 3800 p.s.i.a., and Keyes carried out measurements at 125.4° F. up to a pressure of about 580 p.s.i.a. However, these data do not establish the thermal conductivity with the certainty nor perhaps with the accuracy requisite for industrial purposes, particularly at the higher temperatures.

The application of statistical mechanics to the prediction of the transport properties of the paraffin hydrocarbons has not progressed sufficiently to predict the thermal conductivity with satisfactory accuracy for engineering requirements (*8*). For this reason, experimental measurements of the thermal conductivity of ethane were carried out at pressures up to 5000 p.s.i.a. in the temperature interval between 40° and 340° F. These measurements were made in both the gas and liquid phases at temperatures below the critical temperature of ethane. The thermal conductivity in the critical region was not investigated in detail.

EQUIPMENT AND METHODS

A spherical conductivity cell was employed for these investigations (*11, 12, 13*). In principle, this equipment involved a gold-plated sphere approximately 3.5 inches in diameter located within a slightly larger spherical cavity, yielding a radial transport path of approximately 0.020 inch between the inner sphere and outer shell. The inner sphere was provided with a carefully designed electrical heater that yielded nearly equal flux at all points around its surface (*12*). Thermocouples were used to determine the temperature of the inner spherical surface and of the outer shell. Appropriate corrections have been made for the location of the thermocouples within the stainless steel body of the sphere and shell (*13*). Dimensions of these spherical cavities and the sphere were determined by direct measurement and were checked by measurements upon the thermal conductivity of helium and argon at atmospheric pressure (*2, 3, 5*), where the values are known with high accuracy.

Measurements were carried out for the most part at four different levels of thermal flux. A period of approximately four hours was required to achieve steady state at each thermal flux. Values of $(\dot{q}_m/d\theta)/\Delta t_m$ which are directly related to the apparent thermal conductivity were calculated for each thermocouple at each flux level. Individual corrections for the location of the thermocouples below the surface of the sphere and of the shell were applied after extrapolation to zero flux (*13*).

The measurements, made at different thermal fluxes, were extrapolated to zero thermal flux, assuming a linear relationship between the apparent thermal conductivity and the thermal flux. Least squares techniques were employed in fitting the values obtained from each of the six thermocouples, and an area-weighted average of the values at zero thermal flux was taken from each thermocouple to yield the reported results.

There was some variation in the apparent thermal conductivity with flux as a result of the change in the average temperature of the phase, together with some possible local convection. The onset of gross convection within the spherical transport path could be easily detected by a rapid increase in the apparent thermal conductivity with an increase in the radial temperature gradient. However, measurements were not made under such conditions that gross convection was experienced in the transport path, except in the critical region.

To insure that behavior of the thermal conductivity equipment did not change with time, measurements of the thermal conductivity of helium at pressures of approximately 18 p.s.i.a. and at a temperature of 100° F. were carried out at three different times during the measurements on ethane. The variation in behavior of the instrument from the beginning to the end of the experimental program was not more than 0.5%. Some difficulty in obtaining reproducible measurements apparently resulted from trace quantities of ethane remaining, even after repeated evacuations, to contaminate the helium. The values obtained of 0.0923 and 0.0916 B.t.u./(hr.)(ft.)(° F.) are in good agreement with the critically chosen value of 0.0912 B.t.u./(hr.)(ft.)(° F.) reported by Hilsenrath and Touloukian (*3*).

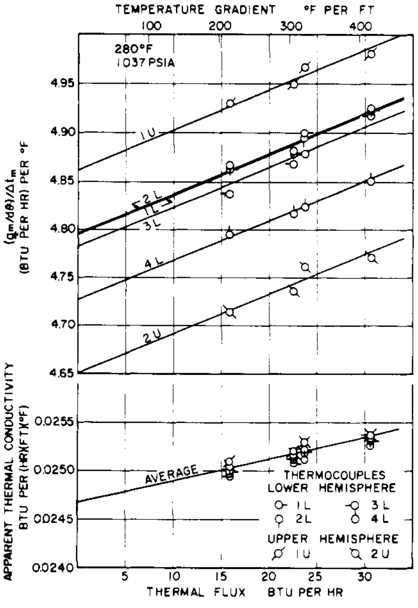

Figure 1. Effect of thermal flux upon apparent thermal conductivity

Table I. Experimental Results

Pressure P.S.I.A.	Thermal Conductivity B.t.u./(hr.) (ft.)(° F.)	Pressure P.S.I.A.	Thermal Conductivity B.t.u./(hr.) (ft.)(° F.)
	40° F.		280° F.
18	0.010971	18	0.021269
219	0.011849	425	0.022262
329	0.013097	1037	0.024660
479	0.049778	3000	0.037558
1006	0.053174	5097	0.046540
2962	0.064962	σ^a	< 0.000030
4805	0.070655		
σ^a	0.000132		
			340° F.
		18	0.023823
	100° F.	422	0.024769
		957	0.026380
17	0.013208	2875	0.035834
410	0.015319	3000	0.036406
725	(0.025239)[b]	4725	0.043853
1005	(0.038334)[b]	σ^a	< 0.000030
1950	0.048221		
2998	0.053520		
5042	0.061620		
σ^a	0.001268		
	160° F.		
17	0.015836		
417	0.017274		
976	(0.023155)[b]		
2041	0.039572		
3012	0.046045		
5310	0.055241		
σ^a	0.000161		

[a] Standard error of estimate $\sigma = \left[\left\{ \sum_{1}^{N} (k_e - k_s)^2 \right\} / N \right]^{1/2}$

[b] Values in parentheses not used in smoothing because of lower accuracy as a result of onset of convection at the higher fluxes.

MATERIAL

The ethane used for this investigation was obtained from the Phillips Petroleum Corporation as research grade material with a reported purity of 0.9993 mole fraction ethane. A spectrographic analysis confirmed this limit of impurities. Furthermore, it was found that the vapor pressure of this material at a temperature of 40° F. did not change more than 1.5 p.s.i. with an increase in quality from 0.1 to 0.9. From the result of these measurements, it is believed that the ethane employed did not contain more than 0.0007 mole fraction of material other than ethane. The principal impurity was probably ethene.

EXPERIMENTAL RESULTS

Figure 1 shows the effect of thermal flux upon the quantity $(q_m/d\theta)/\Delta t_m$ along with the apparent thermal conductivity of ethane for each of the six thermocouples located at different positions around the spherical surface. In each case the values of the apparent thermal conductivity have been individually corrected for their location in the core and shell. The identification refers to the four thermocouples in the lower hemisphere and the two active thermocouples in the upper hemisphere. It is apparent that these values extrapolated to zero flux yield a probable value of the thermal conductivity of ethane of 0.02466 B.t.u./(hr.) (ft.) (° F.) and a standard error of estimate of 0.00005 B.t.u./(hr.)(ft.)(° F.) among the 24 values reported from the curve drawn through the data. The straight lines in Figure 1 were fitted to the points by least squares methods.

The behavior in Figure 1 is typical of the results, except at pressures above 1500 p.s.i.a. where some elastic deformation of the spherical shell was experienced with an attending small eccentricity of the inner sphere within

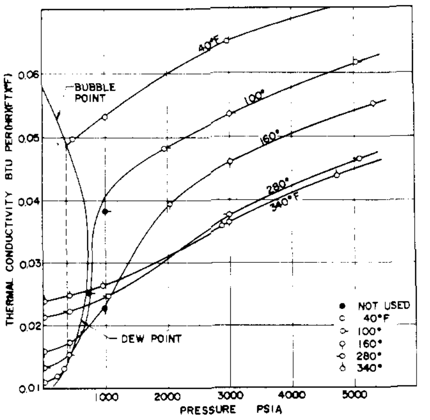

Figure 2. Influence of pressure upon thermal conductivity of ethane

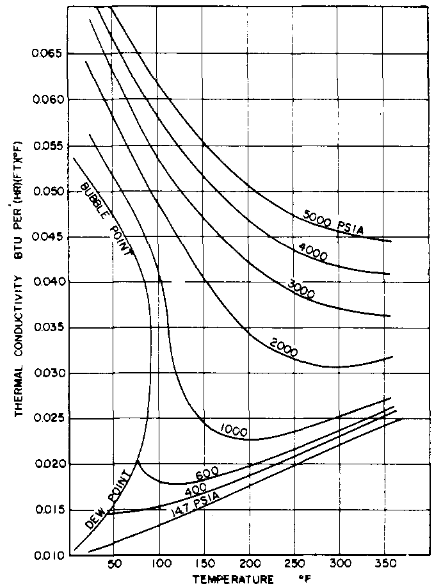

Figure 3. Influence of temperature upon thermal conductivity of ethane

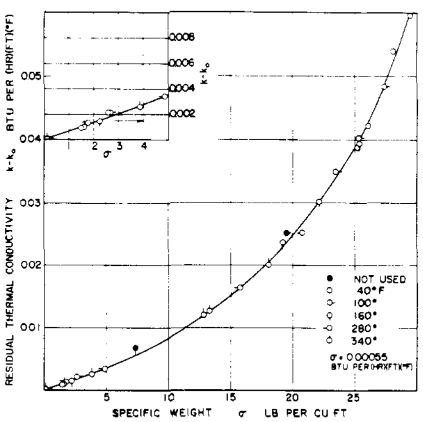

Figure 4. Residual thermal conductivity as a function of specific weight for ethane

the spherical cavity. An analysis of the situation indicated that deviation in measurements from the upper and from the lower hemispheres may be taken into account by a spatial average of the local values obtained. Because of this small eccentricity at the higher pressure, the standard deviation of the measurements when the data in both hemispheres were included was somewhat larger than that shown in Figure 1. The difference in behavior between the upper and lower hemispheres did not introduce more than 0.1% added uncertainty in the experimental results.

In Table I are reported experimental values of the thermal conductivity of ethane as determined by extrapolations of the apparent values to the actual thermal conductivity at zero flux. The standard error of estimate is included for the experimental measurements at each state.

The influence of pressure on the thermal conductivity of ethane is set forth in Figure 2. Each experimental point represents the average of the behavior of the six thermocouples and is the value reported in Table I for the pressure and temperature in question. Each of these points in the figure nearly always represents 24 semi-independent measurements. The solid points are values not used in smoothing because of lower accuracy as a result of the onset of convection at the higher fluxes. The standard error of estimate depicted in Table I is taken from the straight lines of the upper part of Figure 1 used to extrapolate to zero flux. Table II records the smooth values of the thermal conductivity of ethane for even values of pressure and temperature. The standard error of estimate of the experimental measurements from the smooth values was 0.00007 B.t.u./(hr.)(ft.)(° F.).

Figure 3 portrays the influence of temperature upon the thermal conductivity of ethane, as established from the current investigation. The rapid change in the thermal conductivity with change in state in the critical region was in accordance with the expected behavior of this transport property. Insufficient data were obtained in the critical region to permit even an estimate of the thermal conductivity in the critical state.

Abas-Zade (*1*) predicted that the residual thermal conductivity would be a single-valued function of specific weight. Owens and Thodos (*9*) and Schaefer and Thodos (*14*) confirmed this prediction for a number of gases. The "residual thermal conductivity" is defined as the difference between thermal conductivity at a given pressure and at attenuation for the same temperature and is often known as the "thermal conductivity excess."

Figure 4 illustrates the influence of the specific weight of ethane upon the residual thermal conductivity of this material. An earlier study of the volumetric behavior of ethane (*10*) was employed to determine specific weight as a function of pressure and temperature. The behavior near atmospheric pressure is shown on an enlarged scale in an insert to this figure. The solid points in the figure are values not used in smoothing, as in Figure 2. The standard error of estimate of the experimental data for the six temperatures investigated throughout the range of specific weights indicated from the single curve was 0.00055 B.t.u./(hr.)(ft.)(° F.). There was no irregularity in the vicinity of the critical state, confirming the concept that the thermal conductivity may be expressed as the sum of one single-valued function of temperature at attenuation and a second single-valued function of specific weight which is independent of temperature. The standard error of

Table II. Thermal Conductivity of Ethane

Pressure P.S.I.A.	Temperature ° F. 40	100	160	280	340
	(385)[a]				
Dew Point	0.01425				
Bubble Point	0.04880				
14.7	0.01097[b]	0.01320	0.01583	0.02123	0.02379
200	0.01176	0.01390	0.01629	0.02162	0.02421
400	0.04895	0.01523	0.01716	0.02216	0.02470
600	0.05039	0.01804	0.01854	0.02283	0.02523
800	0.05191	0.03460	0.02064	0.02360	0.02584
1000	0.05340	0.04078	0.02356	0.02448	0.02652
1500	0.05684	0.04558	0.03250	0.02730	0.02862
2000	0.06000	0.04851	0.03910	0.03078	0.03111
2500	0.06282	0.05110	0.04310	0.03437	0.03377
3000	0.06517	0.05352	0.04599	0.03756	0.03641
3500	0.06690	0.05575	0.04844	0.04010	0.03888
4000	0.06845	0.05774	0.05060	0.04228	0.04107
4500	0.06987	0.05961	0.05249	0.04426	0.04301
5000	0.07118	0.06149	0.05422	0.04618	0.04482

[a] Vapor pressure of ethane expressed in pounds per square inch.
[b] Thermal conductivity expressed in B.t.u./(hr.)(ft.)(° F.).

estimate was only twice the estimated experimental uncertainty of these measurements. It is therefore believed that for many industrial applications the residual thermal conductivity of ethane may be considered a single-valued function of specific weight.

Figure 5 shows the thermal conductivity of ethane as a function of temperature for atmospheric pressure. The smooth curve is that resulting from the current investigation, and the standard error of estimate of the experimental values from this smooth curve was 0.00003 B.t.u./(hr.)(ft.)(° F.). In addition, the measurements of Keyes (*4*), Leng and Comings (*6*), and Lenoir, Junk and Comings (*7*) have been included. The standard error of estimate of these data from the smooth curve was 0.0014 B.t.u./(hr.)(ft.)(° F.), corresponding to a relative error of 1.8% for the measurements of Leng and Comings and of 2.4% for the measurements of Lenoir, Junk and Comings. The provisional value which Keyes reported at a temperature of 480° F. appeared to fall higher than the current data and was not included in the above standard error of estimate. Agreement of the current data with the earlier measurements at atmospheric pressure is considered to be satisfactory.

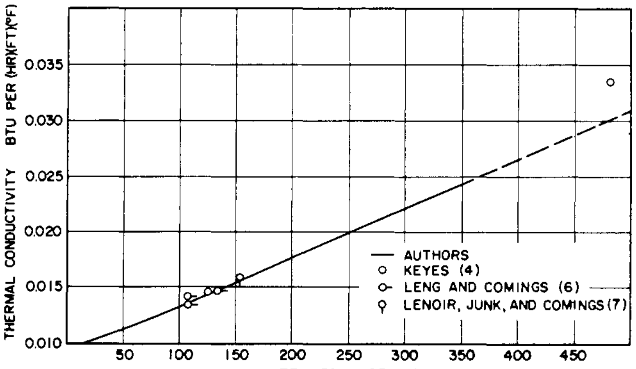

Figure 5. Thermal conductivity of ethane at atmospheric pressure

Figure 6 presents a comparison of the more recent measurements of Lenoir, Junk and Comings, of Leng and Comings, and of Keyes at elevated pressures with the current data. In this instance the smooth curves represent values of the thermal conductivity for the indicated temperatures as interpolated from the current investigation. The standard error of estimate of the experimental data of Lenoir, Junk and Comings at three temperatures from these smooth curves was 0.00255 B.t.u./(hr.(ft.)(° F.), corresponding to a deviation of approximately 6.7% between the two sets of measurements when based on an average value of the thermal conductivity of 0.03785 B.t.u./(hr.)(ft.)(° F.). The data of Keyes at 125.4° F. yielded a standard error of estimate of 0.00072, and the data of Leng and Comings at 154° F. showed a standard error of estimate of 0.00243 B.t.u./(hr.)(ft.)(° F.).

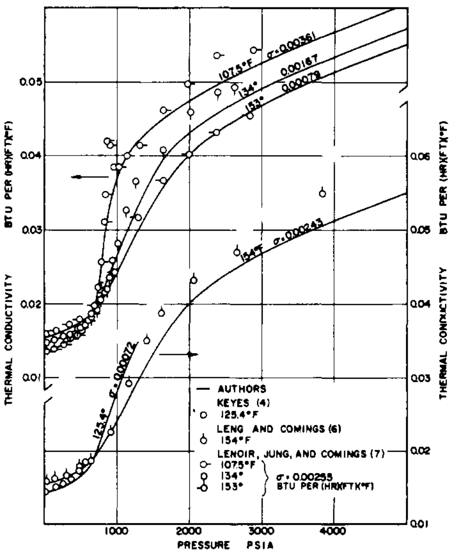

Figure 6. Comparison of results at elevated pressures with data of other investigators

A second method of comparison of available experimental data is shown in Figure 7. In this figure the residual thermal conductivity is again presented as a function of the specific weight of the fluid. The smooth curve corresponds to the present data and is the same as that depicted in Figure 3. The experimental points are based upon the measurements of Keyes (*4*), Leng and Comings (*6*), and Lenoir, Junk and Comings (*7*). These experimental data yielded standard errors of estimate of 0.00252, 0.00446, and 0.00072 B.t.u./(hr.)(ft.)(° F.), respectively. The above standard errors are somewhat larger than the values obtained for the present data of 0.00055 B.t.u./(hr.)(ft.)(° F.) as shown in Figure 4.

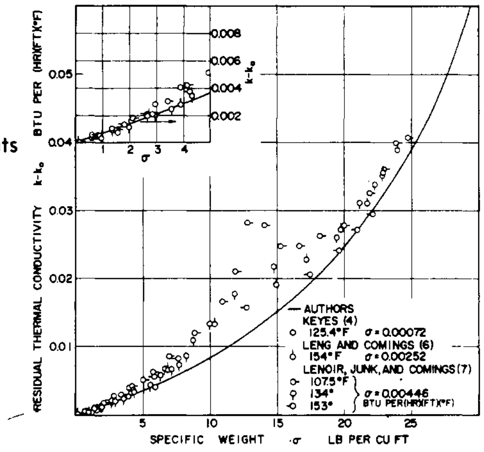

Figure 7. Comparison of measurements of other investigators on the basis of residual thermal conductivity

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NOMENCLATURE

d = differential operator
k = thermal conductivity, B.t.u./(hr.)(ft.)(° F.)
N = number of points
$q_m/d\theta$ = measured rate of energy addition, B.t.u./hr.
Δt_m = measured temperature difference, ° F.
θ = time, hr.
σ = specific weight, lb./cu. ft.
σ = standard error of estimate

Subscripts

e = experimental
o = attenuation
s = smooth

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Improved Formulas for Heat Transfer Calculation in Multipass Exchangers

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Problem of 1–2 exchangers has been re-studied, assuming that overall coefficient of heat transfer varies as a linear function of temperature. Graphs similar to those of Ten Broeck have been drawn, taking into consideration this variation. Differential heat balance and rate equations were changed to appropriate dimensionless form and solved by an iterative procedure using a digital computer. A solution for 2–4 exchangers using the 1–2 charts also discussed.

IN CONVENTIONAL analysis of multipass exchangers, the heat transfer area is calculated from the equation:

$$Q = UAF_T\,(LMTD) \tag{1}$$

Solutions of this equation depend upon whether U is assumed constant or variable. Formulas for the *LMTD* correction factor F_T were derived by Bowman, Mueller, and Nagle (*1*) under the assumption of a constant over-all coefficient U along the exchanger. Values of F_T for multipass exchangers are conveniently presented in form of charts (*4*, *5*), as a function of dimensionless parameters dependent on terminal temperatures.

Assuming linear variation of U with temperature, Colburn (*2*) derived the following expression for the heat exchanged in a countercurrent 1-1 exchanger:

$$\frac{Q}{A} = \frac{U_1\Delta T_2 - U_2\Delta T_1}{\ln(U_1\Delta T_2/U_2\Delta T_1)} \tag{2}$$

Equation 2 involves a "mixed mean" of the coefficient, U, and the temperature difference, ΔT. Colburn's procedure is valid only when $F_T = 1$.

For 1-2 exchangers with variable coefficients of heat transfer, Bowman, Mueller, and Nagle (*1*) combined their results for a 1-2 exchanger involving constant U with those of Colburn for a 1-1 exchanger where U was assumed to be linear with temperature. The resulting equation took the form:

$$Q = AF_T\,\frac{U_1\Delta T_2 - U_2\Delta T_1}{\ln(U_1\Delta T_2/U_2\Delta T_1)} \tag{3}$$

Although of great practical importance and fair accuracy, Equation 3 involves the inconsistency of calculating F_T on the basis of constant U and the mixed mean on the basis of variable U. This procedure will be referred to as the "F_T method" in the remainder of this paper.

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