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The Thermal Conductivity of Oxygen*

Hans M. Roder†

National Bureau of Standards, Boulder, CO 80303

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The paper presents new experimental measurements of the thermal conductivity of oxygen for thirteen isotherms at temperatures from 78 to 310 K with pressures to 70 MPa and densities from 0 to 40 mol/L. The measurements were made with a transient hot wire apparatus and they cover a wide range of physical states including the dilute gas, the moderately dense gas, the near critical region, the compressed liquid states, and the vapor at temperatures below the critical temperature. The thermal conductivity surface is represented with an equation that is based in part on an existing correlation of the dilute gas. The data are compared with the experimental measurements of others through the new correlation. The new measurements show that the critical enhancement extends to quite high temperatures, about 300 K. The precision (2σ) of the oxygen measurements is between 0.5 and 0.8 percent for wire temperature transients of 4 to 5 K, while the accuracy is estimated to be 1.5 percent.

Key words: Hot wire; oxygen; pressure; temperature; thermal conductivity; transient.

1. Introduction

Thermal conductivity values are necessary whenever a heat transfer problem is to be evaluated. In addition, thermal conductivity is a property of fundamental interest in developing the theory of fluids. Accurate measurements of thermal conductivity are of considerable difficulty. Methods and geometries abound, each with its adherents and its inherent drawbacks. The steady state hot wire experiment is one of the older, well established methods. The transient hot wire method used here has come into its own only with recent advances in digital electronics. The evolution of the modern transient hot wire experiment is traced in an earlier paper [1]¹ where a complete description of the apparatus is given.

A search of the literature reveals a relative abundance of papers on the thermal conductivity of oxygen [2]. However, measurements that cover a wide range in both temperature and density or pressure are rare [3,4], and as we shall see, differ considerably. It is, therefore, not surprising that efforts to correlate the thermal conductivity surface of oxygen [5] are beset with difficulties, and that the results are of doubtful accuracy. In this paper,

new experimental measurements are presented that cover a large range in density for every isotherm, i.e., 0 to 19 mol/L for 310 K and 0 to 40 mol/L for 78 K. The new results and a theoretical calculation for the dilute gas [6,7] are used to fashion a new correlation for the thermal conductivity surface of oxygen between 78 and 310 K for pressures up to 70 MPa. The new surface reveals that the critical enhancement extends out to about 300 K.

2. Method

A hot wire system normally involves a vertical, cylindrical symmetry where the wire serves both as heating element and as thermometer. Almost without exception platinum is the wire of choice. The mathematical model that one attempts to approximate is that of an infinite line source of heat suspended vertically in an infinite medium. The method is labelled transient because the power is applied abruptly and the measurement is of short duration. The working equation is based on a specific solution of Fourier's law and can be found in standard texts (see for example reference [8], page 261).

$$T(t) - T_{\text{ref}} = \Delta T = \frac{q}{4\pi\lambda} \ln \left(\frac{4K}{a^2C} \right) t \quad (1)$$

Where $T(t)$ is the temperature of the wire at time t ;

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†Thermophysical Properties Division, National Engineering Laboratory.

¹Figures in brackets indicate literature references at the end of this paper.

- T_{ref} is the reference temperature, the temperature of the cell;
- q is the applied power;
- λ is the thermal conductivity of the fluid, a function of both temperature and density;
- K is the thermal diffusivity of the fluid, i.e., $K = \lambda/\rho C_p$. K is normally taken at the temperature T_{ref} and is nearly constant since the fluid properties do not change drastically with a small increase in temperature;
- a is the radius of the wire; and
- $\ln C = \gamma$, where γ is Euler's constant, $\gamma = 0.5772\dots$

The relation given by eq (1) implies a straight line for a plot of ΔT versus $\ln(t)$. In practice systematic deviations occur at both short and long times. However, for each experimental measurement there exists a range of times over which eq (1) is valid, that is the relation between ΔT and $\ln(t)$ is linear. This range of validity is determined from 250 measured ΔT - t pairs by selecting a beginning time t_1 and an ending time t_2 . The slope of the ΔT vs $\ln(t)$ relation is obtained over the valid range, i.e., between times t_1 and t_2 , and using the applied power the thermal conductivity is calculated from eq (1). The temperature assigned to the measurement of λ is given by

$$T = T_{ref} + \frac{1}{2} [\Delta T(t_1) + \Delta T(t_2)] \quad (2)$$

The density assigned to the measurement of λ is taken from an equation of state using an experimentally measured pressure and the temperature assigned above. The experimentally determined temperature rise of the wire is ΔT_w . A number of corrections account for the departure of the real instrument from the ideal model:

$$\Delta T = \Delta T_w - \sum \delta T_i \quad (3)$$

These corrections δT_i have been fully described elsewhere [9]; the most important at lower times is δT_1 , the effect of the finite heat capacity of the wire.

3. Apparatus

A detailed description of the apparatus, of the experimental procedure, of the wire calibration, of the data reduction, and of the apparatus performance are given in the earlier paper [1]. A brief description of the system follows.

We use a long or primary hot wire approximately 10 cm in length. Its resistance varies from about $20\ \Omega$ at 76 K to $90\ \Omega$ at 298 K. A short or compensating wire is approximately 5 cm in length and its resistance varies from 10 to $45\ \Omega$. Both wires are mounted in a Wheatstone

bridge to provide end effect compensation. Voltages are measured directly with a fast response digital voltmeter (DVM). The DVM is controlled by a minicomputer, which also handles the switching of the power and the logging of the data. The measurement of thermal conductivity for a single point is accomplished by balancing the bridge as close to null as is practical at the cell or reference temperature. The lead resistances, the hot wire resistances, and the ballast resistors are read first with a very small applied voltage. Then the power supply is set to the desired power and the voltage developed across the bridge as a function of time is read and stored. The basic data form a set of 250 voltage readings taken at 3 ms intervals. The other variables measured include the applied power, the cell temperature, and the pressure. All of the pertinent data are written by the minicomputer onto a magnetic tape for subsequent evaluation.

For each isotherm, the data on the magnetic tape are processed on a large computer. In addition to the reduction of the raw data, i.e., the conversion of bridge offset voltages to resistance changes and then to temperature changes, the large computer also handles the wire calibration data and evaluates the best straight line for the ΔT - $\ln(t)$ data and determines the thermal conductivity.

The samples used are research grade oxygen stated by the supplier to be a minimum of 99.994 mol percent oxygen. The impurities listed were 17 ppm hydrocarbons, 3 ppm argon, 20 ppm nitrogen, 16 ppm krypton, and 3 ppm water. The samples were run through molecular sieve and through a 65 micron line filter when routed through the compressor. We used a small diaphragm compressor as a pressure intensifier, and observed normal precautions for high pressure and high vacuum.

One of the additional design considerations for the cell was liquid oxygen safety since the interior of the cell is exposed to very high pressure 70 MPa (10,000 psi) liquid. The materials directly exposed to liquid oxygen have been limited to beryllium copper, copper, stainless steel, silver, teflon, and a polyimide (kapton) all of which have been found to be "oxygen compatible" [10]. Cleaning procedures for cell, wire supports, capillary and sample handling system were extensive [11].

Several changes from the apparatus paper [1] were incorporated into the data reduction process; one involves a digital filter applied to the voltages measured across the bridge, the second changes the deviation plot of experimental temperature rises from the calculated straight line from logarithmic to linear.

The basic data in the experiment are the voltages measured across the bridge which, when plotted against time, form a logarithmic curve as shown in figure 7 of the apparatus paper [1]. Noise levels in the readings were

ascribed to ac pickup. For some of the experimental points the noise level can be reduced considerably by employing a digital filtering process. Briefly, the raw data are fitted to a logarithmic curve. The remainder forms the noise spectrum which was shown to correspond to a frequency of 60 cycles with harmonics at 120 and 240 cycles. The periodicity of the noise spectrum

corresponds to 50 measurements exactly. For those experimental points where the voltages follow a logarithmic curve over all of the measurement time, four or even five cycles of the noise spectrum can be identified uniquely, averaged, and subtracted from the input. Figure 1 illustrates the effect of the digital filtering technique for point 22016. Shown are the plot of ΔT vs

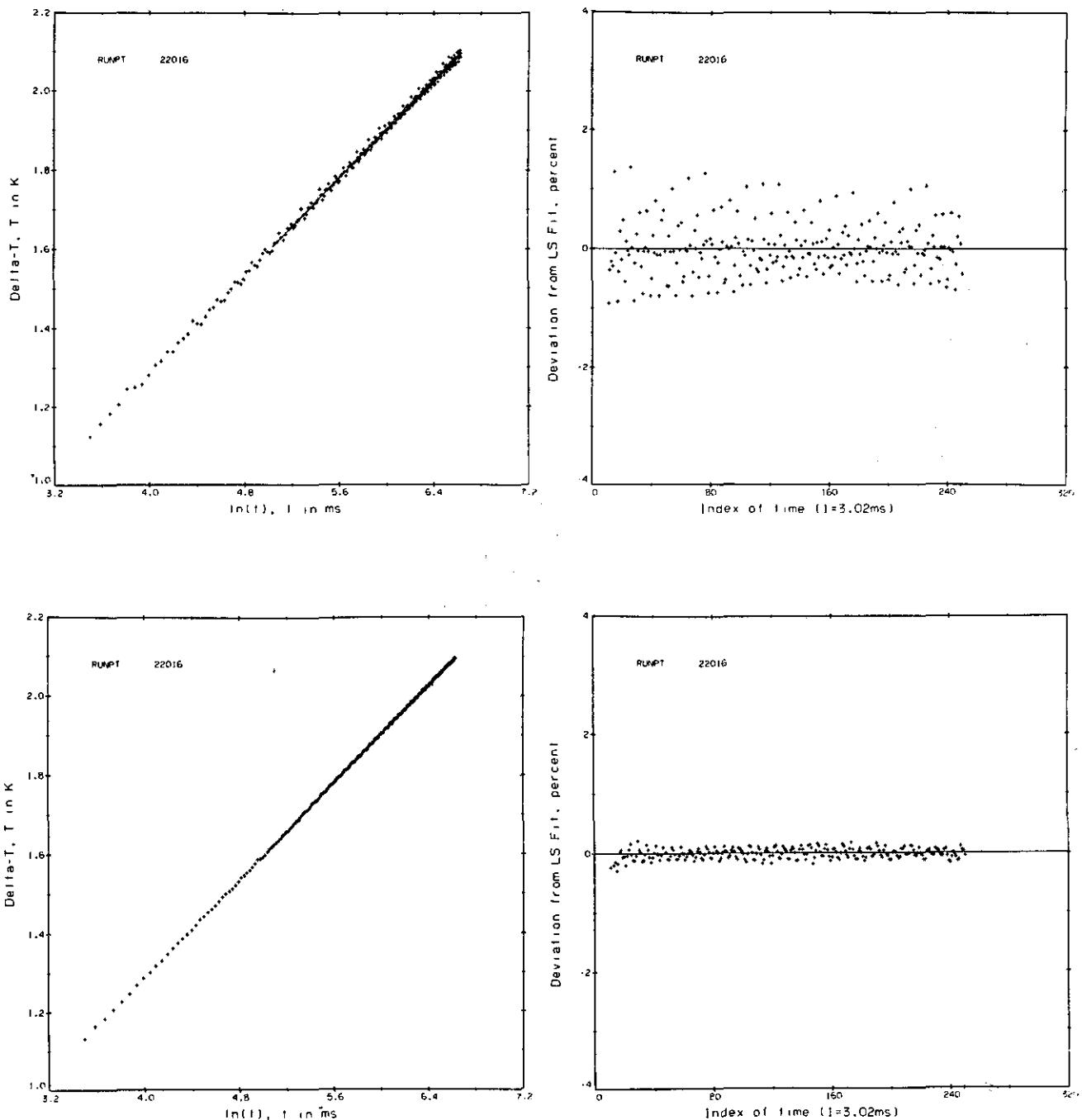


FIGURE 1. Effect of the digital filtering technique for point 22016.

$\ln(t)$ and the deviations of the experimental temperatures rises from the straight line without, and then with filtering.

Application of the digital filtering results only in a reduction of the least squares straight line regression error, STAT. The thermal conductivity values change very little, in rare instances as much as 0.2 percent. Not all of the experimental points are amenable to the filtering process because several cycles of the noise spectrum are required to identify it uniquely. For measurements to be made in the future on other fluids we plan to incorporate an electronic filter into the apparatus.

4. Results

To define the thermal conductivity surface of oxygen a grand total of 1628 points were measured. Of these 162 points involved the alignment of the cell, and 340 points were rejected for experimental reasons such as insufficient experimental time of measurement, inadequate equilibrium, experimental density too low, $\Delta T \cdot \ln(t)$ relation not linear enough, etc. The remaining 1126 valid points are distributed among 13 isotherms as shown in table 1. The portion of the PVT surface covered by the

TABLE 1. Summary table of oxygen thermal conductivity measurements.

Nominal Temperature	Number of Points
77.K	35.
99.	28.
121.	102.
145.	101.
159.	164.
178.	92.
202.	152.
218.	68.
242.	143.
263.	60.
282.	63.
298.	53.
310.	65.

measurements is shown in density-temperature coordinates in figure 2. The fluid states measured in this experiment include the dilute gas, dense gas, the near critical states, vapor at temperatures below critical, compressed liquid states, and metastable liquid states at densities below saturation. On each isotherm measurements were made at a number of different pressure levels. At the low temperatures the spacing was about 7 MPa (1000 psia) in pressure. At higher temperatures the spacing in pressure levels was arranged to give a spacing in density of about 1 mol/L. At each pressure level several different power levels were used, resulting in slightly different experimental temperatures and densities. The

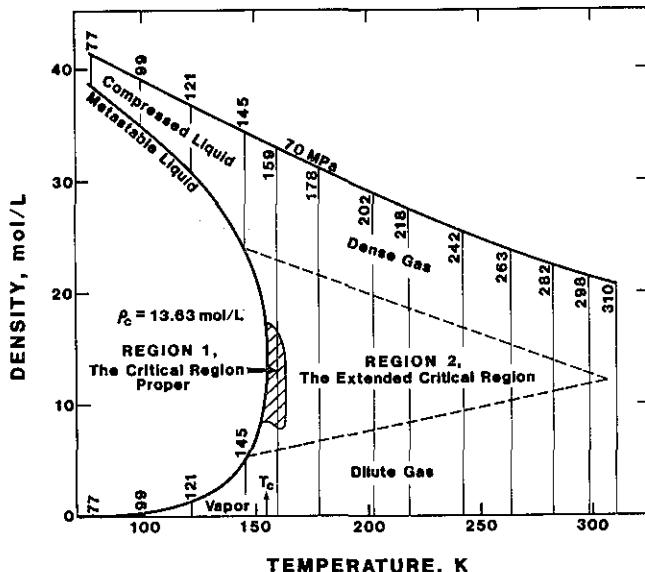


FIGURE 2. Region of the PVT surface covered by the present thermal conductivity measurements.

pressure, temperature, and applied power are measured directly, the thermal conductivity and the associated regression error are obtained through the data reduction program, while the density is calculated from an equation of state [7] using the measured pressure and temperature. Each point is adjusted to the nominal isotherm temperature by a slight shift in temperature using the correlating equation given in the next section. The deviation of the points adjusted to isotherms from the correlation is calculated at the same time. All of the experimental and adjusted data are assembled and presented in table 2.² An overview of the measurements is given in figure 3 where the adjusted data and the isotherms calculated from the correlation are plotted.

The apparatus is not specifically designed to measure thermal conductivity in the critical region. Nevertheless, measurements were made as close to critical as is possible with the present system bearing in mind that the measurements must be free of convection. The measurements closest to critical temperature and critical density are most likely to experience convection. We will, therefore, look at the 159 K isotherm where the actual temperatures range between 158.229 and 162.531 K, i.e., between 1.02 and 1.05 T_c . On this isotherm densities between 5 and 20 mol/L were difficult to execute because rather large changes in density occur near the wire after the power is turned on and the wire starts heating. In extreme cases the change in density was as much as 1 mol/L even though the applied power was reduced considerably resulting in very small temperature

²Table 2 is displayed at the end of this paper, on pages 296-310.

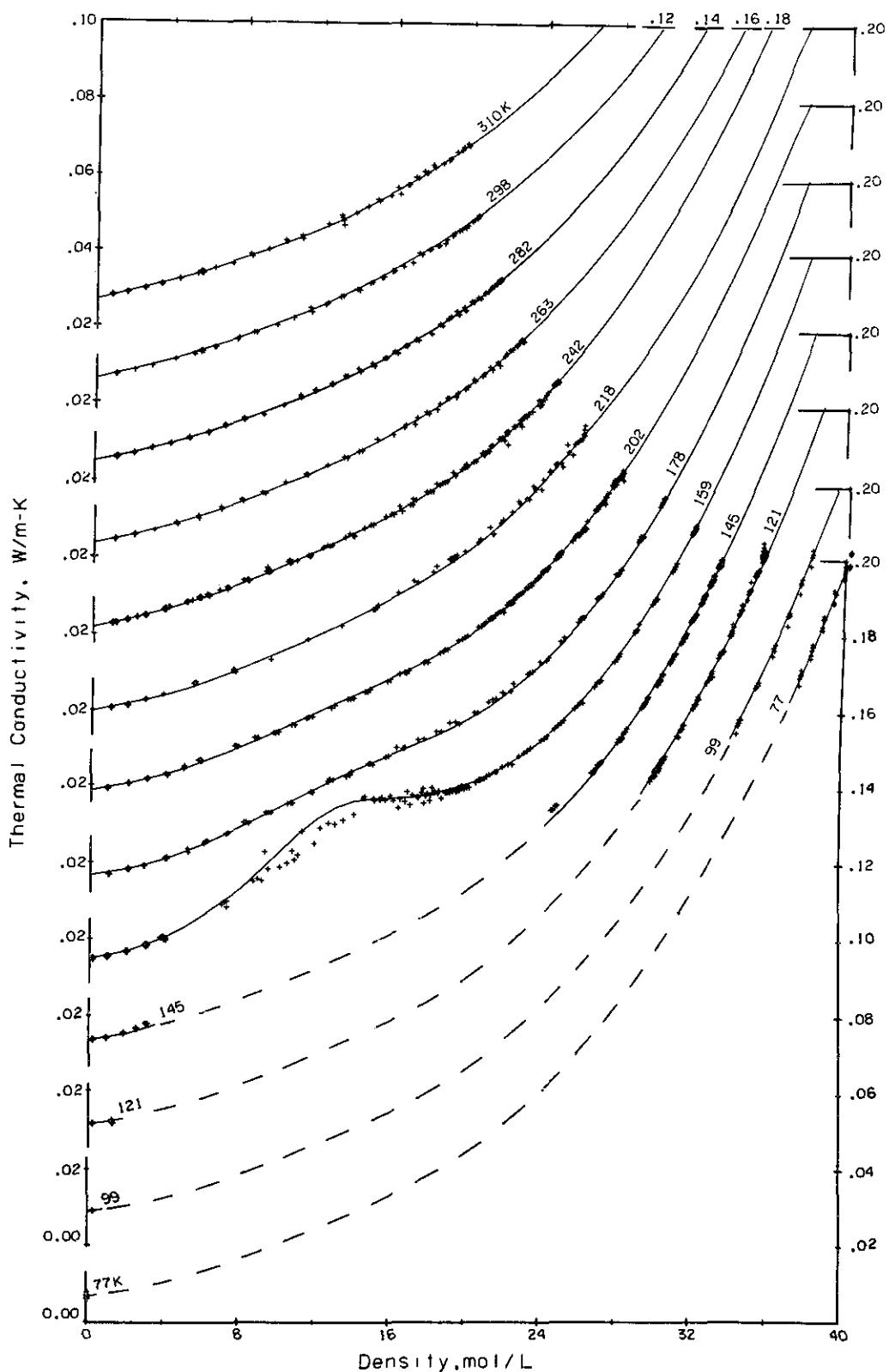


FIGURE 3. Overview of the thermal conductivity measurements on oxygen. Each isotherm is on a separate scale. The scales are offset from each other by 0.02 W/m·K for better visibility.

rises. In addition, the data analysis had to be restricted to shorter times than normal resulting in an increase in the regression statistic, STAT. For these and all measurements the absence of convection is verified by replicate measurements at the same cell temperature and cell pressure with different power levels. This procedure changes the temperature rise in the wire and hence the temperature rise in the gas near the wire. The technique is quite analogous to changing the ΔT for a steady state parallel plate system. Extensive comparisons of the effect of varying the power level for the transient hot wire system are given for N₂ and He in the apparatus paper (figures 12 and 15 in ref. [1]) and for argon in table 2 of ref. [12]. As an example for the present measurements on oxygen consider points 21193, 21194, and 21195 in table 2 at a nominal density of 1.26 mol/L, or 0.92 ρ_c . The power level varies by a factor of 2, and experimental temperature and experimental density are performed somewhat different; however, the measured thermal conductivities differ from each other by no more than 1.8 percent as compared through the correlation. For densities between 4 and 7 mol/L on the 159 K isotherm a convection contribution is inferred from the ΔT vs $\ln(t)$ plots, therefore, these measurements were discarded.

A second argument which implies the absence of convection in the present measurements is to compare them to the best current theoretical predictions. This is done for the 159 K isotherm in figure 7 which will be discussed in the next section. The agreement between predicted and experimental values is found to be within experimental error, the experiment generally being lower. We may thus conclude that convection is absent.

5. Correlation of the Thermal Conductivity Surface

It is generally accepted that the thermal conductivity should be correlated in terms of density and temperature [5] rather than temperature and pressure because over a wide range of experimental conditions the behavior of thermal conductivity is dominated by its density dependence. This preferred technique requires an equation of state [7] to translate measured pressures into equivalent densities. The dependence of thermal conductivity on temperature and density is normally expressed as

$$\lambda(\rho, T) = \lambda_o(T) + \lambda_{\text{excess}}(\rho, T) + \Delta\lambda_{\text{critical}}(\rho, T) \quad (4)$$

The first term on the right of eq (4) 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. An example showing the size and shape of each contributing term is given in figure 4 for the 159 K isotherm.

5.1 Term 1, the Dilute Gas

Values for the dilute gas at zero density have been calculated by Hanley and Ely [6] using kinetic theory equations and an m-6-8 model potential. These results were presented as a curve fit by McCarty [7] in connection with an equation of state for oxygen. The exact expression is

$$\lambda_o(T) = [A_1 T^{-1} + A_2 T^{-2/3} + A_3 T^{-1/3} + A_4 + A_5 T^{1/3} + A_6 T^{2/3} + A_7 T + A_8 T^{4/3} + A_9 T^{5/3}] / 1000. \quad (5)$$

with λ_o in W/m·K and T in kelvin. The coefficients A_i are given in the appendix.

To obtain a value at zero density from the experiment we must extrapolate the measurements at low densities to zero density, usually with a low order polynomial. A comparison of the extrapolations of the experimental data of table 2 and the values obtained from eq (5) is given in table 3. The deviations are seen to be very close to one percent. We will, therefore, use eq (5) to calculate the values of λ_o in the correlation, in effect constraining the new correlation to the kinetic theory expressions.

5.2 Term 2, the Excess Thermal Conductivity

The expression used for the excess thermal conductivity is as follows:

$$\lambda_{\text{excess}}(\rho, T) = \alpha\rho + \delta[e^{\beta\rho\gamma} - 1.0] \quad (6)$$

where the parameters α , β , γ , δ are functions of temperature as follows:

$$\begin{aligned} \alpha &= B_1 T \\ \beta &= B_2 + B_3 T + B_4 T^2 \\ \gamma &= B_5 + B_6 T + B_7 T^2 \\ \delta &= B_8 + B_9 T + B_{10}/T^2. \end{aligned}$$

The B coefficients are given in the appendix.

The use of an exponential function for term 2 is quite conventional [see for example references 13, or 5], however, several remarks regarding the analysis must be made. First, it is customary to omit those points which show a critical enhancement from the fitting of the excess thermal conductivity along an isotherm. For the present set of data the critical enhancement extends to nearly $2T_c$. In the first pass at determining the B coefficients roughly one half of all the data had to be omitted. Second, the expression $\alpha\rho$ is necessary if the exponential

part of the term is to fit the isotherms adequately. At the same time, αq must be restricted to no more than half of the total excess thermal conductivity at the low densities. The other half has to be reserved for the contribution of the exponential part of the term. If this is not done, severe systematic deviations will result at the low densities. Third, since the thermal conductivity varies by

nearly a factor of 10, and since the experimental measurements at high densities predominate, a weighting of $1/\lambda$ was used for this set of data. Fourth, a parameter θ used in the analysis of propane [14] to account for the high density behavior of the excess thermal conductivity was also considered here. The θ is a function of density with different contributions above and

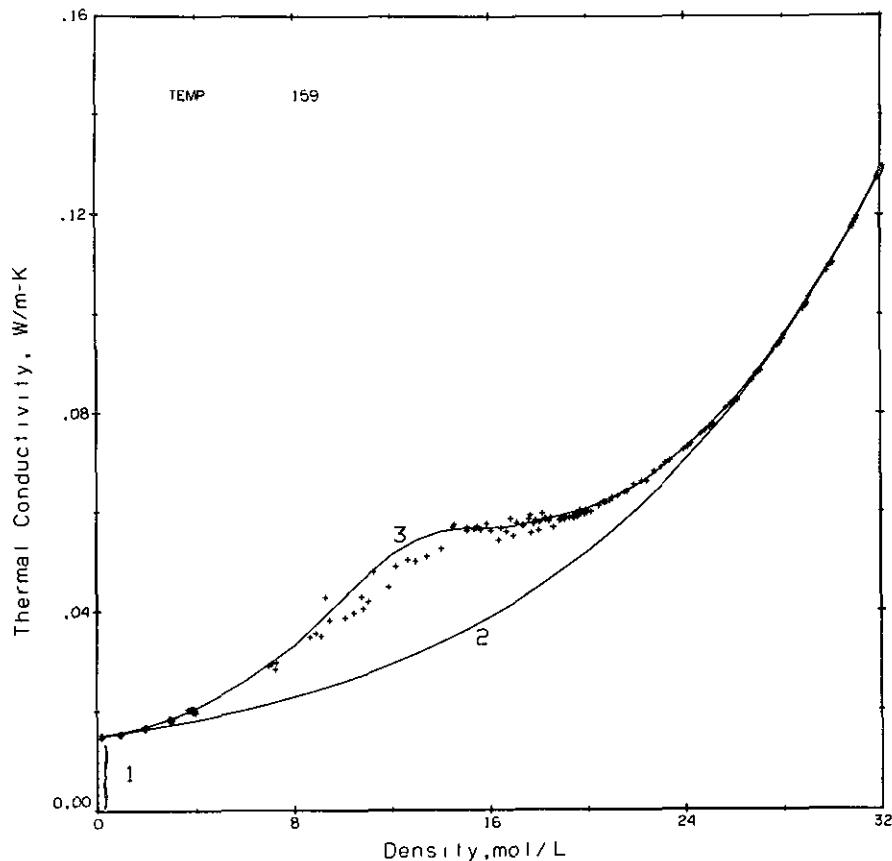


FIGURE 4. Isotherm analysis illustrated for a temperature of 159 K. + experimental points as adjusted to 159 K in table 2; 1 the dilute gas term, λ_o ; 2 the background term, $\lambda_o + \lambda_{\text{excess}}$; 3 the calculated thermal conductivity, $\lambda_o + \lambda_{\text{excess}} + \Delta\lambda_{\text{critical}}$.

TABLE 3. Extrapolated and calculated values of λ_o

Temperature K	λ_o		differences		number of terms in series	cut off density mol/L
	extrapolated $\pm 2\sigma$ W/m·K	calculated, eq (5) W/m·K	W/m·K	percent		
145.	0.01358 \pm 0.00019	0.01340	0.00018	1.31	3	8.5
159.	.01467 \pm .00021	.01472	-.00005	-.34	3	8.5
178.	.01636 \pm .00060	.01644	-.00008	-.51	4	10.5
202.	.01845 \pm .00036	.01851	-.00006	-.31	3	8.5
218.	.01977 \pm .00086	.01984	-.00006	-.32	4	10.5
242.	.02161 \pm .00042	.02177	-.00016	-.73	4	10.5
263.	.02349 \pm .00084	.02341	.00008	.34	4	10.5
282.	.02497 \pm .00037	.02487	.00010	.39	3	8.5
298.	.02599 \pm .00028	.02609	-.00010	-.37	3	8.5
310.	.02725 \pm .00027	.02699	.00026	.95	3	8.5

below critical density. It turns out that a term of this type fails to represent the oxygen thermal conductivity surface adequately. In particular, the isotherms at low temperatures, 77-145 K, are too steep, and the increase in spacing in the λ - ϱ plane required between the 121 and 99 K isotherms and the 99 and 77 K isotherms cannot be achieved correctly. The behavior expected of the thermal conductivity surface over a wide range of temperatures and pressures including the saturation boundary is discussed in reference [15]. With the exception of the parameter δ the parameters are well behaved and vary slowly with temperature. Their dependence on temperature is shown in figure 5.

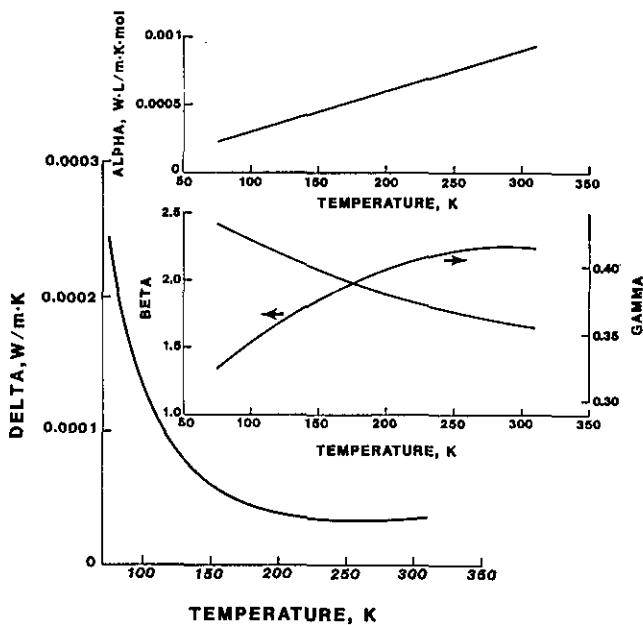


FIGURE 5. Parameters α - δ of the excess thermal conductivity as a function of temperature.

Finally, if we extrapolate all of the isotherms to liquid densities, say around 40 mol/L, then the observation made by Le Neindre [16] seems to be born out. Le Neindre observed that at high pressures at the liquid-solid transition the thermal conductivity coefficient is density dependent only.

5.3 Term 3, The Critical Enhancement

With terms 1 and 2 of the thermal conductivity surface determined, we turn our attention to the remainder, the critical enhancement. The data, shown in figure 6, are obtained by subtracting terms 1 and 2 from the experimental values. For this analysis we will consider two separate regions which are shown in ϱ - T coordinates in figure 2. The first region, which we will call the critical

region proper, is nearly rectangular and corresponds roughly to the range of conditions for which Sengers, et al. [17] recommend the use of a scaled equation of state. Defining the reduced coordinates

$$\Delta T^* = (T - T_c)/T_c \text{ and } \Delta \varrho^* = (\varrho - \varrho_c)/\varrho_c \quad (7)$$

the boundaries of the first region as recommended by Sengers, et al. [17] are

$$|\Delta T^*| < 0.03 \text{ and } |\Delta \varrho^*| < 0.25 \quad (8)$$

For oxygen $T_c = 154.581$ K and $\varrho_c = 13.63$ mol/L. Therefore, the region of concern is bounded approximately by $150 \leq T \leq 160$ K and $10 \leq \varrho \leq 17$ mol/L.

We note that only one isotherm of the present measurements, 159 K, falls within this region, and then it is close to the highest temperature, the extreme edge of the region.

The second region, which we will call the extended critical region, shown in a triangle in figure 2, covers those densities and temperatures for which the present measurements reveal an anomalous increase above the background conductivity, i.e., a critical enhancement. Since nearly all of the present measurements fall into region two, the emphasis of the analysis will be placed here. In addition, we will include the 159 K isotherm into the fitting of the region two in order to provide a smooth transition to region one, even though as mentioned above this isotherm properly belongs into region one.

Region 1, The Critical Region Proper.

Modern theoretical predictions on the calculation of $\Delta \lambda_c$ are given by Hanley, et al. [5] and Sengers, et al. [17]. Both sets of authors recommend a scaling equation in the close vicinity of the critical point and switch to an equation of state, usually a modified Benedict-Webb-Rubin type, further away from the critical point. Hanley, et al. [5] make the switch at $0.025 T_c$ or 158.445 K while Sengers, et al. [17] use $0.03 T_c$ or 159.218 K. A comparison of the $\Delta \lambda_c$ obtained from the experiment and as adjusted to 159 K in table 2 with references [5] and [17] and with the equations developed in the next section is given in figure 7 for a temperature of 159 K. We note that for reference [5] the shift to the BWR equation of state has already taken place. The defects of this equation when used to calculate the compressibility are evident, yielding a distinct asymmetry of the $\Delta \lambda_c$ toward lower densities when compared to the other calculations. The use of a PVT surface by Weber [18], i.e., a polynomial representation of isotherms, with

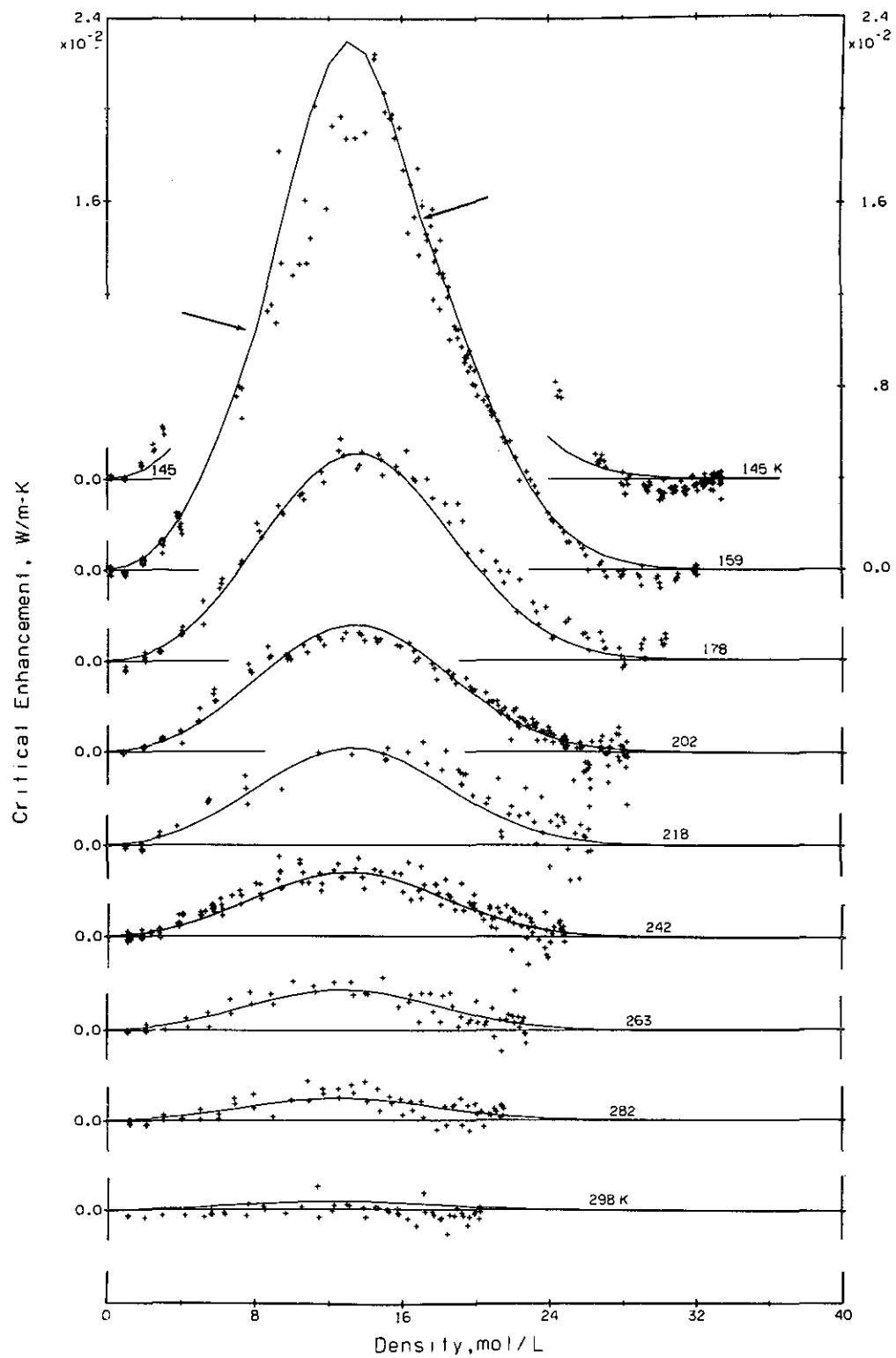


FIGURE 6. Term 3, the critical enhancement or anomalous increase along isotherms. Each isotherm is on a separate scale. The spacing between isotherms is 0.004 W/m · K. For the 159K isotherm the arrows indicate the switch from region 1 to region 2 in the computation.

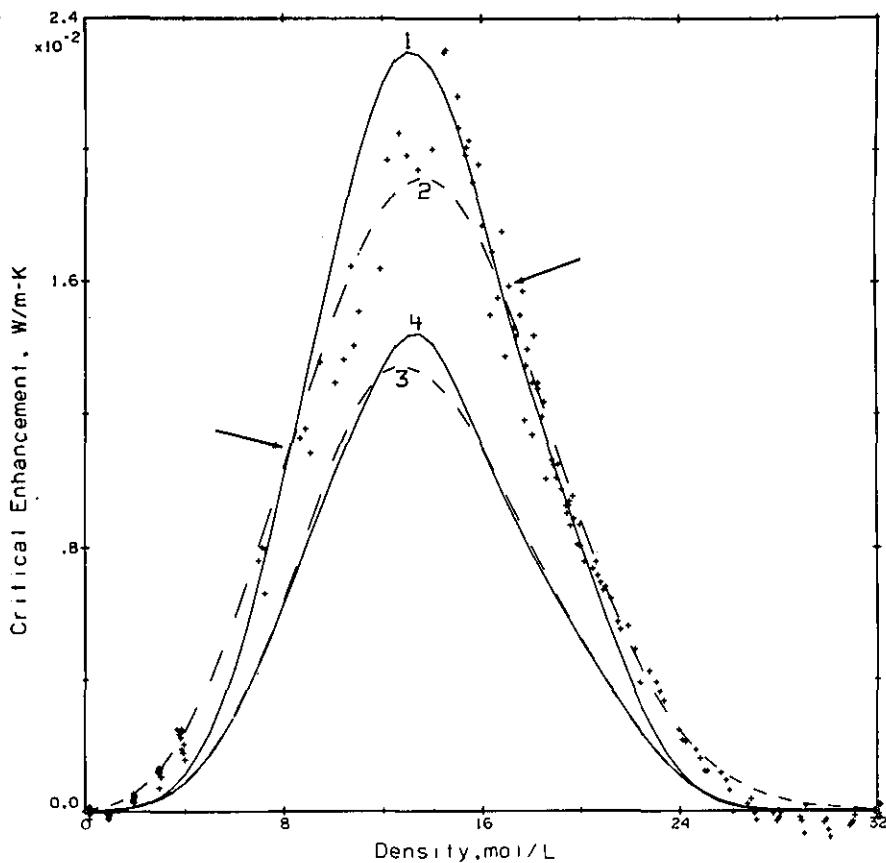


FIGURE 7. Comparison of experimental and calculated $\Delta\lambda_c$ at 159 K. + experimental points as adjusted to 159 K in table 2; 1 $\Delta\lambda_c$ calculated according to [17]; 2 $\Delta\lambda_c$ calculated from eqs (9-13) this paper; 3 $\Delta\lambda_c$ calculated according to [5]; 4 $\Delta\lambda_c$ calculated according to [5] but with derivatives from [18]. The arrows indicate where the switchover in computation from region 1, i.e., reference [17], to region 2, i.e., eqs (9-13), takes place.

the equations in [5] improves the calculated $\Delta\lambda_c$ considerably. For reference [17] the calculation at this temperature is still in the scaled equation mode with but a slight asymmetry toward lower densities. The empirical representation developed in the next section, eqs (9-13), lies intermediate between [5] and [17] and exhibits even less asymmetry toward the lower densities. We conclude that for this temperature the experimental results agree within experimental error with current theoretical predictions.

Region 2, The Extended Critical Region.

What we wish to provide for region two is a mathematical description of the $\Delta\lambda_c(Q, T)$ which will represent the available data. In developing the analytical representation for term 3 we find that the surface to be represented exhibits considerable fine structure. The aspects that must be accommodated in particular are: one, the critical enhancement persists to quite high

temperatures. It persists to somewhere around $2 T_c$ for oxygen quite similar to that initially reported for argon [12,19]. A second aspect is that this increase is centered on a density, Q_{center} , which is a function of temperature. Close to critical Q_{center} is nearly equal to the critical density, but at higher temperatures Q_{center} changes to lower densities as will be seen in figure 6. A third aspect is that the data proved to be slightly asymmetric about Q_{center} .

We started by looking at the prior art in the analysis of the critical point anomaly [5,17,20,21]. However, it became apparent very quickly that the expressions developed previously for $\Delta\lambda_c$ cannot be used at the higher temperatures involved here. Specifically, we tried to use the prescriptions given in references [5] and [17] by adjusting the amplitude, the damping factor, or both to values seen experimentally. This procedure fails to represent the data. The reason for this is as follows. The combination of variables including the correlation length, the compressibility, the viscosity, and the damping factor yields a maximum. However, this maximum

occurs at a density much higher than ρ_c , whereas what is needed is a maximum at a density less than ρ_c . A plot of the densities at which we require the maxima to occur, i.e., ρ_{center} , and the densities where they actually occur for the procedures of references [5] and [17] is given in figure 8b below.

Since the best current prescriptions fail to represent the new data we were forced to develop a new, empirical representation for the $\Delta\lambda_c$ in region 2, the details of which follow.

The expression used is an error function centered upon ρ_{center} multiplied by an amplitude

$$\Delta\lambda_{critical}(\rho, T) = AMPL \cdot e^{-x^2} \quad (9)$$

Both amplitude and centering density are chosen to be simple functions of temperature. Their behavior is shown in figure 8a and b. In figure 8a the error bands shown for the experimental isotherms represent the

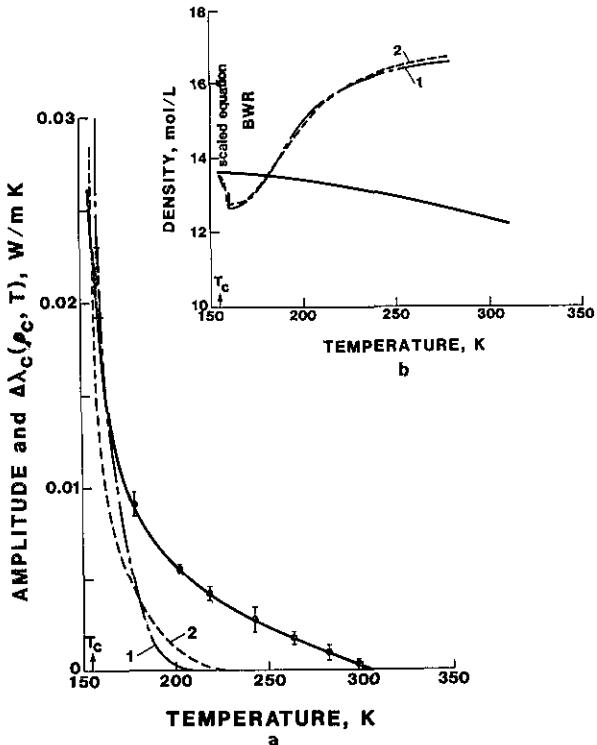


FIGURE 8. Amplitudes and densities at maximum $\Delta\lambda_c$ as a function of temperature.

Amplitudes

- eq (10) this paper, with the range of experimental values I taken from figure 6;
- - - 1 $\Delta\lambda_c(\rho_c, T)$ scaled equation only [17];
- - - 2 $\Delta\lambda_c(\rho_c, T)$ scaled equation and BWR [5].

Densities at maximum $\Delta\lambda_c$

- eq (11) this paper, i.e., ρ_{center} ;
- - - 1 scaled equation and BWR according to [17];
- - - 2 scaled equation and BWR according to [5].

range of values plotted for each isotherm in figure 6 close to the density ρ_{center} . The algebraic representations are

$$AMPL = C_1/(T + C_2) + C_3 + C_4 T \quad (10)$$

$$\rho_{center} = \rho_c + C_5(T - T_c)^{1.5} \quad (11)$$

It is clear that the x in eq (9) is intended to be a function of density. The small asymmetry is achieved by providing different expressions for x above and below ρ_{center} as follows:

$$x = C_6(\rho - \rho_{center}) \quad \text{for } \rho > \rho_{center} \quad (12)$$

and

$$x = C_6(\rho - \rho_{center}) + C_7(\rho - \rho_{center})^5 \quad \text{for } \rho < \rho_{center} \quad (13)$$

Once the analytical representation for term 3 had been determined, a subsequent pass considered all of the data and all terms together in a surface fit. The coefficients C_i as determined in this surface fit are given in the appendix. Values calculated from eqs (9-13) for term 3 are plotted as continuous lines for isotherms 145-298 K in figure 6. We find that the critical enhancement is cut off when the amplitude of eq (10) reaches zero, i.e., approximately at 307 K.

Combining Regions 1 and 2.

The simple functions developed for region 2 are designed to represent the experimental data in region 2, the extended critical region. They were not designed to incorporate the divergence of λ at $T = T_c$. A complete representation of the thermal conductivity surface will, therefore, require a switch from the computational scheme recommended for region 2 to a different one for region 1 that incorporates the proper divergence of λ . The details of this switch are given elsewhere [22] and they include a consideration of the light scattering measurements by Weber [23]. A brief synopsis is as follows. For region 1 we recommend the formulation of Sengers, et al. [17] which is modified in two minor ways. First, the value of Λ adopted to be 1.02 for CO₂ in [17] is chosen to be 1.04 for oxygen. This number is established as a best value for Weber's experimental points [23] for densities close to critical. The second modification is to extend the calculation using the scaled equation out to a temperature of 162.9805 K or 1.054 T_c rather than 1.03 T_c . The second change avoids an abrupt drop of about 10 percent in the value of $\Delta\lambda_c(\rho_c, T)$ in switching from the scaled equation to the BWR at 1.03 T_c . For region 2 we recommend eqs (9-13) of this paper. The boundaries between the two modes of computation are arranged to give as smooth a transition

between them as possible. The temperature 162.9805 K or 1.054 T_c is the point at which the values of $\Delta\lambda_c(\rho_c, T)$ and $\Delta\lambda_c(\rho_{center}, T)$ are equal for regions 1 and 2. The crossover is shown in figure 8a where one of the dashed lines represents the extrapolation of $\Delta\lambda_c(\rho_c, T)$ from [17] for the scaled equation mode and the other represents the extrapolation of $\Delta\lambda_c(\rho_c, T)$ [5] for the BWR equation mode.

A final note concerns the extension of the calculation of $\Delta\lambda_{critical}$ to temperatures below critical. The normal assumption is that the isotherms below T_c mirror the behavior of isotherms above T_c, i.e., the $\Delta\lambda_{critical}$ for the 145 K isotherm is calculated as if that isotherm were at 164.142 K. This was done in figure 6, and it will be seen that the $\Delta\lambda_{critical}$ calculated for 145 K is nowhere near large enough to achieve agreement with experiment. In fact, the experimental $\Delta\lambda_{critical}$ for 145 K is even larger than that calculated or measured for 159 K, a temperature which is considerably closer to critical. To resolve this point additional isotherms below T_c would have to be measured.

5.4 The Thermal Conductivity Surface

Equations (5-13) taken together describe the major part of the thermal conductivity surface, excepting only the critical region proper, region 1 of figure 2. Coefficients for eqs (5-13) were determined by running alternate cycles of a linear least squares routine on six of the coefficients and one parameter, and then a general minimizing routine on the remaining parameters until the change in the total deviation sum became negligible. The three function programs describing dilute gas, the excess thermal conductivity and the $\Delta\lambda_{critical}$ are listed in the appendix. The function program for the $\Delta\lambda_{critical}$ includes the switchover to the formulation of Sengers, et al. [17] at the appropriate conditions. To complete the set of functions needed to describe the entire thermal conductivity surface, a fourth function program is listed in the appendix. This function applies to the critical region proper, region 1 of figure 2. It codes the prescription of reference [17] but restricts it to the scaled equation only. Since the variables normally available to the user are pressure and temperature, an equation of state [7] is required to find the corresponding density. Temperature and density then allow calculation of the thermal conductivity from the functions given in the appendix.

Deviations between experimental values and the calculated surface are shown for all points in figure 9 by isotherms. Some systematic deviations, notably for the 145 K and 159 K isotherms and at low densities remain. Percentage deviations for each experimental point as adjusted to an isotherm have already been shown in table

2. The percentage deviation over all 1126 points is 1.5 percent at the 1 σ level.

5.5 Comparisons to the Results of Others

The comparisons are made through the present correlating surface. A summary of deviations between the experimental thermal conductivities of others and the calculated surface is given in table 4. The deviations for each individual point are shown in figure 10. In comparing the results from the light scattering experiment by Weber [23] we used only those points that fall into the temperature range of our measurements, i.e., above 158 K. The rms deviation of 2.8 percent between the present results and Ziebland and Burton's [3] measurements with a concentric cylinder system represents an excellent agreement. The agreement between Ivanova, et al. [4] who used a steady state hot wire but had to know the thermal conductivity of the supporting glass tube and the present measurements is acceptable, as is the agreement with Weber [23].

TABLE 4. A summary of deviations between experimental thermal conductivities of other authors and the surface calculated in this paper.

Reference	No. of Points	differences in %		RMS
		lowest	highest	
Ziebland and Burton [3]	65	-2.30	8.77	2.82
Ivanova, et al. [4]	88	-11.08	9.90	3.95
Weber [23]	14	-8.38	+17.69	5.68
this paper, total	1126	-14.59	+15.47	1.46
this paper, overlap with region 1	31	-14.59	+8.66	6.67

We can also compare the present correlation to a previous one by Hanley, et al. [5]. The deviations between these two surfaces were defined to be zero at zero density. At higher densities the deviations are systematic and run up to 33 percent at the highest densities. The differences between the two surface representations are illustrated in figure 11 for five isotherms of 80, 120, 160, 200, and 300 K.

Considering the critical enhancement we find that for the isotherm closest to critical, 159 K, the measurements agree with current theoretical predictions [17]. For higher temperatures the present measurements disagree with current theoretical predictions [5,17], the extent of the disagreement is shown for densities near ρ_c in figure 8.

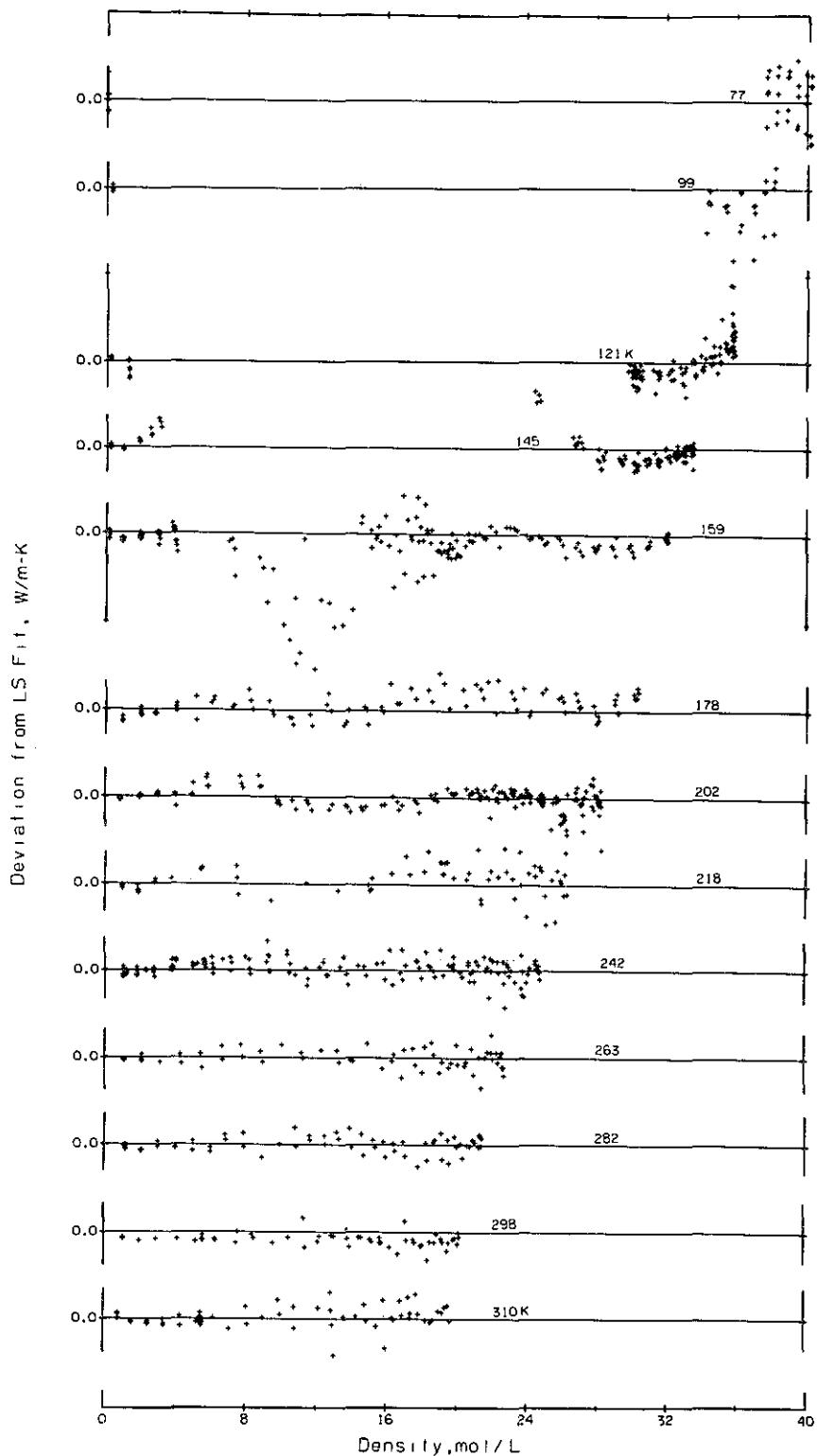


FIGURE 9. Deviations between experimental values and the correlating surface along isotherms. Each isotherm is on a separate scale. The spacing between isotherms or isotherms and tick marks is 0.004 $\text{W}/\text{m}\cdot\text{K}$.

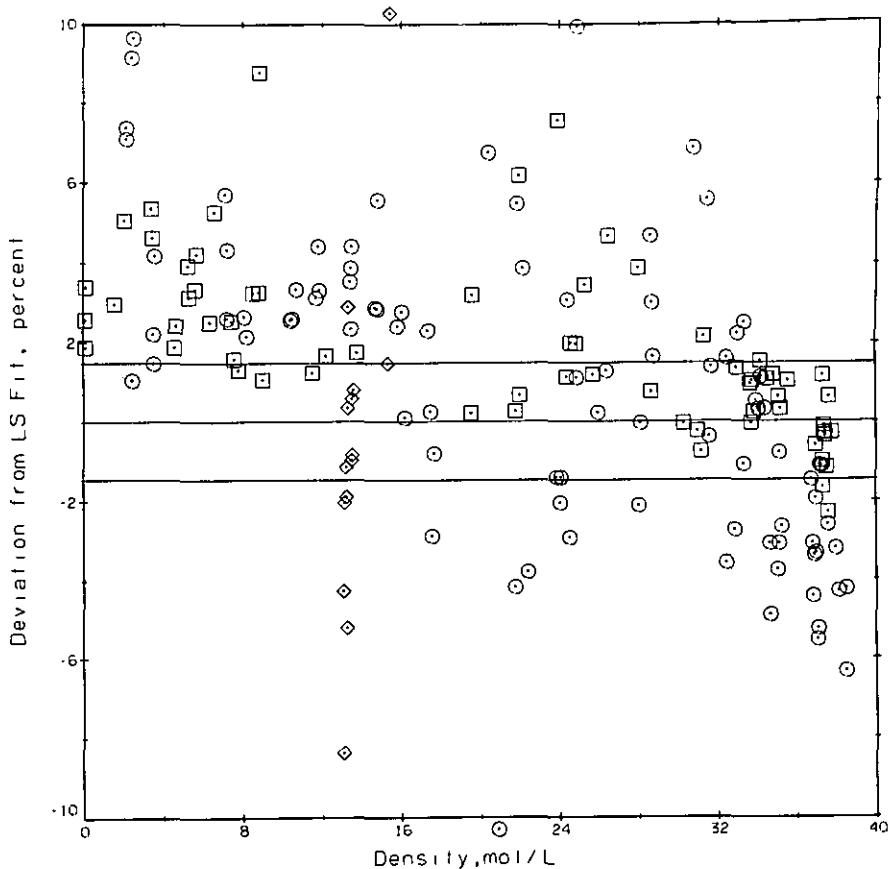


FIGURE 10. Deviations between experimental values of other authors and the correlating surface.

□ Ref. 3 ○ Ref. 4 ◊ Ref. 23
 The horizontal band shows the ± 1.5 percent fit of the correlating surface to the present 1126 points.

There are perhaps three reasons why the present measurements exhibit a critical enhancement to higher temperatures than previously reported. Looking at figure 6 we note that the critical enhancement at any given temperature covers a broad range in density. Therefore, the experimental measurements should be carried out quite high pressures, preferably to a density of about $2\varrho_c$, in order to separate the terms in eq (4) properly. In addition, the precision of the experimental measurements must be fairly high. For the present measurements the precision is a nominal 0.6 percent. Considering the first two elements, we see that at a temperature of 298 K it is nearly impossible to differentiate between potential critical enhancement and experimental precision. Finally, the functional form used to represent term 2, the excess conductivity, should be fairly well constrained. In other words, the excess subtracted at different temperatures should show a slight temperature dependence, the functional form, however, should be the same for all isotherms. In the present

paper an exponential is used rather than the usual power series in density.

6. Summary

The thermal conductivity of oxygen has been measured at temperatures from 77 to 310 K with pressures to 70 MPa. The measurements cover the physical states of the dilute gas, the dense gas, the region near critical, compressed liquid states, metastable liquid states at conditions just below saturation, and vapor states at temperatures below critical and pressures less than the vapor pressure. The results were analyzed in conventional terms to develop a mathematical description of the thermal conductivity surface. The new surface reveals that the critical enhancement, or an anomalous increase in thermal conductivity, persists to reduced temperatures that are quite high, approximately $2 T_c$. The center of the enhancement shifts from the critical density to lower densities at the higher

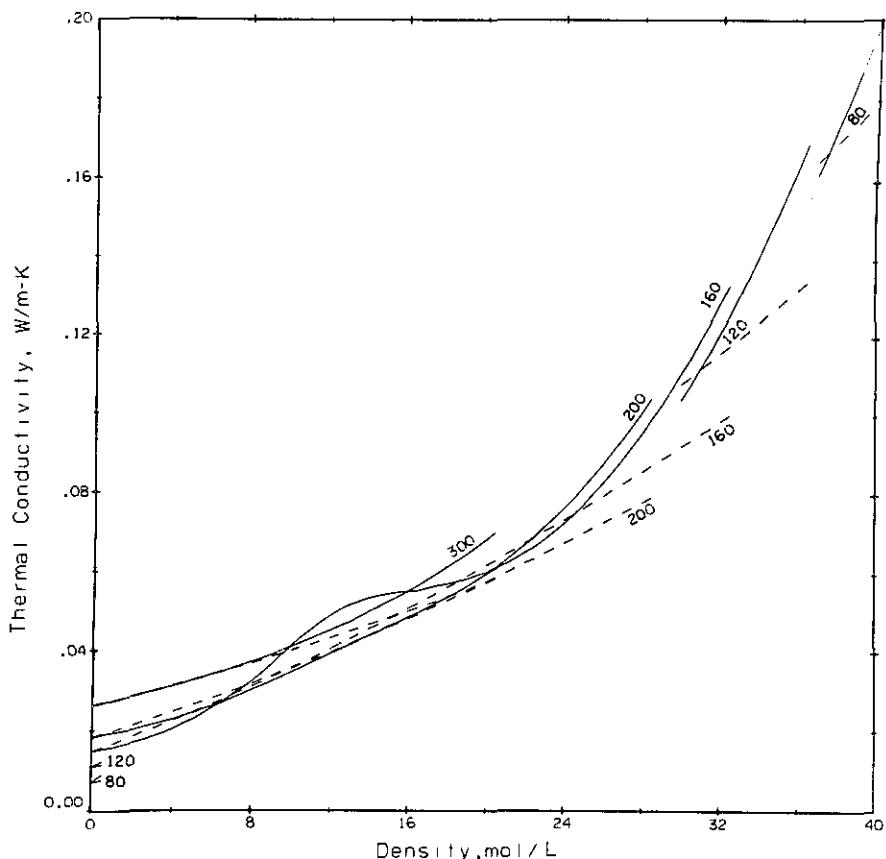


FIGURE 11. Comparison of the correlation by Hanley, et al. [5] - - - and the present correlation — for isotherms of 80, 120, 160, 200, and 300 K.

temperatures, and the enhancement is slightly asymmetric about the center density.

The precision of the measurements as established by varying the applied power is 0.6 percent. The agreement between an extrapolation of the measured values to zero density and dilute gas values calculated from basic theory is around 1 percent. The accuracy of the present measurements is expected to be 1.5 percent (1σ) over much of the surface, as established by the fit of the correlating surface. This accuracy degrades to around 10 percent at 77 K and zero density and to around 6 percent in the region covering the critical enhancement at 159 K. The agreement between the present measurements and those of others ranges between 3 to 5 percent covering a wide range of temperatures, densities and including the region of the critical enhancement.

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8. Appendix

```

C      FUNCTION DILTR(TEMP)
      TC-ZERO FOR OXYGEN FROM TN 1025
      DIMENSION A(9)
      DATA A/-2.0395052193E+5,2.4088141709E+5
      1      ,-1.2014175183E+5,3.295494919E+4
      2      ,-5.4244239598E+3,5.4734865540E+2
      3      ,-3.2854821539E+1,1.0753572103
      4      ,-1.4610986820E-2/
      T=TEMP
      TF=T**(.1./3.)
      TFF=T**(-4./3.)
      SUM=0
      DO 20 I=1,9
      TFF=TFF*TF
      20 SUM=SUM+A(I)*TFF
      DILTR=SUM
      RETURN
      END

      FUNCTION THERMR(RHO,TEMP)
      4TH SURFACE, COEF. FROM TC021 AND MINIMS, 3 MAR 82
      DIMENSION B(10)
      DATA B/.298644E-5
      1,.59842E+00,.11362E-01,-.19520E-04
      2,.47624E+00,-.64769E-03,.83223E-06
      3,-.278141E-4,.153705E-6,.147176E+1/
      T=TEMP
      DEN=RHO
      TCZERO=DILT(T)/1000.
      AL=B(1)*T
      BE=B(2)+B(3)*T+B(4)*T**2
      GA=B(5)+B(6)*T+B(7)*T**2
      DE=B(8)+B(9)*T+B(10)/T**2
      THERMR=TCZERO+AL*DEN+DE*(EXP(BE*DEN**GA)-1.0)
      RETURN
      END

```

```

C      FUNCTION CRITCR(RHO,TEMP)
C      4TH SURFACE, COEF. FROM TC021 AND MINIMS, 3 MAR 82
C      DIMENSION C(7)
C      DATA C/.219200E+0,-145.55,.734512E-02,-.282950E-04
C      1,-.71599E-3,.13804E+0,.12980E-5/
C      DATA (TC=154.581),(RHOC=13.63)
C      T=TEMP
C      DEN=RHO
C      DELD=ABS(DEN-RHOC)/RHOC
C      IF(T.LT.TC) T=TC+(TC-T)
C      IF(T.LT.307.443) GO TO 4
C      CRITCR=0.
C      RETURN
C      4 CONTINUE
C      AMPL=C(1)/(T+C(2))+C(3)+C(4)*T
C      DELT=T-TC
C      RHOCENT=RHOC+C(5)*DELT**1.5
C      DELRHO=DEN-RHOCENT
C      X1=C(6)*DELRHO
C      IF(DELRHO.LT.0.) X1=X1+C(7)*DELRHO**5
C      CRITCR=AMPL*EXP(-X1**2)
C      IF(T.GT.162.9805) RETURN
C      IF(DEN.LT.7.5.OR.DEN.GT.18.) RETURN
C      TEST1=SENG81(DEN,T)
C      IF(TEST1.GT.CRITCR) CRITCR=TEST1
C      RETURN
C      END

C      FUNCTION SENG81(RHO,TEMP)
C      SCALED EQUATION ONLY, VERSION OF 12 FEB 82
C      CRITICAL ENHANCEMENT AS IN SENGERS ET AL 1981 U MARYL. REPORT
C      UNITS, IN MOL/L_K, INTERNAL ALSO ATM, OUT W/M-K, ETA G/CH-S, BK J/K
C      1.02 REPLACED BY 1.04, PARAMETER VARIATION FOR WEBER DATA
C      DATA (TC=154.581),(DC=13.63),(BK=1.38054E-23),(PC=49.77054)
C      1,(ZZ=5.9783E-10)
C      DATA (E=.287),(G=1.190),(B=0.355),(DD=2.36),(XZ=0.183),(DE=4.352)
C      DEN=RHO
C      T=TEMP
C      DELD=ABS(DEN-DC)/DC
C      DELT=ABS(T-TC)/TC
C      DFACT=EXP(-(39.8*DELT**2+5.45*DELD**4))
C      RSTAR=DEN/DC
C      VIS=VIS*(DEN,T)*(1.0E-06)
C      CALL DPDT(DPT,DEN,T)
C      IF(DELD.LE.0.25.AND.DELT.LT.0.03) GO TO 8
C      CALL DPDG(DPD,DEN,T)
C      CHISTAR=PC*DEN/(DC**2*DPD)
C      GO TO 12
C      8 IF(DELD.EQ.0.) GO TO 3
C      X=DELT/DELD**((1.0/B)
C      Y=(X+XZ)/XZ
C      TOP=DELD**(-G/B)*((1.+E)/(1.+E*Y**2*B))**((G-1.)/(2.*B))
C      DIV=DD*(DE+(Y-1.)*(DE-1./B+E*Y**2*B))/(1.+E*Y**2*B)
C      CHISTAR=TOP/DIV
C      12 CHI=CHISTAR**0.468067
C      UPPER=1.04*BK/PC*T*DPT/RSTAR)**2*CHI*DFACT*1.01325E+6
C      SENG81=UPPER/(ZZ*6.*3.14159*VIS)
C      RETURN
C      3 BGAM=XZ**G/DD*((1.+E)/E)**((G-1.)/(2.*B))
C      CHISTAR=BGAM*(DELT)**(-G)
C      GO TO 12
C      END

```

Table 2. The Thermal Conductivity of Oxygen

Run Pt.	Pressure MPa	Temperature K	Density mol/L	Power W/m	Experimental Thermal Conductivity		STAT	Adjusted Thermal Conductivity at a nominal Temperature of 77.K		Deviation from Correlation percent
					W/m.K	W/m.K		W/m.K	W/m.K	
23001	64.519	76.866	40.2622	.20587	.20186	.006		.20192		.38
23002	64.517	77.036	40.2441	.26918	.20215	.005		.20213		.61
23003	64.513	77.173	40.2293	.34099	.20154	.003		.20146		.38
23004	64.510	77.313	40.2143	.41918	.19877	.003		.19863		-.94
23005	64.520	77.610	40.1829	.50890	.19888	.001		.19861		-.74
23006	64.522	77.828	40.1598	.60713	.19825	.001		.19788		-.95
23007	55.437	76.878	39.9627	.23645	.19841	.006		.19846		.67
23008	55.440	77.059	39.9429	.30419	.19725	.003		.19722		.18
23009	55.442	77.201	39.9274	.38050	.19673	.001		.19664		-.01
23010	55.437	77.449	39.8999	.46382	.19512	.001		.19493		-.71
23011	41.740	76.804	39.4881	.20597	.19115	.006		.19123		.16
23012	41.748	77.005	39.4651	.26943	.19140	.004		.19140		.41
23013	41.757	77.320	39.4289	.34219	.19223	.003		.19210		1.01
23014	41.757	77.338	39.4268	.42023	.18923	.002		.18910		-.55
23015	41.758	77.514	39.4065	.46421	.18889	.002		.18868		-.63
23016	27.726	76.830	38.9412	.20620	.18534	.004		.18540		.78
23017	27.726	77.003	38.9199	.26958	.18486	.002		.18486		.63
23018	27.728	77.144	38.9025	.34157	.18473	.002		.18468		.65
23019	27.729	77.410	38.8697	.42083	.18290	.001		.18275		-.17
23020	27.730	77.675	38.8370	.51062	.18212	0.000		.18187		-.43
23021	13.851	76.855	38.3377	.20630	.17812	.005		.17817		.92
23022	13.855	76.995	38.3191	.26955	.17754	.004		.17754		.70
23023	13.861	77.132	38.3013	.34152	.17656	.003		.17652		.24
23024	13.866	77.416	38.2637	.42095	.17541	.002		.17527		-.21
23025	13.872	77.631	38.2352	.51049	.17458	.002		.17437		-.53
23026	1.770	76.664	37.7791	.17761	.17124	.007		.17135		.86
23027	1.773	76.791	37.7610	.23653	.17013	.004		.17020		.31
23028	1.776	77.163	37.7075	.30498	.17027	.003		.17022		.69
23029	1.778	77.266	37.6928	.38123	.16935	.002		.16927		.24
23030	1.777	77.525	37.6554	.46469	.16750	.002		.16734		-.65
28006	.025	78.734	.0391	.02260	.00642	.134		.00626		-.842
28007	.025	79.375	.0388	.02805	.00724	.115		.00702		3.32
28008	.025	80.248	.0384	.03427	.00833	.106		.00803		15.47
28011	.025	78.728	.0391	.02258	.00645	.155		.00629		-.790
28012	.025	79.320	.0388	.02803	.00723	.130		.00701		3.26
Run Pt.	Pressure MPa	Temperature K	Density mol/L	Power W/m	Experimental Thermal Conductivity		STAT	Adjusted Thermal Conductivity at a nominal Temperature of 99.K		Deviation from Correlation percent
					W/m.K	W/m.K	W/m.K	W/m.K		
22001	68.411	98.836	38.1211	.34047	.18361	.004		.18368		.55
22002	68.401	99.097	38.0943	.43771	.18276	.002		.18272		.22
22003	68.384	99.395	38.0633	.54783	.18217	.002		.18200		.05
22004	68.377	99.663	38.0359	.66601	.17984	.001		.17956		-1.11
22005	55.474	98.794	37.5845	.34014	.17617	.003		.17625		.25
22006	55.470	99.064	37.5553	.43744	.17540	.002		.17537		-.04
22007	55.469	99.330	37.5265	.54736	.17512	.002		.17499		-.05
22008	55.461	99.730	37.4831	.66636	.17273	.001		.17244		-1.21
22009	41.961	98.577	36.9801	.33948	.16750	.003		.16766		-.41
22010	41.961	98.812	36.9529	.43655	.16693	.002		.16700		-.61
22011	41.964	99.262	36.9010	.54699	.16676	.002		.16666		-.44
22012	41.958	99.400	36.8846	.66437	.16418	.001		.16403		-.93
22013	27.692	98.666	36.2124	.29657	.15909	.003		.15920		-.05
22014	27.693	98.737	36.2034	.38713	.15748	.002		.15757		-1.02
22015	27.696	99.272	36.1358	.49195	.15834	.002		.15825		-.09
22016	27.697	99.580	36.0969	.60482	.15625	.001		.15605		-1.22
22017	14.022	98.527	35.3802	.25574	.14908	.004		.14923		-.47
22018	14.027	98.714	35.3539	.34051	.14853	.003		.14862		-.68
22019	14.030	99.059	35.3053	.43823	.14836	.002		.14834		-.52
22020	14.034	99.476	35.2463	.54912	.14785	.002		.14770		-.52
22021	1.667	98.612	34.4380	.21845	.13913	.005		.13924		-.48
22022	1.678	98.914	34.3898	.29749	.13933	.003		.13935		-.04
22023	1.683	99.126	34.3558	.38884	.13855	.002		.13851		-.40
22024	1.685	99.504	34.2942	.49334	.13795	.001		.13781		-.45
22025	1.682	99.978	34.2162	.60711	.13594	.001		.13567		-1.45
26004	.222	101.183	.2784	.03978	.00928	.066		.00906		-.60
26007	.222	100.306	.2813	.03211	.00908	.090		.00895		-1.90
26008	.222	101.821	.2763	.04827	.00953	.051		.00925		1.44

Run Pt.	Pressure MPa	Temperature K	Density mol/L	Power W/m	Experimental Thermal Conductivity W/m.K	STAT	Adjusted Thermal Conductivity at a nominal Temperature of 121.K		Deviation from Correlation percent
							W/m.K	W/m.K	
17001	66.830	120.725	35.8415	.16153	.16230	.010	.16238	.16238	.23
17002	66.827	121.079	35.8058	.19941	.16308	.007	.16306	.16306	.90
17003	66.823	121.014	35.8121	.24084	.16310	.006	.16310	.16310	.88
17004	66.821	121.104	35.8031	.28636	.16281	.005	.16278	.16278	.75
17005	66.819	121.326	35.7806	.33606	.16196	.004	.16187	.16187	.36
17006	66.818	121.476	35.7656	.38985	.16233	.003	.16219	.16219	.67
17007	66.817	121.588	35.7543	.44748	.16177	.002	.16160	.16160	.39
17008	66.810	121.880	35.7246	.50957	.16168	.002	.16143	.16143	.50
17009	66.812	122.030	35.7096	.57552	.16133	.002	.16103	.16103	.37
17010	66.807	122.074	35.7050	.64516	.16099	.001	.16068	.16068	.18
17011	66.803	122.475	35.6646	.72021	.16161	.002	.16119	.16119	.79
17012	66.804	122.764	35.6356	.80010	.16080	.001	.16030	.16030	.45
17013	66.802	121.785	35.7337	.44805	.16229	.002	.16206	.16206	.82
17014	66.800	121.854	35.7267	.44817	.16261	.003	.16236	.16236	1.06
17015	66.794	121.952	35.7166	.44831	.16436	.003	.16409	.16409	2.17
17016	66.793	121.960	35.7157	.44836	.16190	.006	.16162	.16162	.68
17017	66.791	122.039	35.7076	.44856	.16546	.004	.16516	.16516	2.87
17018	66.790	122.446	35.6668	.64652	.16221	.003	.16180	.16180	1.15
17019	66.786	122.482	35.6630	.64675	.16264	.002	.16222	.16222	1.43
17020	66.785	122.621	35.6490	.64715	.16378	.002	.16332	.16332	2.20
17021	59.914	120.808	35.4695	.16156	.15808	.010	.15813	.15813	.32
17022	59.916	121.015	35.4480	.24080	.15794	.006	.15794	.15794	.35
17023	59.919	121.241	35.4246	.33602	.15779	.004	.15772	.15772	.39
17024	59.920	121.699	35.3770	.44768	.15763	.003	.15743	.15743	.56
17025	59.926	122.098	35.3357	.57576	.15708	.002	.15678	.15678	.45
17026	59.932	122.555	35.2884	.72069	.15694	.001	.15651	.15651	.63
17027	52.721	120.785	35.0664	.16150	.15498	.010	.15504	.15504	1.32
17028	52.728	121.026	35.0406	.24075	.15279	.006	.15278	.15278	.05
17029	52.730	121.300	35.0110	.33594	.15245	.004	.15237	.15237	-.00
17030	52.735	121.661	34.9720	.44761	.15287	.003	.15269	.15269	.50
17031	52.743	122.104	34.9243	.57572	.15210	.002	.15180	.15180	.27
17032	52.747	122.608	34.8697	.72075	.15076	.001	.15033	.15033	-.30
17033	45.937	120.724	34.6609	.16145	.14872	.006	.14879	.14879	.22
17034	45.943	120.949	34.6357	.24068	.14897	.004	.14898	.14898	.54
17035	45.949	121.287	34.5976	.33592	.14784	.002	.14776	.14776	.00
17036	45.955	121.709	34.5500	.44770	.14773	.002	.14754	.14754	.21
17037	45.963	122.148	34.5005	.57585	.14692	.001	.14662	.14662	-.05
17038	45.970	122.767	34.4304	.72143	.14668	.001	.14623	.14623	.20
17039	38.451	120.792	34.1569	.16162	.14314	.009	.14319	.14319	.14
17040	38.458	121.094	34.1211	.24097	.14381	.006	.14379	.14379	.82
17041	38.465	121.429	34.0812	.33628	.14215	.003	.14204	.14204	-.10
17042	38.471	121.781	34.0391	.44803	.14157	.003	.14137	.14137	-.26
17043	38.478	122.245	33.9837	.57643	.14117	.001	.14086	.14086	-.21
17044	38.484	122.833	33.9132	.72205	.14119	.001	.14074	.14074	.23
17045	31.221	120.887	33.6143	.16169	.13674	.009	.13677	.13677	-.39
17046	31.229	121.094	33.5883	.24102	.13643	.005	.13641	.13641	-.46
17047	31.237	121.473	33.5402	.33660	.13670	.003	.13659	.13659	.04
17048	31.250	121.857	33.4918	.44840	.13629	.002	.13608	.13608	.03
17049	31.257	122.391	33.4236	.57699	.13586	.001	.13553	.13553	.13
17050	31.263	122.870	33.3623	.72253	.13520	.001	.13476	.13476	.02
17051	24.034	120.891	33.0206	.16174	.12972	.009	.12975	.12975	-1.20
17052	24.041	120.755	33.0400	.12800	.13126	.014	.13132	.13132	-.14
17053	24.053	121.100	32.9932	.24111	.13073	.005	.13071	.13071	-.25
17054	24.060	121.427	32.9485	.33659	.12970	.003	.12960	.12960	-.77
17055	24.071	121.932	32.8793	.44864	.12924	.002	.12903	.12903	-.69
17056	24.082	122.394	32.8160	.57724	.12915	.002	.12883	.12883	-.36
17057	24.095	122.959	32.7382	.72293	.12881	.001	.12837	.12837	-.13
17058	16.732	120.750	32.3684	.12802	.12402	.011	.12408	.12408	-.59
17059	16.739	120.956	32.3177	.19941	.12463	.006	.12464	.12464	.10
17060	16.744	121.329	32.2611	.28692	.12377	.003	.12370	.12370	-.23
17061	16.754	121.763	32.1956	.39079	.12279	.002	.12262	.12262	-.61
17062	16.761	122.190	32.1307	.51103	.12267	.001	.12241	.12241	-.29
17063	16.770	122.789	32.0393	.64842	.12182	.001	.12144	.12144	-.40
17064	9.823	120.750	31.5707	.12802	.11705	.010	.11710	.11710	-.47
17065	9.829	121.049	31.5199	.19945	.11682	.005	.11681	.11681	-.33
17066	9.837	121.359	31.4671	.28696	.11608	.003	.11601	.11601	-.62
17067	9.847	121.841	31.3848	.39100	.11576	.002	.11559	.11559	-.36
17068	9.854	122.331	31.3002	.51164	.11415	.002	.11388	.11388	-1.21
17069	9.864	122.964	31.1906	.64895	.11439	.001	.11399	.11399	-.27
17070	2.634	120.844	30.5303	.12808	.10792	.010	.10795	.10795	-.67
17071	2.641	121.060	30.4867	.19952	.10772	.005	.10771	.10771	-.56
17072	2.644	121.440	30.4080	.28707	.10710	.003	.10702	.10702	-.60
17073	2.646	121.992	30.2919	.39122	.10650	.002	.10631	.10631	-.37
17074	2.657	122.405	30.2063	.51180	.10582	.001	.10555	.10555	-.43
17075	2.664	123.103	30.0579	.64974	.10489	.001	.10450	.10450	-.29
17076	2.656	120.805	30.5747	.12812	.10864	.007	.10868	.10868	-.33
17077	2.657	121.098	30.5146	.19960	.10784	.003	.10782	.10782	-.67

17078	2.858	121.501	30.4311	.28727	.10784	.002	.10774	-.10
17079	2.859	121.922	30.3434	.39134	.10694	.001	.10676	-.34
17080	2.860	122.517	30.2181	.51222	.10602	.001	.10573	-.35
17081	2.861	123.084	30.0975	.64998	.10537	.001	.10498	-.14
17082	1.074	120.673	30.2995	.09834	.10553	.009	.10559	-1.11
17083	1.074	120.799	30.2719	.12810	.10538	.006	.10542	-1.06
17084	1.074	120.932	30.2427	.16184	.10519	.005	.10520	-1.04
17085	1.074	121.025	30.2224	.19956	.10486	.003	.10486	-1.22
17086	1.074	121.194	30.1852	.24131	.10522	.003	.10518	-.62
17087	1.073	121.427	30.1336	.28723	.10522	.002	.10514	-.26
17088	1.073	121.674	30.0788	.33722	.10459	.002	.10446	-.49
17089	1.073	121.928	30.0221	.39135	.10367	.003	.10350	-.98
17090	1.073	122.197	29.9617	.44964	.10359	.002	.10337	-.64
17091	1.073	122.426	29.9099	.51207	.10350	.001	.10324	-.37
17092	1.073	122.835	29.8169	.57925	.10315	.001	.10281	-.07
17093	1.072	123.145	29.7455	.65023	.10233	.001	.10194	-.37
27003	1.056	121.949	1.2468	.03306	.01147	.056	.01137	-6.21
27004	1.056	122.925	1.2299	.05147	.01196	.037	.01176	-2.56
27006	1.056	121.592	1.2531	.02541	.01135	.092	.01129	-7.04
27007	1.056	122.455	1.2379	.04175	.01179	.053	.01164	-3.70
27008	1.056	123.522	1.2199	.06231	.01232	.035	.01206	.05
27009	1.056	124.121	1.2100	.07420	.01245	.026	.01213	.69
27012	.210	122.778	.2122	.03322	.01155	.071	.01137	.92
27013	.210	124.061	.2098	.05182	.01171	.041	.01140	1.21
27016	.210	123.390	.2110	.04197	.01170	.047	.01146	1.69

Run Pt.	Pressure MPa	Temperature K	Density mol/L	Experimental			Adjusted Thermal Conductivity at a nominal Temperature of 145.K		
				Power W/m	Thermal Conductivity W/m.K	STAT	from Correlation percent	Deviation	
16001	65.387	143.353	33.4978	.19927	.14106	.005	.14138	.05	
16002	65.388	143.518	33.4813	.24561	.14114	.004	.14143	.21	
16003	65.391	143.651	33.4684	.29692	.14051	.003	.14077	-.16	
16004	65.390	143.840	33.4494	.35318	.13966	.004	.13988	-.65	
16005	65.390	144.065	33.4270	.41444	.14026	.002	.14044	-.08	
16006	65.390	144.266	33.4071	.48067	.14031	.002	.14045	.07	
16007	65.389	144.617	33.3721	.55209	.13967	.001	.13974	-.17	
16008	65.390	144.862	33.3478	.62851	.13989	.001	.13992	.13	
16009	65.391	145.161	33.3182	.71001	.13959	.001	.13956	.10	
16010	65.391	145.414	33.2931	.79658	.13947	.001	.13939	.17	
16011	59.096	143.181	33.0930	.15774	.13691	.010	.13726	.12	
16012	59.097	143.370	33.0734	.19929	.13680	.006	.13711	.16	
16013	59.096	143.555	33.0542	.24572	.13589	.004	.13616	-.39	
16014	59.097	143.706	33.0386	.29705	.13631	.003	.13656	.01	
16015	59.098	143.846	33.0242	.35331	.13597	.003	.13619	-.15	
16016	59.098	144.107	32.9970	.41465	.13572	.002	.13589	-.16	
16017	59.094	144.390	32.9675	.48097	.13556	.001	.13567	-.10	
16018	59.096	144.624	32.9433	.55226	.13564	.001	.13571	.11	
16019	59.098	144.960	32.9086	.62881	.13470	.001	.13471	-.38	
16020	59.098	145.177	32.8861	.71030	.13493	.001	.13490	-.07	
16021	59.098	145.530	32.8495	.79712	.13459	.001	.13449	-.09	
16022	52.975	143.222	32.6448	.15779	.13200	.010	.13233	-.18	
16023	52.980	143.414	32.6244	.19930	.13191	.007	.13221	-.12	
16024	52.982	143.555	32.6092	.24576	.13194	.005	.13221	-.00	
16025	52.987	143.779	32.5853	.29708	.13152	.004	.13175	-.17	
16026	52.991	143.966	32.5652	.35340	.13178	.003	.13197	.15	
16027	52.994	144.224	32.5375	.41478	.13111	.003	.13125	-.19	
16028	52.997	144.341	32.5250	.48097	.13092	.002	.13104	-.26	
16030	53.004	144.947	32.4597	.62887	.13037	.002	.13038	-.28	
16031	53.006	145.233	32.4288	.71048	.13024	.001	.13020	-.18	
16032	53.009	145.596	32.3897	.79729	.13003	.001	.12992	-.10	
16033	46.690	145.697	31.8638	.79764	.12517	.002	.12505	.03	
16035	46.708	144.490	32.0037	.48106	.12594	.002	.12603	-.24	
16036	46.716	143.931	32.0683	.35330	.12646	.003	.12665	-.23	
16037	46.723	143.532	32.1146	.24565	.12689	.005	.12716	-.18	
16038	46.726	143.207	32.1520	.15768	.12689	.010	.12722	-.42	
16039	46.734	145.410	31.9005	.71057	.12554	.001	.12547	.09	
16040	46.740	144.643	31.9888	.55221	.12580	.002	.12586	-.26	
16041	46.494	145.921	31.2765	.79802	.11961	.001	.11945	-.13	
16042	46.503	143.246	31.6032	.15772	.12178	.009	.12209	-.40	
16043	46.511	145.136	31.3739	.62915	.11993	.001	.11991	-.48	
16044	46.516	143.615	31.5595	.24570	.12143	.005	.12168	-.41	
16045	46.523	144.558	31.4454	.48113	.12063	.002	.12071	-.35	
16046	46.526	143.931	31.5221	.35327	.12091	.003	.12110	-.61	
16047	46.530	144.297	31.4779	.41466	.12089	.002	.12101	-.34	
16048	34.503	143.223	31.0185	.15768	.11641	.004	.11672	-.49	
16049	34.506	143.586	30.9715	.24567	.11623	.003	.11648	-.34	
16050	34.511	144.051	30.9114	.35340	.11580	.001	.11596	-.33	
16051	34.515	144.590	30.8414	.48118	.11498	.001	.11505	-.54	
16052	34.518	145.202	30.7617	.62918	.11463	.001	.11460	-.34	
16053	34.528	145.585	30.7127	.71107	.11426	.001	.11416	-.4	

16054	28.783	143.335	30.3661	.157778	.11066	.008	.11094	-.64
16055	28.786	143.676	30.3184	.24581	.11093	.005	.11116	-.08
16056	28.790	144.080	30.2616	.35351	.10969	.003	.10985	-.84
16057	28.796	144.406	30.2163	.41507	.10941	.002	.10951	-.81
16058	28.798	144.649	30.1822	.48138	.10935	.002	.10941	-.64
16059	28.802	144.943	30.1410	.55306	.10916	.001	.10917	-.55
16060	28.807	145.285	30.0930	.62965	.10840	.001	.10835	-.94
16061	28.810	145.694	30.0353	.71169	.10842	.001	.10830	-.55
16062	22.869	143.350	29.5938	.15790	.10466	.009	.10494	-.36
16063	22.871	143.763	29.5292	.24600	.10434	.004	.10455	-.25
16064	22.871	144.178	29.4642	.35394	.10349	.003	.10363	-.64
16065	22.874	144.491	29.4154	.41545	.10320	.002	.10329	-.60
16066	22.875	144.751	29.3747	.48192	.10303	.002	.10307	-.50
16067	22.876	145.144	29.3127	.55377	.10265	.002	.10263	-.47
16068	22.877	145.531	29.2517	.63074	.10233	.001	.10224	-.38
16070	16.026	143.454	28.4621	.15798	.09635	.007	.09661	-.10
16071	16.033	143.880	28.3847	.24621	.09549	.004	.09568	-.48
16072	16.041	144.371	28.2947	.35424	.09511	.002	.09521	-.29
16073	16.046	144.622	28.2488	.41582	.09420	.002	.09426	-.95
16074	16.051	144.931	28.1921	.48248	.09384	.002	.09385	-.96
16075	16.056	145.374	28.1098	.55432	.09369	.002	.09363	-.58
16076	16.061	145.730	28.0437	.63140	.09385	.001	.09373	.02
16077	16.068	146.057	27.9834	.71345	.09300	.001	.09282	-.50
16078	10.151	143.438	27.1527	.15799	.08748	.007	.08774	.07
16079	10.157	143.883	27.0506	.24621	.08715	.003	.08734	.36
16080	10.161	144.397	26.9311	.35440	.08674	.002	.08684	.67
16081	10.165	144.744	26.8502	.41603	.08604	.002	.08608	.39
16082	10.170	145.114	26.7636	.48282	.08538	.002	.08536	.19
16083	10.176	145.393	26.6983	.55469	.08506	.001	.08499	.23
16084	10.180	145.865	26.5854	.63175	.08478	.002	.08463	.63
16088	4.202	143.760	24.7491	.19972	.07577	.004	.07602	2.90
16089	4.204	143.969	24.6661	.24640	.07566	.004	.07587	3.25
16090	4.206	144.299	24.5317	.29809	.07472	.003	.07486	2.84
16091	4.207	144.574	24.4166	.35471	.07475	.003	.07484	3.56
25002	2.661	144.035	3.0767	.04058	.01761	.061	.01775	5.05
25003	2.661	144.805	3.0326	.06301	.01790	.033	.01793	6.39
25004	2.661	145.666	2.9859	.09048	.01810	.018	.01800	7.20
25007	2.337	144.202	2.5391	.04061	.01652	.058	.01662	3.45
25008	2.335	144.955	2.5073	.06306	.01652	.029	.01653	3.15
25009	2.333	145.945	2.4676	.09062	.01693	.016	.01681	5.10
25014	1.837	144.349	1.8488	.04061	.01536	.055	.01543	1.67
25015	1.845	145.215	1.8384	.06312	.01538	.026	.01536	1.24
25016	1.844	146.388	1.8126	.09076	.01567	.015	.01551	2.42
25019	1.029	144.631	.9392	.04066	.01420	.050	.01424	-.12
25020	1.029	145.726	.9299	.06324	.01417	.026	.01410	-.1.07
25021	1.029	146.415	.9242	.07648	.01430	.017	.01416	-.61
25024	.257	144.603	.2180	.03132	.01362	.071	.01366	.09
25025	.256	145.163	.2168	.04073	.01369	.048	.01367	.21
25026	.256	145.834	.2157	.05147	.01386	.035	.01378	.98
25027	.256	146.466	.2144	.06349	.01376	.025	.01362	-.19

Run Pt.	Pressure MPa	Temperature K	Density mol/L	Power W/m	Experimental Thermal Conductivity W/m.K		STAT	Temperature of 159.K	Adjusted Thermal Conductivity at a nominal Temperature of 159.K From Correlation W/m.K	Deviation percent
					Conductivity W/m.K	STAT				
21001	67.810	159.357	32.0954	.27777	.12979	.005		.12973		.10
21002	67.813	159.626	32.0696	.33589	.12920	.003		.12910		-.19
21003	67.815	159.809	32.0521	.39939	.12948	.003		.12935		.13
21004	67.818	160.151	32.0193	.46868	.12890	.002		.12872		-.11
21005	67.820	160.355	31.9999	.54353	.12864	.001		.12843		-.20
21006	67.824	160.671	31.9696	.62408	.12855	.001		.12829		-.08
21007	67.827	161.014	31.9368	.71034	.12839	.001		.12807		-.00
21008	67.829	161.455	31.8945	.80236	.12803	.001		.12764		-.02
21009	67.833	161.736	31.8678	.90035	.12781	.001		.12738		-.03
21010	55.242	159.633	31.0659	.33567	.11990	.003		.11980		-.19
21011	55.247	160.272	30.9984	.46853	.11922	.002		.11903		-.34
21012	55.249	160.867	30.9354	.62406	.11869	.001		.11841		-.39
21013	55.252	161.587	30.8594	.80257	.11805	.001		.11766		-.45
21014	44.878	159.732	30.0625	.33573	.11056	.003		.11045		-.83
21015	44.873	160.260	30.0000	.46862	.11033	.002		.11015		-.64
21016	44.873	160.935	29.9206	.62436	.11009	.001		.10981		-.36
21017	44.874	161.744	29.8255	.80301	.10931	.001		.10891		-.47
21018	36.308	159.484	29.1005	.27768	.10370	.006		.10363		-.04
21019	36.310	160.013	29.0314	.39935	.10238	.002		.10224		-.89
21020	36.312	160.749	28.9351	.54377	.10211	.001		.10187		-.53
21021	36.313	161.458	28.8421	.71119	.10161	.001		.10128		-.43
21022	29.319	159.616	28.0905	.27776	.09590	.003		.09582		-.42
21023	29.320	160.127	28.0152	.39955	.09526	.002		.09512		-.61
21024	29.320	160.852	27.9082	.54392	.09447	.002		.09424		-.75
21025	29.321	161.631	27.7931	.71151	.09398	.001		.09366		-.53
21026	23.472	159.331	27.1028	.22520	.08869	.004		.08866		-1.02

21027	23.472	159.892	27.0084	.93565	.08834	.002	.08825	-.80
21028	23.472	160.564	26.8953	.46907	.08808	.001	.08792	-.36
21029	23.473	161.409	26.7524	.62525	.08708	.002	.08683	-.58
21030	19.091	159.278	26.1394	.22539	.08268	.004	.08266	-1.20
21031	19.092	159.934	26.0133	.33633	.08258	.002	.08251	-.50
21032	19.093	160.728	25.8599	.46992	.08199	.002	.08186	-.23
21033	19.095	161.632	25.6805	.62664	.08120	.001	.08100	-.06
21034	15.462	161.244	24.6608	.54564	.07582	.001	.07575	-.03
21035	15.463	159.170	25.1317	.17849	.07781	.002	.07780	-.41
21036	15.464	159.728	25.0066	.27821	.07710	.001	.07707	-.53
21037	15.464	160.508	24.8928	.40046	.07651	.001	.07646	-.19
21038	12.955	158.967	24.2640	.13701	.07382	.007	.07382	-.13
21039	12.955	159.545	24.1128	.22553	.07305	.004	.07306	-.24
21040	12.955	160.113	23.9626	.33648	.07254	.003	.07256	-.03
21042	10.977	158.792	23.3814	.10133	.07043	.005	.07041	.34
21043	10.978	159.325	23.2169	.17907	.06985	.003	.06988	.48
21044	10.979	159.940	23.0239	.27918	.06912	.002	.06920	.55
21045	10.979	160.730	22.7707	.40192	.06813	.002	.06829	.56
21047	9.527	159.023	22.3968	.13733	.06614	.007	.06614	-.77
21048	9.528	159.587	22.1844	.22612	.06606	.004	.06616	.27
21049	9.528	160.365	21.8826	.33735	.06525	.002	.06549	.64
21051	8.460	159.006	21.4979	.13724	.06392	.007	.06392	-.16
21052	8.460	159.628	21.2085	.22602	.06320	.003	.06337	.13
21055	8.461	158.786	21.5996	.10119	.06419	.010	.06414	-.24
21056	7.671	158.813	20.6850	.10116	.06192	.009	.06185	-.40
21057	7.671	159.199	20.4617	.17875	.06109	.005	.06117	-.78
21060	7.131	158.642	19.9436	.07063	.06059	.015	.06042	-.43
21061	7.131	158.994	19.6888	.13713	.06032	.007	.06032	.10
21064	6.828	158.546	19.3945	.07061	.05918	.015	.05893	-1.50
21065	6.828	158.912	19.0785	.13711	.05906	.007	.05901	-.60
21067	6.828	158.322	19.5784	.04560	.05938	.032	.05901	-1.82
21069	6.538	158.643	18.4994	.07063	.05908	.017	.05883	.34
21070	6.538	158.968	18.1305	.13714	.05961	.008	.05959	2.30
21073	6.433	158.531	18.2535	.07063	.05890	.016	.05856	.35
21074	6.433	158.993	17.6664	.13714	.05940	.008	.05939	2.82
21077	6.293	158.582	17.5822	.07032	.05876	.010	.05841	1.34
21081	6.292	158.391	17.8517	.04540	.05874	.009	.05825	.58
21082	6.195	158.547	17.1056	.07058	.05820	.016	.05779	1.14
21084	6.195	158.700	16.8410	.10103	.05893	.010	.05861	3.00
21087	5.923	158.423	15.0757	.07056	.05756	.018	.05614	-1.09
21088	5.924	158.625	14.5447	.10100	.05836	.014	.05735	1.40
21091	5.845	158.450	14.0037	.07055	.05428	.017	.05261	-6.54
21092	5.845	158.658	13.4259	.10098	.05207	.015	.05104	-8.15
21094	5.717	158.554	11.9018	.07055	.04595	.014	.04478	-13.76
21097	5.594	158.777	10.0501	.07122	.03890	.011	.03859	-10.77
21099	5.594	158.519	10.4229	.04601	.04049	.022	.03970	-12.16
21100	5.594	158.294	10.8133	.02627	.04183	.047	.04044	-14.59
21106	5.451	158.229	9.4244	.01205	.03896	.323	.03812	-4.23
21124	3.705	159.284	3.8699	.04586	.01981	.020	.01982	-1.88
21126	3.705	160.004	3.8236	.07114	.02009	.012	.02012	.15
21127	3.705	160.848	3.7716	.10212	.02015	.008	.02019	1.05
21128	3.705	161.869	3.7118	.13884	.02027	.005	.02029	2.22
21129	3.110	158.885	3.0365	.02617	.01822	.046	.01822	-1.48
21130	3.110	159.473	3.0125	.04589	.01847	.020	.01846	.07
21131	3.110	160.304	2.9787	.07124	.01832	.012	.01829	-.54
21132	3.109	161.236	2.9427	.10228	.01846	.007	.01839	.38
21133	2.207	158.997	1.9641	.02618	.01674	.045	.01674	-.36
21134	2.207	159.647	1.9512	.04594	.01669	.019	.01665	-.81
21135	2.207	160.661	1.9314	.07135	.01664	.011	.01653	-1.38
21136	2.206	161.786	1.9094	.10250	.01675	.006	.01656	-1.04
21137	1.179	159.143	.9637	.02620	.01541	.037	.01540	-1.67
21139	1.178	160.026	.9563	.04601	.01542	.017	.01533	-2.05
21140	1.178	161.070	.9486	.07146	.01554	.009	.01536	-1.80
21141	1.177	162.531	.9373	.10276	.01568	.005	.01538	-1.64
21143	.209	159.505	.1594	.02624	.01508	.037	.01503	.70
21144	.209	160.610	.1583	.04610	.01494	.017	.01480	-.90
21145	.208	161.963	.1566	.07168	.01524	.010	.01497	.31
21146	7.982	158.944.	21.0082	.10117	.06288	.010	.06286	.08
21147	7.982	159.147	20.9020	.13715	.06226	.004	.06231	-.42
21148	7.982	159.379	20.7788	.17871	.06191	.002	.06203	-.43
21149	7.982	159.654	20.6310	.22581	.06182	.003	.06204	.09
21150	7.120	158.588	19.9616	.07058	.06004	.006	.05985	-1.45
21151	7.120	158.729	19.8613	.10104	.05965	.008	.05952	-1.72
21152	7.120	158.948	19.7022	.13700	.05972	.006	.05969	-.98
21153	7.120	159.161	19.5428	.17854	.05952	.004	.05960	-.72
21154	7.120	158.357	20.1232	.04558	.06031	.030	.06002	-1.64
21155	6.831	158.429	19.4979	.04558	.05961	.030	.05930	-1.12
21156	6.831	158.514	19.4275	.07059	.05908	.016	.05881	-1.78
21157	6.831	158.726	19.2482	.10109	.05902	.008	.05886	-1.25
21158	6.831	158.960	19.0424	.13708	.05850	.008	.05848	-1.43
21159	6.603	158.430	18.9193	.04559	.05878	.028	.05842.	-1.26
21160	6.603	158.497	18.8531	.07058	.05865	.015	.05833	-1.27

21161	6.603	158.737	18.6085	.10108	.05707	.009	.05689	-3.29
21162	6.603	158.894	18.4412	.13707	.05826	.007	.05819	-.65
21163	6.402	158.423	18.2675	.04560	.05885	.029	.05842	.09
21164	6.403	158.607	18.0427	.07061	.05815	.014	.05785	-.47
21165	6.403	158.806	17.7830	.10110	.05769	.009	.05754	-.53
21166	6.403	159.089	17.3924	.13711	.05710	.006	.05717	-.46
21167	6.283	158.248	18.0076	.04556	.05678	.027	.05619	-.38
21168	6.283	158.471	17.6972	.07057	.05605	.015	.05562	-.84
21169	6.283	158.717	17.3311	.10108	.05750	.010	.05726	-.20
21171	6.144	158.459	16.9412	.04561	.05568	.028	.05518	-.24
21172	6.145	158.601	16.6821	.07060	.05654	.016	.05603	-.138
21173	6.145	158.721	16.4510	.10107	.05715	.010	.05676	-.05
21175	6.043	158.386	16.3470	.04559	.05530	.029	.05436	-.46
21176	6.043	158.517	16.0619	.07055	.05709	.016	.05627	-.92
21177	6.043	158.709	15.6283	.10102	.05702	.012	.05645	-.61
21181	6.034	158.558	15.8870	.07062	.05843	.015	.05763	1.45
21182	6.034	158.786	15.3567	.10114	.05705	.011	.05660	-.34
21185	5.989	158.547	15.4821	.04560	.05808	.032	.05712	.57
21186	5.989	158.579	15.4027	.07060	.05762	.015	.05671	-.15
21189	5.905	158.353	15.0518	.04557	.05854	.030	.05692	.30
21190	5.905	158.562	14.4821	.07056	.05819	.017	.05698	.83
21193	5.769	158.427	12.9769	.04556	.05182	.032	.05002	-8.50
21194	5.769	158.550	12.6474	.07052	.05163	.016	.05029	-6.23
21195	5.769	158.742	12.1713	.10093	.04960	.017	.04891	-6.16
21197	5.621	158.366	11.0163	.02602	.04317	.028	.04184	-12.95
21198	5.621	158.529	10.7160	.04555	.04381	.011	.04294	-6.87
21202	5.622	158.264	11.2394	.01193	.04968	.138	.04800	-.51
21203	5.433	158.234	9.2741	.01196	.04348	.406	.04271	8.66
21204	5.433	158.412	9.0985	.02608	.03555	.097	.03502	-9.00
21205	5.433	158.691	8.8605	.04567	.03569	.043	.03545	-4.46
21206	5.433	159.001	8.6308	.07073	.03483	.028	.03483	-3.19
21210	5.093	158.415	7.2671	.01196	.02991	.266	.02963	-2.42
21211	5.093	158.487	7.2402	.02608	.02852	.077	.02828	-6.98
21212	5.093	158.851	7.1117	.04568	.02958	.035	.02952	-.95
21213	5.093	159.300	6.9675	.07079	.02879	.020	.02891	-1.32
21241	3.758	158.450	4.0129	.01196	.01968	.143	.01965	-4.45
21242	3.758	158.775	3.9896	.02611	.02010	.050	.02009	-1.89
21243	3.758	159.327	3.9517	.04578	.01976	.025	.01978	-3.06
21244	3.758	160.053	3.9030	.07102	.02038	.013	.02042	.73
21245	3.758	160.836	3.8527	.10191	.02036	.009	.02041	1.23
21247	3.073	158.919	2.9864	.02612	.01785	.046	.01785	-3.07
21248	3.073	159.548	2.9615	.04581	.01834	.020	.01833	-.15
21249	3.073	160.313	2.9321	.07109	.01829	.012	.01825	-.27
21250	3.073	161.316	2.8949	.10207	.01835	.006	.01827	.19
21251	2.213	159.072	1.9695	.02614	.01669	.048	.01669	-.73
21252	2.213	159.801	1.9549	.04586	.01656	.020	.01651	-1.70
21253	2.213	160.689	1.9376	.07119	.01662	.010	.01651	-1.56
21254	2.213	161.887	1.9148	.10230	.01697	.012	.01677	.20
21255	1.141	159.198	.9297	.02615	.01540	.044	.01538	-1.55
21256	1.141	160.078	.9234	.04591	.01531	.017	.01522	-2.61
21257	1.140	161.204	.9150	.07134	.01543	.010	.01524	-2.40
21258	1.140	162.548	.9057	.10255	.01565	.006	.01534	-1.65
21259	.226	158.833	.1737	.01198	.01464	.125	.01465	-1.96
21260	.226	159.562	.1726	.02619	.01487	.041	.01482	-.82
21261	.226	160.640	.1714	.04600	.01499	.017	.01484	-.65
21262	.225	162.062	.1696	.07155	.01523	.009	.01495	.11

Run Pt.	Pressure MPa	Temperature K	Density mol/L	Power W/m	Experimental Thermal Conductivity W/m.K	STAT	Adjusted Thermal Conductivity at a nominal Temperature of 178.K from Correlation		
							W/m.K	Deviation percent	
24001	68.349	178.050	30.3567	.15601	.11748	.023	.11747	.75	
24002	68.347	178.543	30.3102	.25674	.11738	.007	.11730	.95	
24003	68.345	179.133	30.2547	.38265	.11652	.002	.11636	.55	
24004	68.345	179.884	30.1844	.53412	.11601	.002	.11575	.54	
24005	68.343	180.827	30.0959	.71135	.11559	.002	.11520	.71	
24006	56.467	178.210	29.2320	.15600	.10737	.017	.10734	-.02	
24007	56.471	178.666	29.1852	.25665	.10706	.010	.10697	-.02	
24008	56.474	179.269	29.1232	.38270	.10750	.006	.10733	.76	
24009	56.475	180.114	29.0359	.53420	.10671	.003	.10642	.56	
24010	56.477	180.528	28.9934	.61950	.10622	.003	.10587	.35	
24011	46.625	178.142	28.1214	.15615	.09863	.018	.09861	-.38	
24012	46.624	178.738	28.0529	.25705	.09841	.009	.09831	-.18	
24013	46.622	179.399	27.9768	.38329	.09762	.005	.09743	-.53	
24014	46.622	180.240	27.8803	.53507	.09756	.003	.09726	.00	
24015	46.621	180.792	27.8168	.62084	.09750	.003	.09712	.33	
24017	39.666	178.782	27.0838	.25705	.09215	.007	.09205	.27	
24018	39.664	179.543	26.9874	.38334	.09157	.004	.09137	.23	
24019	39.661	180.396	26.8796	.53544	.09130	.003	.09099	.58	
24020	39.658	181.164	26.7823	.62101	.09111	.003	.09070	.96	
24021	33.641	178.284	26.1449	.15622	.08584	.016	.08580	-.02	

24022	33.639	178.862	26.0639	.25707	.08593	.008	.08582	.58
24023	33.638	179.710	25.9452	.38348	.08550	.005	.08529	.79
24024	33.637	180.618	25.8182	.53559	.08480	.003	.08447	.73
24027	29.187	179.745	25.0259	.38358	.08059	.003	.08038	1.30
24028	29.187	180.741	24.8728	.53573	.07969	.002	.07937	1.09
24029	25.039	178.367	24.2220	.15623	.07514	.015	.07510	-.01
24030	25.039	179.040	24.1065	.25719	.07447	.008	.07436	-.23
24032	25.041	180.962	23.7763	.53598	.07429	.003	.07398	1.44
24033	22.058	178.021	23.3931	.11521	.07125	.022	.07125	.19
24034	22.058	178.756	23.2532	.20352	.07116	.009	.07109	.86
24035	22.058	179.528	23.1061	.31729	.07090	.005	.07076	1.32
24037	19.306	178.095	22.3668	.11523	.06816	.023	.06815	2.14
24038	19.306	178.733	22.2300	.20359	.06615	.010	.06609	-.07
24040	19.305	180.753	21.7943	.45693	.06603	.003	.06584	2.09
24041	17.340	178.096	21.4696	.11522	.06391	.013	.06390	.99
24042	17.340	178.795	21.3024	.20361	.06375	.006	.06371	1.61
24043	17.340	179.713	21.0818	.31747	.06325	.004	.06316	1.96
24045	15.672	178.193	20.5050	.11523	.06033	.009	.06032	.47
24046	15.672	178.919	20.3094	.20366	.06045	.003	.06042	1.63
24049	14.309	178.174	19.5542	.11525	.05739	.015	.05739	.23
24050	14.309	179.020	19.2989	.20372	.05784	.006	.05784	2.19
24051	14.308	179.949	19.0173	.31767	.05757	.004	.05758	3.02
24053	13.213	178.285	18.5648	.11527	.05514	.016	.05515	.78
24054	13.214	179.035	18.3140	.20376	.05506	.007	.05509	1.76
24057	12.353	178.268	17.6529	.11530	.05315	.016	.05316	1.03
24058	12.353	179.093	17.3511	.20379	.05294	.008	.05300	1.97
24061	11.563	178.182	16.6688	.08062	.05082	.026	.05083	.64
24062	11.562	178.501	16.5413	.11546	.05053	.016	.05057	.64
24063	11.562	179.367	16.1993	.20403	.05068	.009	.05079	2.47
24066	10.970	178.168	15.7724	.08053	.04861	.025	.04863	-.05
24067	10.971	178.447	15.6558	.11532	.04853	.012	.04857	.34
24071	10.421	177.892	14.9305	.05204	.04628	.038	.04627	-1.35
24072	10.421	178.126	14.8286	.08059	.04669	.014	.04670	.06
24073	10.421	178.411	14.7055	.11541	.04653	.005	.04657	.34
24076	9.835	177.842	13.7895	.05203	.04447	.044	.04445	.11
24077	9.835	178.138	13.6603	.08058	.04358	.022	.04360	-1.18
24078	9.835	178.482	13.5126	.11540	.04305	.016	.04311	-1.55
24081	9.385	177.852	12.8004	.05202	.04213	.043	.04211	.03
24082	9.385	178.247	12.6347	.08055	.04246	.033	.04249	1.85
24083	9.384	178.474	12.5406	.11538	.04171	.014	.04176	.70
24086	8.922	177.876	11.7189	.05201	.03873	.025	.03872	-1.81
24087	8.922	178.177	11.6030	.08056	.03893	.013	.03895	-.45
24091	8.432	177.919	10.5510	.05201	.03605	.036	.03604	-.93
24092	8.430	178.325	10.4141	.08056	.03568	.020	.03571	-.88
24096	8.428	177.636	10.6388	.02970	.03598	.083	.03595	-1.85
24097	7.989	178.032	9.5093	.05202	.03341	.035	.03341	-.62
24098	7.987	178.409	9.4035	.08060	.03327	.022	.03329	-.14
24099	7.987	178.984	9.2525	.11547	.03330	.012	.03335	1.22
24102	7.433	178.065	8.3303	.05204	.03055	.029	.03055	.05
24103	7.431	178.540	8.2273	.08063	.03067	.013	.03068	1.33
24104	7.430	179.226	8.0897	.11552	.03082	.008	.03084	2.97
24107	6.876	178.232	7.2499	.05204	.02806	.014	.02806	.77
24108	6.874	178.691	7.1758	.08065	.02781	.009	.02781	.51
24112	6.218	178.363	6.1471	.05205	.02589	.025	.02588	2.25
24113	6.212	178.890	6.0821	.08067	.02561	.013	.02558	1.67
24114	6.209	179.663	5.9977	.11567	.02533	.009	.02527	1.18
24116	5.536	178.468	5.1569	.05212	.02277	.028	.02275	-2.15
24117	5.535	179.023	5.1136	.08083	.02378	.017	.02373	2.43
24120	4.610	177.980	4.0278	.02975	.02146	.049	.02146	1.30
24121	4.609	178.654	3.9942	.05214	.02114	.021	.02109	-.16
24122	4.609	179.348	3.9608	.08086	.02129	.012	.02119	.57
24123	4.608	180.314	3.9158	.11600	.02117	.007	.02100	.02
24124	3.519	178.132	2.8532	.02977	.01925	.044	.01924	-.94
24125	3.519	178.832	2.8331	.05217	.01929	.019	.01922	-.89
24127	3.518	180.753	2.7811	.11614	.01939	.008	.01916	-.85
24128	2.614	178.229	2.0064	.02977	.01812	.041	.01810	-1.55
24129	2.613	178.956	1.9935	.05220	.01856	.029	.01848	.60
24130	2.612	179.975	1.9766	.08100	.01832	.012	.01815	-1.10
24131	2.612	180.520	1.9679	.09783	.01846	.007	.01824	-.53
24132	1.326	178.394	.9499	.02978	.01688	.041	.01684	-2.79
24133	1.325	179.249	.9442	.05225	.01710	.017	.01699	-1.89
24134	1.325	180.432	.9365	.08111	.01698	.009	.01676	-3.22

Run Pt.	Pressure MPa	Temperature K	Experimental				Adjusted Thermal Conductivity		
			Density mol/L	Power W/m	Thermal Conductivity W/m.K	STAT	at a nominal Temperature of 202.K	Deviation from Correlation percent	
15001	64.673	200.900	27.8712	.17868	.10040	.031	.10054	.17	
15002	64.669	201.006	27.8610	.23272	.09967	.021	.09980	-.50	
15003	64.669	201.484	27.8167	.29389	.10087	.015	.10094	.95	
15004	64.669	201.810	27.7866	.36230	.10038	.011	.10040	.63	
15005	64.665	202.159	27.7540	.43783	.09923	.008	.09921	-.33	
15007	64.663	203.047	27.6717	.61115	.09978	.006	.09965	.69	
15009	60.534	201.086	27.3932	.23262	.09731	.020	.09743	.40	
15010	60.536	201.731	27.3315	.36224	.09664	.011	.09667	.06	
15012	60.539	202.592	27.2495	.52077	.09466	.007	.09458	-1.56	
15013	60.541	203.006	27.2103	.61096	.09574	.005	.09561	-.19	
15014	56.501	201.103	26.9064	.23257	.09418	.019	.09430	.56	
15015	56.504	201.393	26.8778	.29375	.09345	.013	.09353	-.05	
15016	56.511	201.791	26.8392	.36200	.09333	.010	.09336	.04	
15017	56.513	202.082	26.8106	.43788	.09344	.008	.09343	.31	
15018	56.515	202.518	26.7676	.52084	.09290	.006	.09283	-.02	
15020	52.066	201.190	26.3146	.23261	.09006	.018	.09016	.23	
15022	52.088	201.857	26.2482	.36226	.08812	.010	.08814	-1.59	
15023	52.090	202.371	26.1950	.43788	.08845	.007	.08840	-.91	
15024	52.091	202.741	26.1569	.52082	.08812	.006	.08803	-1.08	
15025	52.091	203.179	26.1114	.61116	.08814	.005	.08799	-.80	
15026	47.913	201.310	25.6983	.23258	.08621	.017	.08630	.13	
15027	47.914	201.573	25.6697	.29387	.08583	.013	.08588	-.15	
15030	47.916	202.861	25.5297	.52117	.08513	.005	.08502	-.20	
15032	43.443	201.277	24.9745	.23269	.08177	.017	.08186	-.17	
15033	43.446	201.522	24.9467	.29392	.08187	.013	.08193	.10	
15034	43.450	201.979	24.8945	.36241	.08133	.009	.08133	-.27	
15035	43.451	202.355	24.8513	.43813	.08144	.007	.08140	.10	
15036	43.454	202.798	24.8008	.52125	.08131	.005	.08121	.22	
15037	43.456	203.450	24.7262	.61145	.08091	.004	.08073	.13	
15038	39.473	201.309	24.2379	.23255	.07805	.016	.07813	.16	
15039	39.476	201.592	24.2038	.29391	.07759	.011	.07764	-.25	
15040	39.478	201.986	24.1560	.36243	.07769	.009	.07769	.14	
15041	39.478	202.462	24.0979	.43821	.07747	.006	.07741	.17	
15042	39.483	202.999	24.0331	.52134	.07734	.005	.07722	.35	
15043	39.483	203.560	23.9647	.61186	.07721	.004	.07702	.55	
15044	35.181	201.003	23.3637	.17866	.07314	.023	.07326	-.49	
15045	35.185	201.380	23.3148	.23275	.07371	.016	.07378	.54	
15046	35.187	201.750	23.2665	.29397	.07330	.011	.07333	.24	
15047	35.191	202.210	23.2071	.36262	.07316	.008	.07314	.37	
15048	35.192	202.661	23.1480	.43844	.07294	.006	.07286	.38	
15049	35.194	203.228	23.0742	.52154	.07287	.004	.07273	.67	
15050	31.371	201.078	22.3987	.17870	.06941	.022	.06951	.46	
15051	31.371	201.397	22.3332	.23272	.06879	.014	.06886	-.20	
15052	31.375	201.843	22.2912	.29404	.06873	.010	.06875	.03	
15053	31.376	202.295	22.2272	.36260	.06847	.007	.06844	-.02	
15054	31.378	202.747	22.1639	.43849	.06887	.006	.06879	.89	
15055	31.379	203.442	22.0659	.52168	.06835	.004	.06819	.63	
15056	28.064	201.119	21.4072	.17874	.06515	.019	.06524	.23	
15057	28.068	201.516	21.3473	.23274	.06480	.014	.06485	-.01	
15058	28.069	201.876	21.2924	.29414	.06467	.010	.06468	.07	
15059	28.070	202.431	21.2080	.36275	.06464	.007	.06460	.44	
15060	28.071	202.946	21.1299	.43863	.06457	.006	.06448	.71	
20001	67.997	200.197	26.2809	.09196	.10074	.089	.10097	-2.33	
20002	67.991	200.402	26.2618	.13157	.10267	.052	.10287	-.30	
20003	67.985	200.625	26.2410	.17840	.10323	.030	.10341	.36	
20004	67.990	200.891	26.2176	.23233	.10260	.021	.10274	-.12	
20005	67.990	201.157	26.1928	.29346	.10184	.014	.10195	-.72	
20006	67.990	201.553	26.1579	.36171	.10210	.010	.10216	-.26	
20007	67.991	201.807	26.1352	.43725	.10201	.008	.10203	-.22	
20008	67.985	202.281	26.0919	.52019	.10199	.005	.10195	.01	
20009	67.983	202.696	26.0544	.60980	.10163	.005	.10154	-.13	
20010	67.982	203.132	26.0152	.70751	.10171	.004	.10157	.17	
20011	59.170	200.693	27.2716	.17842	.09610	.026	.09627	.06	
20012	59.173	201.197	27.2230	.29354	.09504	.012	.09514	-.77	
20013	59.168	201.995	27.1450	.43759	.09512	.007	.09512	-.24	
20014	59.170	202.852	27.0622	.61076	.09468	.004	.09457	-.24	
20015	49.829	200.734	26.0461	.17848	.08707	.026	.08723	-1.21	
20016	49.830	201.391	25.9760	.29366	.08706	.011	.08714	-.83	
20017	49.832	202.170	25.8932	.43775	.08624	.007	.08622	-1.32	
20018	49.830	203.073	25.7969	.61091	.08683	.004	.08669	-.10	
20019	42.597	200.552	24.9109	.13167	.08115	.038	.08133	-.39	
20020	42.602	201.097	24.8478	.23252	.08140	.016	.08151	.27	
20021	42.602	201.847	24.7601	.36220	.08064	.008	.08066	-.19	
20022	42.602	202.718	24.6585	.52096	.08031	.005	.08022	-.04	
20023	37.182	200.559	23.8635	.13173	.07602	.035	.07619	.15	
20024	37.177	201.212	23.7792	.23262	.07537	.015	.07546	-.26	
20025	37.175	201.982	23.6811	.36240	.07533	.008	.07533	.22	
20026	37.172	202.987	23.5530	.52131	.07476	.005	.07464	.14	
20027	33.073	200.593	22.9120	.13172	.07137	.033	.07153	.06	
20028	33.071	201.270	22.8185	.23265	.07109	.014	.07117	.16	
20029	33.070	202.113	22.7027	.36248	.07083	.007	.07082	.39	
20030	33.069	203.205	22.5531	.52151	.07034	.004	.07021	.48	
20031	29.342	200.412	21.9140	.09204	.06608	.052	.06625	-1.33	
20032	29.342	200.974	21.6302	.17866	.06666	.019	.06677	-.02	

20033	29.340	201.755	21.7135	.29400	.06637	.009	.06640	.13
20034	29.340	202.726	21.5695	.43843	.06617	.005	.06610	.55
20035	26.332	200.474	20.9162	.09203	.06335	.050	.06350	.44
20036	26.331	201.044	20.8240	.17867	.06304	.018	.06313	.41
20037	26.330	201.852	20.6938	.29407	.06257	.008	.06258	.30
20038	26.330	202.889	20.5282	.43858	.06234	.005	.06226	.73
20039	23.773	200.442	19.9185	.09204	.05983	.047	.05996	.42
20040	23.772	201.077	19.8078	.17868	.05944	.017	.05952	.29
20041	23.772	201.948	19.6576	.29415	.05908	.008	.05908	.39
20042	23.770	203.149	19.4510	.43876	.05874	.005	.05865	.77
20043	21.560	200.485	18.8745	.09207	.05618	.044	.05629	.26
20044	21.560	201.181	18.7454	.17872	.05619	.015	.05625	.34
20045	21.558	201.595	18.6683	.23281	.05577	.011	.05580	.05
20046	21.558	202.570	18.4890	.36289	.05549	.006	.05545	.25
20047	19.717	200.507	17.8455	.09206	.05279	.042	.05287	-1.24
20048	19.717	201.199	17.7092	.17872	.05289	.014	.05293	-43
20049	19.716	201.694	17.6123	.23286	.05278	.010	.05280	-21
20051	18.171	200.489	16.8409	.09207	.05053	.037	.05060	.66
20052	18.171	201.202	16.6945	.17875	.04999	.013	.05002	-1.08
20053	18.170	201.736	16.5860	.23288	.05012	.010	.05013	-33
20054	18.169	202.863	16.3596	.36297	.04986	.005	.04982	.16
20055	16.888	200.601	15.8536	.09207	.04817	.036	.04822	-65
20056	16.887	201.428	15.6801	.17877	.04774	.014	.04776	-78
20059	15.656	200.689	14.7841	.09209	.04557	.037	.04560	.94
20060	15.655	201.455	14.6225	.17882	.04505	.013	.04506	-1.32
20061	15.655	201.973	14.5153	.23299	.04497	.008	.04497	-98
20063	14.725	200.647	13.9116	.09208	.04334	.035	.04337	-1.49
20064	14.724	201.543	13.7255	.17885	.04313	.013	.04314	-1.04
20065	14.724	202.127	13.5071	.23305	.04298	.009	.04298	-78
20067	13.748	200.754	12.8843	.09211	.04129	.032	.04132	-70
20068	13.748	201.612	12.7138	.17889	.04067	.012	.04068	-1.39
20071	12.676	200.743	11.7017	.09213	.03824	.030	.03827	-1.58
20072	12.676	201.899	11.4909	.17899	.03810	.011	.03810	-73
20073	12.676	202.434	11.3965	.23334	.03802	.007	.03801	-40
20075	11.902	200.804	10.7963	.09222	.03617	.028	.03621	-1.51
20076	11.902	201.916	10.6109	.17913	.03619	.011	.03619	-35
20079	11.159	200.934	9.9027	.09221	.03428	.027	.03432	-1.02
20080	11.159	201.448	9.8253	.13208	.03429	.015	.03431	-52
20081	11.158	202.081	9.7316	.17917	.03400	.010	.03400	-82
20082	11.158	202.748	9.6363	.23354	.03408	.007	.03405	-02
20083	10.258	201.192	8.8144	.09224	.03262	.016	.03266	1.43
20084	10.257	201.851	8.7308	.13216	.03245	.009	.03246	1.39
20085	10.257	202.636	8.6351	.17928	.03280	.006	.03277	2.98
20087	9.344	201.320	7.7639	.09227	.03029	.014	.03033	1.41
20088	9.344	202.071	7.6870	.13219	.03032	.009	.03032	1.90
20089	9.344	202.898	7.6043	.17941	.03054	.006	.03049	3.02
20095	7.517	201.022	5.8512	.05959	.02649	.020	.02656	1.69
20096	7.517	201.850	5.7978	.09232	.02646	.008	.02647	1.72
20097	7.517	202.588	5.7514	.13229	.02697	.005	.02693	3.70
20098	7.517	203.590	5.6900	.17952	.02679	.005	.02667	3.19
20099	6.601	201.197	4.9513	.05957	.02510	.037	.02516	2.48
20100	6.601	201.901	4.9166	.09230	.02457	.013	.02458	.39
20101	6.601	202.845	4.8711	.13229	.02455	.008	.02448	.31
20103	5.530	200.717	3.9999	.03399	.02248	.024	.02259	-2.02
20104	5.530	201.271	3.9801	.05955	.02301	.016	.02307	.25
20106	5.528	203.063	3.9171	.13230	.02316	.007	.02307	.64
20107	4.309	200.732	2.9781	.03400	.02160	.042	.02171	.34
20108	4.308	201.354	2.9632	.05957	.02177	.019	.02183	.96
20109	4.308	202.308	2.9414	.09233	.02175	.010	.02172	.62
20110	4.307	203.421	2.9161	.13241	.02174	.006	.02162	.28
20111	3.006	200.784	1.9829	.03400	.02041	.043	.02052	.28
20112	3.005	201.562	1.9720	.05959	.02046	.019	.02050	.25
20113	3.005	202.555	1.9589	.09239	.02046	.010	.02041	-10
20114	3.004	203.831	1.9420	.13250	.02054	.006	.02038	-17
20115	1.381	200.971	.8625	.03401	.01922	.038	.01931	-14
20116	1.381	201.949	.8575	.05962	.01921	.016	.01921	-61
20117	1.381	203.027	.8521	.09248	.01929	.008	.01920	-64
20118	1.380	204.509	.8448	.13267	.01941	.006	.01919	-65

Run Pt.	Pressure MPa	Temperature K	Density mol/L	Power W/m	Experimental Thermal Conductivity W/m.K	STAT	Adjusted Thermal Conductivity at a nominal Temperature of 210.K from Correlation	
							W/m.K	Deviation percent
14004	63.772	216.715	26.3276	.19390	.09148	.058	.09164	-.44
14005	63.773	217.159	26.2881	.25249	.09402	.042	.09412	2.48
14006	63.772	217.499	26.2576	.31894	.09306	.028	.09312	1.63
14007	63.773	217.954	26.2171	.39322	.09187	.020	.09188	.58
14008	63.776	218.450	26.1733	.47533	.09067	.016	.09062	-.51
14009	61.728	217.145	26.0370	.25245	.09028	.039	.09038	.17
14010	61.733	218.025	25.9577	.39313	.08998	.020	.08998	.26
14011	59.738	217.226	25.7739	.25243	.08923	.039	.08932	.77
14012	59.739	218.042	25.6988	.39313	.08652	.021	.08651	-1.93
14013	57.531	217.155	25.4847	.25244	.08708	.038	.08718	.31
14014	57.533	218.050	25.4009	.39310	.08901	.021	.08900	2.90
14015	55.350	217.232	25.1710	.25266	.08319	.036	.08328	-2.18
14016	55.353	218.057	25.0923	.39370	.08420	.019	.08419	-.54
14017	53.341	217.270	24.8715	.25282	.08400	.035	.08409	.82

14018	53.343	218.158	24.7849	.39370	.08380	.017	.08378	1.03
14019	51.181	217.262	24.5379	.25284	.08193	.034	.08202	.55
14020	51.182	218.108	24.4534	.39381	.08204	.018	.08203	1.12
14021	48.674	217.320	24.1204	.25283	.07983	.033	.07991	.72
14022	48.677	218.203	24.0301	.39381	.07748	.017	.07746	-1.82
14023	46.380	217.345	23.7161	.25286	.07720	.030	.07728	.02
14024	46.383	218.346	23.6110	.39379	.07832	.017	.07828	1.98
14025	44.287	217.283	23.3323	.25291	.07473	.033	.07481	-.72
14026	44.290	218.427	23.2091	.39384	.07516	.018	.07511	.47
14027	42.045	217.459	22.8661	.25284	.07371	.029	.07377	.87
14028	42.047	218.398	22.7617	.39392	.07442	.017	.07437	2.33
14029	39.933	217.430	22.4166	.25282	.07143	.029	.07149	.59
14031	37.909	217.413	21.9519	.25289	.06965	.028	.06972	.97
14032	37.908	218.544	21.8183	.39392	.06883	.015	.06877	.43
14035	35.645	217.029	21.4324	.19419	.06593	.043	.06603	-1.27
14036	35.644	217.433	21.3827	.25289	.06599	.026	.06605	-.94
14038	35.643	218.636	21.2356	.39397	.06779	.016	.06772	2.42
14040	33.299	217.655	20.7087	.25279	.06459	.027	.06463	.91
14041	33.301	218.693	20.5777	.39385	.06388	.015	.06381	.41
14043	31.082	218.934	19.8622	.39377	.06141	.017	.06132	.57
14044	28.891	217.813	19.2605	.25354	.05946	.025	.05948	.89
14046	28.942	216.641	19.4396	.06485	.06048	.172	.06060	1.76
14049	28.941	217.592	19.3087	.19480	.06009	.037	.06013	1.70
14050	28.941	218.094	19.2401	.25346	.05942	.025	.05941	.89
14051	28.941	218.714	19.1558	.32023	.05969	.017	.05963	1.71
14052	28.941	219.330	19.0724	.39491	.05952	.013	.05940	1.79
14054	26.727	218.200	18.3732	.25338	.05773	.024	.05771	2.67
14055	26.728	219.596	18.1775	.39476	.05633	.013	.05620	1.09
14056	24.415	218.390	17.3279	.25338	.05367	.024	.05364	.87
14057	24.416	219.682	17.1416	.39487	.05410	.012	.05398	2.43
14058	22.418	218.472	16.3090	.25336	.05103	.021	.05100	1.03
14060	20.090	216.906	15.1937	.10018	.04793	.073	.04799	.61
14061	20.090	217.412	15.1163	.14340	.04727	.047	.04730	-.43
14062	20.090	217.897	15.0426	.19449	.04705	.031	.04706	-.58
14063	20.090	218.595	14.9379	.25333	.04709	.021	.04706	-.04
14066	17.465	218.113	13.2194	.19477	.04275	.029	.04274	-.65
14068	15.066	217.702	11.3916	.14377	.03887	.037	.03889	.19
14070	12.809	218.029	9.4263	.14382	.03366	.039	.03366	-2.27
14073	10.596	217.485	7.5485	.10044	.03000	.049	.03004	-1.58
14074	10.595	218.278	7.4876	.14390	.03067	.029	.03065	.84
14075	10.595	219.251	7.4155	.19521	.03118	.018	.03109	2.70
14079	8.145	217.897	5.4763	.10049	.02745	.041	.02746	2.72
14080	8.145	218.862	5.4310	.14399	.02740	.027	.02733	2.54
14081	8.145	219.889	5.3839	.19540	.02735	.018	.02720	2.35
14083	5.972	219.342	3.7689	.14406	.02443	.025	.02431	.97
14084	4.594	217.549	2.8380	.06491	.02303	.066	.02307	.95
14085	4.594	219.652	2.7990	.14414	.02302	.021	.02288	.33
14087	3.168	217.762	1.8861	.06491	.02140	.067	.02142	-1.49
14088	3.168	218.746	1.8752	.10060	.02139	.036	.02133	-1.89
14089	3.168	220.143	1.8600	.14419	.02157	.021	.02139	-1.53
14090	3.168	221.664	1.8437	.19582	.02193	.013	.02162	-.36
14092	1.738	217.970	.9986	.06492	.02074	.060	.02074	-.40
14093	1.738	219.183	.9923	.10062	.02072	.034	.02062	-.97
14095	1.737	221.512	.9799	.16913	.02101	.016	.02071	-.45

Run Pt.	Pressure MPa	Temperature K	Density mol/L	Power W/m	Experimental Thermal Conductivity W/m.K	STAT	Adjusted Thermal Conductivity at a nominal Temperature of 242.K from Correlation		
							W/m.K	Deviation percent	
10001	64.660	242.903	24.2073	.21945	.08277	.038	.08268	.18	
10003	64.653	243.730	24.1396	.36091	.08221	.019	.08203	-.17	
10005	64.648	244.993	24.0372	.53768	.08143	.011	.08112	-.63	
10006	62.093	243.314	23.8165	.28582	.08059	.023	.08045	-.05	
10007	62.097	244.376	23.7299	.44492	.08104	.014	.08079	.91	
10009	59.868	244.388	23.4018	.44495	.07816	.013	.07791	-.64	
10010	57.704	243.301	23.1615	.28530	.07739	.025	.07725	.03	
10011	57.705	244.434	23.0655	.44440	.07680	.012	.07654	-.29	
10012	55.570	243.266	22.8223	.28551	.07409	.024	.07396	-2.23	
10013	55.573	244.338	22.7302	.44458	.07488	.013	.07463	-.73	
10014	53.426	243.323	22.6559	.28547	.07398	.023	.07384	-.09	
10015	53.430	244.466	22.3564	.44455	.07416	.014	.07390	.60	
10016	51.310	243.363	22.0770	.28548	.06941	.028	.06927	-4.24	
10017	51.312	244.503	21.9756	.44452	.07261	.011	.07235	.82	
10018	49.325	243.402	21.7023	.28549	.07074	.023	.07059	.03	
10019	49.325	244.526	21.6003	.44459	.07106	.011	.07080	.93	
10020	47.112	243.475	21.2560	.28549	.06914	.024	.06899	.40	
10021	47.115	244.583	21.1561	.44464	.06901	.012	.06875	.66	
10022	44.975	243.434	20.8125	.28552	.06659	.021	.06645	-.71	
10023	44.978	244.693	20.6943	.44462	.06701	.011	.06674	.44	
10024	42.944	243.481	20.3534	.28556	.06499	.021	.06484	-.45	
10025	42.946	244.693	20.2377	.44475	.06489	.011	.06463	-.11	

10026	40.835	243.509	19.8470	.28535	.06372	.021	.06357	.50
10027	40.837	243.506	19.8477	.28533	.06407	.021	.06392	1.04
10029	38.635	243.591	19.2743	.28545	.06110	.020	.06103	-.33
10030	38.636	244.843	19.1501	.44465	.06203	.011	.06177	1.55
10031	35.622	243.578	18.4276	.28563	.05881	.018	.05867	.42
10032	35.623	244.999	18.2835	.44489	.05908	.010	.05882	1.45
10033	33.413	243.645	17.7348	.28570	.05686	.019	.05672	.80
10035	31.582	243.710	17.1122	.28567	.05480	.018	.05466	.43
10036	31.582	245.241	16.9534	.44487	.05520	.010	.05494	1.76
10037	29.404	243.063	16.3846	.21906	.05182	.023	.05174	-1.25
10038	29.404	244.392	16.2447	.36052	.05310	.012	.05292	1.73
10039	27.213	243.144	15.4975	.21912	.05041	.025	.05033	.60
10041	24.734	243.256	14.3858	.21913	.04751	.023	.04743	.43
10043	22.685	243.312	13.3788	.21917	.04505	.020	.04496	.37
10045	20.444	243.445	12.1721	.21924	.04223	.020	.04214	.33
10047	18.097	243.524	10.8114	.21903	.03886	.019	.03876	-.93
10049	15.678	243.813	9.3038	.21919	.03655	.018	.03642	1.81
10050	15.678	244.823	9.2308	.28543	.03715	.014	.03695	3.61
10051	13.498	243.055	7.9648	.16153	.03378	.026	.03370	1.79
10053	11.514	243.340	6.6690	.16165	.03131	.023	.03120	1.59
13013	10.024	243.424	5.7138	.11326	.02930	.038	.02918	.36
13016	10.024	244.351	5.6778	.16220	.02944	.023	.02925	.78
13018	10.024	245.442	5.6362	.22001	.02970	.016	.02942	1.58
10055	9.257	243.585	5.2240	.16151	.02871	.023	.02858	1.01
13030	7.367	244.685	4.0319	.16222	.02716	.023	.02693	1.59
13031	7.367	245.967	4.0009	.22003	.02729	.015	.02695	1.83
10057	6.991	242.840	3.8493	.11281	.02632	.035	.02625	.00
10059	6.991	245.235	3.7946	.21916	.02693	.014	.02665	1.81
13035	5.183	245.196	2.7642	.16223	.02516	.021	.02489	.38
10060	4.396	243.185	2.3256	.11284	.02435	.034	.02425	-.15
10061	4.395	246.022	2.2910	.21926	.02461	.013	.02427	.11
10062	2.368	242.415	1.2188	.07287	.02287	.055	.02284	-.93
10063	2.367	243.574	1.2118	.11287	.02303	.030	.02290	-.62
10064	2.367	245.053	1.2034	.16173	.02322	.018	.02297	-.28
10065	2.365	246.748	1.1932	.21937	.02340	.010	.02301	-.05
18031	67.261	239.643	24.8126	.15974	.08516	.065	.08541	-.46
18032	67.258	239.942	24.7881	.21666	.08536	.043	.08558	-.10
18033	67.258	240.362	24.7543	.28216	.08554	.025	.08571	.27
18034	67.256	240.899	24.7110	.35632	.08513	.018	.08525	.01
18035	67.256	241.411	24.6700	.43923	.08502	.014	.08508	.08
18036	67.255	241.995	24.6232	.53089	.08487	.011	.08487	.13
18037	67.254	242.671	24.5691	.63127	.08500	.009	.08493	.55
18038	67.253	243.377	24.5129	.74047	.08466	.006	.08452	.42
18039	60.668	239.741	23.9095	.15979	.07955	.055	.07979	-1.48
18040	60.672	240.585	23.8389	.28209	.07936	.026	.07951	-1.38
18041	60.670	241.606	23.7528	.43924	.07932	.014	.07936	-1.02
18043	54.839	239.705	23.0134	.15984	.07649	.060	.07674	.28
18044	54.839	240.635	22.9314	.28209	.07634	.026	.07649	.47
18045	54.840	241.756	22.8330	.43924	.07558	.013	.07561	-.07
18046	54.840	243.144	22.7119	.63136	.07567	.008	.07555	.61
18047	49.399	239.433	22.0814	.11163	.07245	.097	.07272	.68
18048	49.401	240.265	22.0045	.21658	.07170	.037	.07188	-.01
18049	49.400	241.375	21.9021	.35625	.07015	.018	.07022	-1.74
18050	49.399	242.693	21.7812	.53084	.07115	.010	.07108	.23
18051	44.338	239.593	21.0420	.11164	.06711	.088	.06736	-.70
18052	44.335	240.311	20.9717	.21666	.06738	.034	.06755	.01
18053	44.332	241.475	20.8588	.35631	.06693	.016	.06698	-.17
18054	44.328	242.834	20.7277	.53113	.06707	.009	.06699	.61
18056	39.714	240.397	19.8758	.21663	.06326	.027	.06342	.08
18057	39.713	241.672	19.7472	.35632	.06303	.015	.06306	.26
18058	39.713	243.125	19.6023	.53118	.06276	.008	.06265	.44
18060	35.670	239.880	18.8253	.16000	.05924	.041	.05943	-.48
18061	35.669	241.033	18.7042	.28255	.05924	.019	.05933	.02
18062	35.668	242.489	18.5529	.44000	.05903	.010	.05899	.27
18064	33.172	240.016	18.0395	.16021	.05669	.042	.05686	-.59
18065	33.170	241.166	17.9160	.28278	.05689	.016	.05696	.25
18066	33.169	242.747	17.7491	.44021	.05681	.010	.05675	.77
18068	30.056	240.063	16.9534	.16010	.05339	.041	.05354	-.80
18069	30.055	241.293	16.8195	.28267	.05344	.018	.05350	-.19
18072	27.526	240.148	15.9518	.16012	.05065	.042	.05079	-.85
18073	27.525	241.503	15.8033	.28270	.05112	.019	.05116	.65
18076	25.091	240.224	14.8751	.16006	.04807	.039	.04819	-.51
18077	25.090	241.629	14.7228	.28270	.04821	.017	.04824	.37
18079	22.852	239.597	13.8504	.07230	.04509	.118	.04525	-1.49
18080	22.851	240.575	13.7459	.16018	.04540	.033	.04549	-.39
18081	22.851	242.061	13.5906	.28272	.04592	.016	.04592	1.34
18083	20.668	239.642	12.6718	.07217	.04279	.111	.04294	-.68
18084	20.667	240.736	12.5604	.15995	.04261	.034	.04269	-.46
18085	20.666	242.286	12.4065	.28243	.04294	.014	.04292	.90
18089	18.811	241.616	11.4059	.21728	.04034	.020	.04036	.23
18090	18.810	240.764	11.4843	.16026	.03969	.033	.03977	-1.71
18091	18.809	240.089	11.5473	.11196	.04009	.050	.04021	-.94

18093	17.149	242.615	10.3125	.28310	.03865	.014	.03861	1.88
18094	17.146	241.663	10.3901	.21731	.03891	.021	.03893	2.26
18095	17.144	240.886	10.4547	.16026	.03800	.030	.03807	.30
18096	17.142	240.164	10.5160	.11191	.03851	.052	.03863	.80
18098	15.378	242.939	9.1781	.28311	.03595	.013	.03588	1.05
18099	15.375	241.897	9.2526	.21732	.03634	.018	.03635	1.89
18100	15.374	241.085	9.3121	.16023	.03567	.028	.03573	.13
18101	15.372	240.296	9.3710	.11191	.03575	.048	.03587	.09
18104	13.712	240.502	8.2656	.11189	.03340	.044	.03351	.51
18105	13.710	241.241	8.2162	.16025	.03358	.026	.03364	.15
18106	13.708	242.189	8.1543	.21732	.03397	.017	.03396	1.45
18108	12.021	239.954	7.1749	.07227	.03181	.083	.03197	1.10
18109	12.019	240.587	7.1390	.11191	.03140	.043	.03151	.13
18110	12.017	241.471	7.0902	.16025	.03199	.025	.03203	1.78
18113	10.479	242.839	6.0272	.21745	.03024	.016	.03017	1.89
18114	10.476	241.685	6.0746	.16031	.02993	.022	.02996	.92
18115	10.472	240.691	6.1156	.11195	.02974	.041	.02985	.33
18116	10.470	239.966	6.1463	.07229	.02945	.080	.02962	.63
18003	9.776	240.876	5.6549	.11194	.02923	.038	.02932	1.16
18026	9.779	241.798	5.6207	.16022	.02916	.023	.02918	.86
18029	9.781	242.879	5.5804	.21728	.02934	.015	.02927	1.39
18117	8.794	243.151	4.9493	.21749	.02826	.014	.02816	1.08
18118	8.791	242.012	4.9847	.16033	.02810	.023	.02810	.65
18119	8.789	240.933	5.0193	.11195	.02805	.038	.02814	.61
18121	6.880	240.289	3.8413	.07229	.02624	.056	.02639	.57
18122	6.879	241.220	3.8186	.11196	.02614	.034	.02621	.01
18123	6.877	242.319	3.7923	.16035	.02630	.019	.02627	.40
18124	6.876	243.737	3.7593	.21748	.02640	.014	.02625	.49
18125	5.138	239.727	2.8020	.04126	.02435	.149	.02454	-1.31
18127	5.137	241.431	2.7749	.11198	.02483	.033	.02488	.19
18128	5.136	242.640	2.7556	.16041	.02475	.020	.02470	.46
18129	3.441	243.126	1.7948	.16047	.02360	.020	.02351	.72
18130	3.441	241.765	1.8071	.11200	.02363	.033	.02365	.16
18131	3.440	240.597	1.8174	.07231	.02335	.064	.02347	.99
18132	3.440	239.732	1.8255	.04128	.02366	.128	.02385	.59
18133	1.990	239.902	1.0304	.04128	.02237	.133	.02254	-1.37
18134	1.990	240.756	1.0263	.07233	.02290	.062	.02300	.67
18135	1.990	242.075	1.0198	.11202	.02264	.031	.02263	.91
18136	1.989	243.581	1.0126	.16052	.02295	.019	.02282	.06

Run Pt.	Pressure MPa	Temperature K	Density mol/L	Power W/m	Experimental Thermal Conductivity W/m.K	STAT	Adjusted Thermal Conductivity at a nominal Temperature of 263.K from Correlation		
							W/m.K	Deviation percent	
11001	65.109	262.180	22.7739	.23772	.07654	.006	.07661	-1.06	
11002	65.105	262.731	22.7324	.30959	.07678	.004	.07680	-.56	
11003	65.104	263.325	22.6883	.39095	.07668	.005	.07665	-.49	
11004	65.101	263.958	22.6412	.48187	.07716	.003	.07708	.35	
11005	65.098	264.688	22.5871	.58221	.07679	.005	.07664	.11	
11006	63.123	262.775	22.4377	.30961	.07568	.004	.07570	-.23	
11007	63.124	263.888	22.3547	.48201	.07584	.003	.07576	.35	
11008	61.108	262.672	22.1374	.30971	.07449	.005	.07452	-.00	
11009	61.110	263.979	22.0390	.48200	.07444	.003	.07435	.36	
11010	59.112	262.724	21.8157	.30970	.07341	.004	.07343	.44	
11011	59.112	264.020	21.7166	.48199	.07285	.003	.07276	.11	
11012	56.897	262.702	21.4488	.30972	.07018	.005	.07021	-1.90	
11013	56.899	264.096	21.3411	.48190	.07124	.004	.07114	.07	
11014	54.638	262.798	21.0464	.30961	.06910	.008	.06912	-1.09	
11015	54.639	264.086	20.9454	.48199	.07002	.004	.06992	.66	
11016	52.381	262.778	20.6324	.30962	.06803	.005	.06805	-.24	
11017	52.384	264.132	20.5252	.48199	.06756	.004	.06746	-.49	
11018	49.965	262.778	20.1619	.30969	.06608	.005	.06610	-.44	
11019	49.968	264.191	20.0485	.48200	.06668	.004	.06658	.92	
11020	47.930	262.793	19.7413	.30956	.06459	.006	.06461	-.33	
11021	47.932	264.190	19.6278	.48190	.06411	.004	.06401	-.63	
11022	45.670	262.795	19.2487	.30968	.06285	.004	.06287	-.29	
11023	45.671	264.318	19.1232	.48198	.06206	.005	.06195	-1.07	
11024	43.617	262.857	18.7686	.30966	.06154	.004	.06155	.27	
11025	43.619	264.420	18.6387	.48191	.06178	.004	.06166	1.15	
11026	41.525	262.911	18.2504	.30941	.06018	.004	.06019	.87	
11027	41.527	264.471	18.1198	.48181	.05872	.008	.05860	-1.10	
11028	39.449	262.944	17.7052	.30957	.05762	.005	.05762	-.52	
11029	39.451	264.568	17.5682	.48183	.05808	.002	.05795	.78	
11030	37.255	262.987	17.0891	.30956	.05643	.004	.05643	.68	
11031	37.256	264.605	16.9516	.48197	.05485	.008	.05472	-1.67	
11032	35.188	262.944	16.4747	.30968	.05443	.002	.05443	.33	
11033	35.188	263.852	16.3971	.39088	.05395	.007	.05389	-.27	
11034	32.964	262.313	15.8155	.23776	.05189	.004	.05194	-.90	
11037	30.854	263.935	14.9493	.39081	.05084	.004	.05077	1.32	
11038	28.357	262.387	14.1473	.23768	.04789	.006	.04793	-.28	
11039	28.358	264.152	14.0016	.39084	.04769	.009	.04761	-.20	

11040	26.404	262.485	13.3525	.23763	.04588	.005	.04591	-.47
11041	26.404	264.242	13.2108	.39082	.04622	.006	.04614	.75
11042	24.025	262.648	12.3112	.23763	.04403	.007	.04405	.80
11044	21.793	262.675	11.2747	.23772	.04136	.005	.04138	-.01
11045	21.793	263.706	11.2006	.30948	.04152	.005	.04147	.60
11047	19.540	263.915	10.0856	.30956	.03951	.005	.03945	1.50
11048	17.217	262.256	8.9910	.17525	.03638	.010	.03643	-.59
11049	17.217	264.209	8.8791	.30954	.03679	.012	.03670	.74
11050	15.060	262.292	7.8326	.17535	.03443	.006	.03448	.11
11051	15.059	264.550	7.7221	.30954	.03495	.006	.03483	1.69
11052	12.982	262.356	6.6879	.17522	.03226	.012	.03230	-.37
11053	12.981	263.661	6.6424	.23752	.03290	.005	.03285	1.56
11054	10.801	261.734	5.5215	.12244	.02991	.008	.03001	-1.60
11055	10.800	263.934	5.4513	.23765	.03063	.007	.03055	.55
11056	8.657	261.953	4.43487	.12247	.02837	.008	.02846	-.94
11057	8.657	264.375	4.2916	.23771	.02888	.003	.02877	.43
11059	6.491	264.833	3.1513	.23776	.02703	.003	.02688	-.76
11060	4.421	262.458	2.1268	.12249	.02588	.007	.02592	.47
11061	4.420	265.420	2.0977	.23783	.02585	.003	.02565	-.46
11062	4.420	263.842	2.1129	.17536	.02568	.004	.02561	-.68
11063	2.354	262.808	1.1059	.12235	.02452	.008	.02454	-.41
11064	2.354	264.284	1.0990	.17530	.02459	.005	.02449	-.58
11065	2.354	266.069	1.0908	.23774	.02481	.004	.02456	-.23

Run Pt.	Pressure MPa	Temperature K	Density mol/L	Power W/m	Conductivity W/m.K	STAT	Experimental Thermal Conductivity at a nominal Temperature of 282. K	Adjusted Thermal Conductivity from Correlation Deviation percent
							W/m.K	W/m.K
12001	65.415	281.052	21.4801	.18921	.07345	.042	.07352	.43
12002	65.413	281.663	21.4385	.25644	.07298	.027	.07300	-.03
12003	65.415	282.236	21.4001	.33390	.07329	.020	.07327	.55
12004	65.415	282.894	21.3559	.42150	.07322	.013	.07316	.64
12005	65.415	283.682	21.3033	.51942	.07250	.009	.07238	-.12
12006	63.305	281.666	21.1152	.25635	.07180	.025	.07182	.18
12007	63.306	283.619	20.9830	.51933	.07153	.009	.07141	.35
12008	61.205	281.653	20.7812	.25637	.07030	.026	.07033	-.04
12009	61.206	283.627	20.6465	.51933	.06994	.010	.06982	.00
12010	59.061	281.667	20.4240	.25632	.06835	.026	.06837	-.84
12011	59.062	283.784	20.2782	.51910	.06857	.010	.06844	.08
12012	57.008	281.656	20.0688	.25629	.06749	.025	.06752	-.11
12013	57.008	283.803	19.9196	.51909	.06755	.010	.06742	.57
12014	54.632	281.711	19.6332	.25623	.06511	.026	.06513	-.1.29
12015	54.633	283.067	19.5381	.42106	.06596	.012	.06588	.39
12016	52.671	281.828	19.2515	.25616	.06394	.026	.06395	-.1.01
12017	52.673	283.111	19.1611	.42109	.06490	.012	.06482	.83
12018	50.496	281.742	18.8234	.25621	.06331	.025	.06333	.36
12019	50.497	283.179	18.7212	.42106	.06298	.011	.06289	.23
12020	48.397	281.733	18.3838	.25622	.06088	.024	.06090	-.1.16
12021	48.400	283.263	18.2747	.42107	.06144	.012	.06135	.16
12022	45.987	281.924	17.8361	.25612	.05883	.022	.05884	-.1.67
12024	42.975	281.847	17.1271	.25619	.05707	.023	.05708	-.91
12025	42.976	283.453	17.0112	.42105	.05750	.011	.05740	.26
12026	40.671	281.993	16.5307	.25613	.05553	.022	.05553	-.51
12027	40.672	283.560	16.4180	.42106	.05567	.012	.05556	.13
12028	38.676	282.025	15.5910	.25614	.05371	.021	.05371	-.1.04
12029	38.676	283.650	15.8741	.42103	.05418	.014	.05407	.24
12030	36.592	282.024	15.3975	.25620	.05253	.020	.05253	-.17
12031	36.593	283.727	15.2762	.42111	.05260	.010	.05248	.37
12032	34.472	282.134	14.7495	.25613	.05041	.019	.05040	-.98
12033	34.473	283.935	14.6229	.42094	.05116	.010	.05103	.92
12034	32.259	282.205	14.0342	.25610	.04898	.018	.04897	-.20
12035	32.260	284.024	13.9089	.42101	.04963	.010	.04950	1.51
12036	30.141	282.251	13.3091	.25614	.04756	.018	.04754	.54
12037	30.141	284.241	13.1753	.42102	.04770	.009	.04756	1.24
12038	28.060	282.405	12.5475	.25612	.04584	.019	.04551	.04
12039	28.060	283.325	12.0874	.33345	.04584	.012	.04575	.87
12040	25.809	282.450	11.6844	.25607	.04378	.017	.04375	.46
12041	25.809	283.382	11.6266	.33348	.04393	.011	.04384	.95
12042	23.816	282.585	10.8737	.25618	.04177	.017	.04173	-.16
12043	23.815	283.585	10.8149	.33350	.04258	.011	.04247	1.88
12044	21.620	282.672	9.9425	.25623	.03997	.016	.03992	.11
12046	19.361	283.020	8.9304	.25617	.03739	.018	.03732	-.1.56
12048	17.121	283.124	7.9062	.25617	.03599	.015	.03591	-.28
12049	17.120	284.340	7.8546	.33360	.03661	.011	.03644	1.44
12050	14.964	283.409	6.8894	.25617	.03455	.012	.03444	.60
12051	14.964	284.651	6.8448	.33362	.03481	.009	.03461	1.29
12052	13.068	283.632	5.9869	.25624	.03276	.013	.03263	-.39
12053	13.067	282.431	6.0237	.18899	.03251	.020	.03248	-1.05
12054	10.991	282.647	5.0258	.18904	.03105	.019	.03100	-.89
12055	10.990	283.793	4.9971	.25630	.03156	.012	.03142	.59
12056	8.921	282.849	4.0366	.18904	.02976	.018	.02969	-.52

12057	8.921	284.135	4.0122	.25626	.02983	.012	.02966	-.52
12058	6.795	283.111	3.0338	.18906	.02871	.018	.02862	.44
12059	6.794	284.631	3.0131	.25626	.02856	.011	.02835	-.43
12060	4.757	283.445	2.0925	.18899	.02717	.017	.02705	-.95
12061	4.757	284.994	2.0791	.25628	.02727	.012	.02703	-.98
12062	2.744	281.135	1.2002	.08534	.02620	.055	.02627	.04
12063	2.743	282.381	1.1942	.13209	.02609	.029	.02606	-.74
12064	2.743	283.912	1.1869	.18907	.02621	.017	.02606	-.71
12065	2.743	285.643	1.1790	.25634	.02649	.011	.02620	-.13
12066	2.743	287.789	1.1691	.33376	.02661	.008	.02615	-.27

Run Pt.	Pressure MPa	Temperature K	Density mol/L	Experimental Thermal Conductivity		STAT	Adjusted Thermal Conductivity at a nominal Temperature of 298.1 K from Correlation W/m.K		Deviation percent
				Power W/m	Conductivity W/m.K		Temperature of 298.1 K	from Correlation W/m.K	
6001	64.203	297.095	20.2487	.35206	.06909	.003	.06916	-.29	
6002	64.199	297.774	20.2057	.44449	.06915	.003	.06916	-.02	
6003	64.199	298.586	20.1552	.54758	.06851	.003	.06848	-.75	
6004	62.467	297.134	19.9685	.35117	.06800	.003	.06805	-.35	
6005	62.468	298.585	19.8777	.54649	.06769	.002	.06765	-.45	
6006	60.411	297.030	19.6344	.35189	.06657	.003	.06663	-.66	
6007	60.411	298.451	19.5449	.54743	.06593	.016	.06590	-1.28	
6008	58.437	297.041	19.2938	.35114	.06538	.004	.06544	-.62	
6009	58.440	298.803	19.1828	.54618	.06523	.002	.06518	-.42	
6010	56.365	297.039	18.9228	.35131	.06440	.004	.06446	-.13	
6011	56.368	298.652	18.8207	.54650	.06378	.003	.06374	-.71	
6012	54.314	297.128	18.5343	.35134	.06276	.003	.06282	-.64	
6013	54.319	298.639	18.4386	.54672	.06169	.016	.06165	-2.02	
6014	52.215	297.135	18.1246	.35139	.06124	.005	.06130	-.91	
6015	52.225	298.640	18.0300	.54675	.06098	.020	.06094	-.99	
6016	50.117	297.089	17.6998	.35145	.05996	.003	.06002	-.77	
6017	50.124	298.681	17.5989	.54678	.05988	.024	.05984	-.54	
6018	47.824	297.251	17.1987	.35141	.05852	.003	.05857	-.58	
6019	47.829	298.727	17.1048	.54687	.05917	.039	.05912	.85	
6020	45.725	297.282	16.7246	.35144	.05644	.005	.05649	-1.74	
6022	43.758	297.263	16.2620	.35145	.05539	.003	.05544	-1.21	
6024	41.669	296.504	15.7944	.27008	.05420	.005	.05429	-.88	
6025	41.676	298.353	15.6777	.44368	.05402	.002	.05400	-.82	
6026	41.680	298.257	15.6847	.44370	.05423	.002	.05421	-.46	
6027	39.538	296.687	15.2276	.26993	.05271	.004	.05279	-.78	
6028	39.543	298.542	15.1112	.44354	.05261	.005	.05258	-.59	
6029	37.303	296.617	14.6179	.27004	.05125	.004	.05134	-.48	
6030	37.310	298.523	14.5004	.44369	.05109	.003	.05106	-.42	
6031	35.010	296.718	13.9451	.27002	.04911	.004	.04919	-1.36	
6032	35.019	298.838	13.8179	.44373	.04932	.006	.04927	-.56	
6033	32.198	296.804	13.0695	.27004	.04748	.003	.04755	-.36	
6034	32.201	298.890	12.9468	.44376	.04735	.007	.04730	-.29	
6035	29.737	296.957	12.2486	.27004	.04559	.005	.04565	-.37	
6036	29.741	298.897	12.1392	.44389	.04522	.012	.04516	-.91	
6037	27.356	297.137	11.4073	.26989	.04323	.004	.04328	-1.58	
6038	27.359	299.036	11.3056	.44376	.04447	.026	.04441	1.47	
6039	24.774	297.273	10.4489	.26999	.04168	.003	.04173	-.57	
6041	22.553	297.512	9.5790	.27000	.03972	.004	.03975	-1.23	
6043	19.670	296.548	8.4557	.19929	.03778	.003	.03788	-.69	
6044	19.674	298.815	8.3640	.35153	.03793	.002	.03787	-.28	
6045	17.516	296.704	7.5444	.19910	.03647	.003	.03656	.06	
6046	17.517	299.063	7.4595	.35132	.03598	.011	.03590	-1.37	
6047	14.725	297.120	6.3291	.19909	.03409	.003	.03416	-1.11	
6048	14.728	299.312	6.2656	.35136	.03423	.034	.03413	-.89	
7065	13.018	296.033	5.6124	.19829	.03291	.003	.03306	-1.08	
7015	12.970	297.328	5.5577	.19887	.03315	.013	.03320	-.41	
7026	12.973	298.842	5.5202	.26978	.03300	.004	.03294	-1.05	
6049	12.064	297.118	5.1656	.19913	.03225	.003	.03232	-.133	
6051	9.725	297.510	4.1301	.19917	.03090	.002	.03094	-1.04	
6053	6.981	297.780	2.9302	.19916	.02933	.003	.02935	-1.03	
6055	4.807	298.104	1.9942	.19920	.02811	.002	.02810	-1.31	
6057	2.590	298.652	1.0591	.19920	.02711	.001	.02706	-1.08	
6058	2.590	298.746	1.0587	.19918	.02716	.002	.02710	-.92	

Run Pt.	Pressure MPa	Temperature K	Density mol/L	Power W/m	Experimental Thermal Conductivity		STAT	Adjusted Thermal Conductivity at a nominal Temperature of 310.K		Deviation from Correlation percent
					W/m.K	W/m.K		W/m.K	W/m.K	
8001	65.257	310.587	19.6011	.56770	.06831	.005		.06827		.91
8002	65.259	308.839	19.7033	.36506	.06786	.009		.06793		-.13
8003	63.342	310.480	19.3020	.56723	.06694	.005		.06691		.47
8004	63.344	308.792	19.4012	.36479	.06741	.008		.06749		.81
8006	61.375	308.882	19.0717	.36468	.06611	.009		.06619		.59
8007	59.241	310.711	18.5987	.56714	.06409	.005		.06404		-.23
8008	59.242	308.862	18.7081	.36470	.06444	.008		.06452		-.05
8010	57.077	308.862	18.3229	.36476	.06314	.009		.06322		-.07
8011	54.792	310.911	17.7771	.56753	.06271	.004		.06264		1.82
8012	54.793	309.089	17.8851	.36489	.06203	.007		.06210		.41
8013	52.489	311.035	17.3223	.56756	.06114	.004		.06106		1.61
8014	52.491	309.025	17.4417	.36527	.06043	.007		.06051		.10
8015	52.491	308.271	17.4869	.28070	.06074	.012		.06088		.48
8016	50.052	310.173	16.8763	.46084	.05955	.006		.05954		1.38
8017	50.052	308.313	16.9873	.28064	.05907	.011		.05921		.27
8018	47.901	310.206	16.4148	.46099	.05744	.006		.05742		.14
8019	47.903	308.348	16.5255	.28065	.05749	.010		.05763		-.07
8020	45.636	310.215	15.9068	.46112	.05676	.006		.05674		1.51
8021	45.636	308.329	16.0184	.28066	.05475	.010		.05489		-2.38
8023	43.622	308.430	15.5395	.28069	.05439	.010		.05453		-.60
8024	41.256	310.447	14.8389	.46100	.05365	.006		.05361		1.21
8025	41.257	308.431	14.9561	.28065	.05307	.010		.05321		-.12
8027	38.927	308.644	14.3382	.28054	.05166	.010		.05178		.24
8029	36.437	308.614	13.6564	.28059	.04993	.009		.05006		.23
8030	34.164	310.856	12.8761	.46090	.04935	.005		.04927		2.42
8031	34.165	309.786	12.9342	.36514	.04860	.006		.04862		.84
8032	34.167	308.695	12.9943	.28059	.04800	.009		.04812		-.48
8033	34.167	307.855	13.0408	.20711	.04665	.015		.04685		-3.44
8035	31.616	308.826	12.2078	.28068	.04695	.009		.04706		1.10
8039	27.317	308.994	10.7855	.28066	.04395	.008		.04405		1.26
8040	27.317	308.051	10.8309	.20711	.04299	.013		.04318		-.94
8041	24.993	310.356	9.9083	.36489	.04263	.006		.04260		2.02
8043	24.991	308.105	10.0085	.20706	.04197	.011		.04215		.52
8045	22.377	308.112	9.0452	.20698	.04000	.011		.04018		.20
8046	20.111	310.744	8.0806	.36507	.03899	.005		.03892		1.41
8047	20.111	308.305	8.1701	.20700	.03813	.011		.03829		-.62
8049	17.519	308.452	7.1418	.20696	.03619	.011		.03633		-1.23
8051	15.214	308.654	6.2040	.20704	.03522	.010		.03534		.19
7084	13.617	309.141	5.5380	.14525	.03413	.016		.03421		-.15
7085	13.617	310.333	5.5096	.20773	.03420	.009		.03417		-.13
7086	13.618	311.626	5.4794	.28135	.03458	.006		.03443		.77
7094	13.620	309.078	5.5407	.14507	.03400	.016		.03408		-.53
7095	13.620	310.215	5.5135	.20752	.03424	.010		.03422		-.00
7096	13.620	311.525	5.4826	.28123	.03438	.006		.03424		.20
7104	13.569	307.822	5.5499	.14464	.03391	.016		.03411		-.50
7105	13.569	308.681	5.5291	.20712	.03403	.010		.03415		-.28
7106	13.569	310.149	5.4941	.28055	.03423	.006		.03422		.07
7114	13.574	307.657	5.5559	.14486	.03392	.016		.03413		-.45
7115	13.574	308.760	5.5293	.20725	.03386	.010		.03397		-.80
7116	13.574	310.130	5.4969	.28081	.03427	.007		.03426		.18
8055	12.980	308.855	5.2827	.20689	.03364	.010		.03374		-.40
8056	10.694	310.570	4.3068	.28037	.03266	.006		.03261		.42
8057	10.694	307.811	4.3566	.14471	.03203	.014		.03222		-.99
8058	8.434	310.857	3.3751	.28051	.03127	.006		.03120		-.01
8059	8.434	308.026	3.4135	.14473	.03080	.013		.03097		-.91
8060	8.434	309.260	3.3966	.20701	.03096	.008		.03102		-.66
8061	6.282	311.318	2.4926	.28042	.03004	.005		.02993		-.40
8062	6.282	309.588	2.5090	.20703	.02981	.008		.02984		-.76
8063	6.282	308.167	2.5227	.14471	.02971	.015		.02986		-.76
8064	4.015	311.862	1.5766	.28042	.02900	.006		.02885		-.20
8065	4.015	310.019	1.5868	.20703	.02880	.008		.02880		-.43
8066	4.015	308.320	1.5966	.14474	.02865	.014		.02878		-.52
8067	2.046	312.535	.7947	.28032	.02843	.005		.02823		.93
8068	2.045	310.562	.7998	.20695	.02824	.007		.02820		.78
8069	2.045	308.833	.8045	.14468	.02794	.013		.02803		.17

Measurements of the Octanol/Water Partition Coefficient by Chromatographic Methods

Stanley P. Wasik,* Yadu B. Tewari,* Michele M. Miller*

National Bureau of Standards, Washington, DC 20234
and

J. H. Purnell

Department of Chemistry, University College of Swansea, Swansea, Wales, U.K.

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A theoretical relationship is developed to provide a quantitative definition of hydrophobicity using established theoretical and semi-empirical relationships. A method of predicting partition coefficients of relatively water-insoluble third components between water and an immiscible second component is devised and tested. Comparison with experimental data for four classes of compounds in the water/*n*-octanol system at 25° C shows excellent agreement, indicating that values for substances for which direct determination is experimentally precluded can be calculated with confidence.

Key words: Activity coefficients; alkybenzenes; gas chromatography; octanol/water partition coefficients.

1. Introduction

In recent years there has been an increased interest in the use of hydrophobic parameters to study the fate of toxic substances in the marine environment since the ability of organic compounds to bioconcentrate is believed to depend upon the partition behaviour of molecules between lipid and aqueous phases [1,2].¹ An important and simplifying observation has been that by Neely, Branson and Blau [1] who demonstrated that bioconcentration factors for chlorobenzenes and chlorophenols between trout muscles and dilute solutions in water could be successfully correlated with their partition coefficients in the *n*-octanol/water system, $K_{o/w}$. Subsequently, Dunn and Hansch [3] compiled hydrophobic interaction data for a large number of organic compounds and showed that these could, indeed, be quantitatively correlated with partition coefficients of organic/water systems. The weight of evidence has led Leo [4] to suggest not only that hydrophobicity is the most important parameter in bioaccumulation and biotransport but that this can be confidently determined in terms of octanol/water partition coefficients.

Because of the thousands of compounds being studied as potential hazards to the environment through bioac-

cumulation, simple economics makes it desirable to devise some system whereby we measure values of $K_{o/w}$ for key compounds which may be used to calculate values for related compounds. In the only approach to date, Hansch, Quinlan and Lawrence [5] have developed a method for estimating $K_{o/w}$ based on additive group contributions; these group contributions or "Π values" being as defined by eq (1),

$$\Pi_x = \log K_{o/w}^x - \log K_{o/w}^h \quad (1)$$

where $K_{o/w}^x$ and $K_{o/w}^h$ are the octanol/water partition coefficients for the derivative and the parent compound, respectively. Not surprisingly, in the light of the numerous such correlations established in GLC studies [6], Π values are often additive, and the method has met with acceptance. However, because of steric, electronic and hydrogen bonding effects there are many series of compounds for which the method fails. Some alternative would, therefore, be useful, particularly if the correlation method involved real and measurable physical properties of the molecules concerned rather than a purely empirical set of parameters. This paper outlines one such approach and an indication of its applicability.

Partition coefficients are generally determined by some variant on the traditional shake-flask method. This method is slow, tedious, often wasteful, and demanding in the standard of purity of materials it requires. Conse-

*Center for Chemical Physics, National Measurement Laboratory.

¹Figures in brackets indicate literature references at the end of this paper.

quently there have been many attempts to develop chromatographic methods to which, in principle, and normally in practice, none of the above objections apply. In the method presented in this paper $K_{o/w}$ is defined, as proved later, by eq (2),

$$K_{o/w} = \gamma_\phi^w / \gamma_\phi^o \quad (2)$$

where γ_ϕ^w and γ_ϕ^o are the activity coefficients at infinite dilution, based on volume fraction, for the solute in water and n-octanol, respectively. The quantity, γ_ϕ^w , is calculated from the solute aqueous solubility, C_w , and the solute molar volume, V [7], and γ_ϕ^o is determined from the corrected retention volume of the solute eluting from a column containing n-octanol as the stationary phase. Thus $K_{o/w}$ (at infinite dilution) can be calculated from γ_ϕ^w and γ_ϕ^o , which can be measured by two independent methods having all the advantages of the chromatographic approach, while the recognition of eq (2) opens the route to the alternative approach to be described.

2. Theoretical

The octanol/water partition coefficient, $K_{o/w}$, is defined as the equilibrium ratio of the molar concentration of solute x in octanol, C_o , and the concentration in water, C_w , in an octanol/water system, viz.

$$K_{o/w} = \frac{C_o}{C_w} \quad (3)$$

But, self evidently, $K_{o/w}$ may also be defined by eq (4)

$$K_{o/w} = \frac{K_{a/o}}{K_{a/w}} \quad (4)$$

where $K_{a/o}$ is the air/octanol (saturated with water) and $K_{a/w}$ is the air/water (saturated with octanol) partition coefficient. GLC theory yields the expression for $K_{a/o}$

$$K_{a/o} = \frac{C_o RT}{P} = \frac{n_x RT}{(V_x + V_o + V_w) P} \quad (5)$$

where n_x is the number of moles of solute x in the octanol (saturated with water), V_x , V_o and V_w are the volumes of solute, octanol and water, in the octanol phase, respectively, R is the gas constant, and P is the partial pressure of solute x above the solution at temperature, T .

For an ideal vapour the ratio P/P^o , where P^o is the solute saturation vapour pressure, is equal to the activity (a). We may define the activity in terms of any quantity that defines relative amount, and an appropriate activity

coefficient, e.g., we may write,

$$a = \gamma_x x = \gamma_\phi \Phi = \gamma_w W = \gamma_c C/C^o \quad (6)$$

where x represents mole fraction, Φ the volume fraction, W the weight fraction, and C/C^o the ratio of concentration in solution to that in the pure solute liquid. Although the first of these definitions is the one most widely used we choose the second for reasons that will emerge.

Thus, setting

$$\frac{P}{P^o} = \Phi \gamma_\phi \quad (7)$$

substitution for P in eq (5) yields

$$K_{a/o} = \frac{n_w}{V_x + V_o + V_w} \cdot \frac{RI}{\gamma_\phi^o \Phi P^o} = \frac{RT}{V(x) \gamma_\phi^o P^o} \quad (8)$$

where γ_ϕ^w is the activity coefficient in water saturated with n-octanol. Provided there is no significant excess volume of mixing in either solvent, the normal solution,

$$K_{a/w} = \frac{RT}{V(x) \gamma_\phi^w P^o} \quad (9)$$

where γ_ϕ^w is the activity coefficient in water saturated with n-octanol. Provided there is no significant excess volume of mixing in either solvent, the normal solution,

$$K_{o/w} = \gamma_\phi^w / \gamma_\phi^o \quad (10)$$

It remains only to emphasize again that γ_ϕ^o and γ_ϕ^w are values. An immediate and obvious attraction of eq (10) is the absence of explicit solvent parameters, which is not the case if γ_x is used.

3. Dependence of the thermodynamic functions associated with solute partitioning between an organic and an aqueous phase on vapour pressure.

Hoare and Purnell [8] have shown that for solutes of similar chemical structure the GLC specific retention volume of solute x , $V_g(x)$, is related to the saturation vapour pressure of the solute, P^o , by the expression

$$\log V_g^o(x) = -a \log P^o + \text{constant} \quad (11)$$

where a is a series constant. The validity of eq (11) has subsequently been further established for a wide range of

chemical types of both solvent and solute [9, 10, 11] and in a summary by Purnell [8]. In so far as data are available there seems to be no recorded exception to the rule. Further since

$$V_g^o(x) = \frac{RT}{\gamma_\phi^o P^o V(x)\rho}$$

where ρ is the solvent density, eq (11) yields

$$\log \gamma_\phi^o V(x) = (a^o - 1) \log P^o + \text{constant} \quad (12)$$

where a^o is the slope of the $\log V_g^o(x)$ vs $\log P^o$ plot for each series of solutes in *n*-octanol.

In similar manner we obtain

$$\log \gamma_\phi^w V(x) = (a^w - 1) \log P^o + \text{constant} \quad (13)$$

where a^w is the slope of the $\log V_g^o(x)$ vs $\log P^o$ plot for each series of solutes in water. Combining eqs (10), (12), and (13) we obtain

$$\log K_{o/w} = (a^o - a^w) \log P^o + \text{constant} \quad (14)$$

Thus for solutes of similar chemical structure the thermodynamic functions, $\log P^o$, $\log \gamma_\phi^o V(x)$ and $\log \gamma_\phi^w V(x)$, associated with the partitioning of a solute between an organic and aqueous phase may each be expressed in the form

$$\text{function} = B + A \log P \quad (15)$$

where B and A are numerically defined by the function being considered.

4. Results

The solute activity coefficients in octanol, γ_ϕ^o and in water γ_ϕ^w listed in columns 1 and 2 of table 1 were obtained from an earlier publication of Wasik *et al* (12). γ_ϕ^o were calculated from the solute specific retention volume V_g^o , obtained from retention times of solutes eluting from a GC column containing *n*-octanol as the stationary phase. γ_ϕ^w values were calculated from solubility data using the following equation

$$\gamma_\phi^w = \frac{1}{\phi_w} \quad (16)$$

where ϕ_w is the solute aqueous solubility in volume fraction. The last two columns show a comparison between the calculated $K_{o/w}$ (using eq (10)) and the experimental values. The agreement between the two sets of data is excellent.

TABLE 1. Solute Activity Coefficients and Octanol/Water Partition Coefficients at 25.0°C.

Solute	Log γ_ϕ^o (GLC)	Log γ_ϕ^w (Generator column /HPLC or GC)	Log $K_{o/w}$	
			Calculated*	Experimental
n-Pentane	0.555	4.19	3.63 (3.68)	3.62
n-Hexane	.530	4.73	4.20 (4.22)	4.11
n-Heptane	.517	5.28	4.76 (4.77)	4.66
n-Octane	.512	5.80	5.29 (5.29)	5.18
1-Hexene	.504	3.98	3.48 (3.47)	3.39
1-Heptene	.491	4.58	4.09 (3.07)	3.99
1-Octene	.479	5.24	4.76 (4.73)	4.57
1-Nonene	.470	5.81	5.34 (5.30)	5.15
Toluene	.509	3.17	2.66 (2.66)	2.65
Ethylbenzene	.505	3.66	3.15 (3.15)	3.13
n-Propylbenzene	.494	4.22	3.73 (3.71)	3.69
Ethylacetate	.621	1.15	0.53 (0.64)	0.68
n-Propylacetate	.534	1.64	1.11 (1.13)	1.24
n-Butylacetate	.425	2.15	1.73 (1.64)	1.82

*Values in parentheses were calculated using the hydrophobicity equation (eq 17).

5. Discussion

Our approach of defining $K_{o/w}$ in terms of volume fraction based activity coefficients has several important consequences. First, the infinite dilution coefficients $\log K_{o/w}$, $\log \gamma_\phi^o$, and $\log \gamma_\phi^w$ for a given solute type are clearly described by a linear relationship with the solute saturation vapour pressure.

The extent to which this is true may be gauged by consideration of the values of the correlation coefficients, r , listed in table 2 derived from data of table 1 via linear regression as a consequence of the above.

The data in table 1 indicate that values of $\log \gamma_\phi^w$ are large and change rapidly with $\log P^o$; whereas, $\log \gamma_\phi^o$ are much smaller and remain fairly constant (0.510 ± 0.045) for all compounds. Thus the relevant values of $\log K_{o/w}$ are determined by $\log \gamma_\phi^w$. Our approach leads us to a quantitative theoretical definition of the hitherto empirical concept of hydrophobicity, H ,

$$H = \log K_{o/w} = \log \gamma_\phi^w - 0.510 \quad (17)$$

$$= \log \gamma_\phi^w \cdot k$$

The numerical constant k will vary for different solvents which means that H can be defined with respect to solvents other than *n*-octanol. The values of hydrophobicity (H) calculated using eq (17) are listed in table 1 in parenthesis. A quantitative definition of H is

TABLE 2. Coefficients of the Regression Equation and the Coefficient of Correlation for the Solute

Type of Correlation	Type of Solute	Slope	Intercept	Coefficient of Correlation (r)
$\log K_{o/w} = A \log P^o + B$	Alkanes	-0.9957	6.298	0.999
	Alkenes	-1.1400	5.981	.999
	Aromatics	-0.8809	3.770	.998
	Acetates	-0.7700	2.484	.999
$\log K_{o/w} = k_1 n_c + k_2$	Alkanes	0.5230	0.993	0.999
	Alkenes	.5860	-0.1200	.999
	Aromatics	.5200	2.117	.999
	Acetates	.5700	-0.4633	.999
$\log K_{o/w} = k_3 T_b + k_4$	Alkanes	0.01748	-1.8210	0.998
	Alkenes	.02110	-3.7309	.999
	Aromatics	.02136	-5.5677	.997
	Acetates	.02306	-7.3981	.999

important in order to correlate other solute properties for estimation purposes such as bioconcentration and soil adsorption.

The advantages in using a $\log \gamma_\phi^w$ instead of $\log K_{o/w}$ in defining H are: (1) solubility data are more readily available in the literature than $K_{o/w}$ data, and (2) γ_ϕ^w is independent of any solvent/water system.

The utility of the gas chromatographic technique for measuring activity coefficients in organic solutions and the validity of the data obtained are now well established. The technique is particularly applicable to measurements at infinite dilution, the condition of primary interest and least accessible otherwise. There are several important advantages to this method for measuring γ_ϕ^w : (1) the speed with which the measurements are made, (2) the accuracy of the measurements, (3) the measurements are made at infinite dilution, and (4) several solutes may be injected into the gas chromatograph simultaneously thus increasing the productivity rate. Although absolute γ_ϕ^w value may be obtained by this method, the method is best suited for measuring values relative to some carefully studied standards because of the relatively high volatility of octanol.

In the octanol/water system at equilibrium the water phase is saturated with octanol(wo), and the octanol phase is saturated with water(ow). In order to derive an expression relating $K_{o/w}$ to the solute aqueous solubility,

we assume that $\gamma_\phi^w \approx \gamma_\phi^o$ and $\gamma_\phi^{wo} \approx \gamma_\phi^w$ where γ_ϕ^o and γ_ϕ^w are the solute activity coefficients in pure water and pure octanol, respectively. The extent to which these assumptions are valid may be judged by the very good agreement between $K_{o/w}$ values calculated via eq (10) and experimental values (table 1) measured by a generator column method [12,13].

The above method for determining $K_{o/w}$ is best suited for volatile compounds. There are drawbacks to the method for relatively nonvolatile solutes. These compounds depending on their γ_ϕ^o value could require a relatively long time to elute through the GC column, thus making the method impractical.

For the cases where vapour pressure data are not available, Purnell has shown that carbon number (n_c) or boiling point (T_b) may be substituted for $\log P^o$, i.e.

$$\log K_{o/w} = k_1 n_c + k_2 \quad (18)$$

$$\log K_{o/w} = k_3 T_b + k_4 \quad (19)$$

where the k 's are constants.

Equation (19) is particularly useful when the homologous series cannot be described by the carbon numbers. The results listed in the table 2 show that there is an excellent correlation with these quantities.

In summary it is clear that the chromatographic technique, particularly in association with the developments reported here, offers a primary route to rapid collection of large volumes of reliable values of $K_{o/w}$ and other thermodynamic functions associated with the partitioning of organic material in the environment. The infinite dilution method proposed in this paper has all the advantages of a chromatographic method in that there are no stringent demands placed on the purity of the solute or the amount of material required to determine $K_{o/w}$.

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Curve Fitting With Clothoidal Splines

Josef Stoer*

Universität Würzburg, Federal Republic of Germany

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Clothoids, i.e. curves $Z(s)$ in R^2 whose curvatures $x(s)$ are linear fitting functions of arclength s , have been used for some time for curve fitting purposes in engineering applications. The first part of the paper deals with some basic interpolation problems for clothoids and studies the existence and uniqueness of their solutions.

The second part discusses curve fitting problems for clothoidal splines, i.e. C^2 -curves, which are composed of finitely many clothoids. An iterative method is described for finding a clothoidal spline $Z(s)$ passing through given points $Z_i \in R^2$, $i = 0, 1, \dots, n+1$, which minimizes the integral $\int_Z x(s)^2 ds$.

This algorithm is superlinearly convergent and needs only $O(n)$ operations per iteration. A similar algorithm is given for a related problem of smoothing by clothoidal splines.

Key words: Approximation; clothoids; computer-aided design; Cornu-spirals; curvature; curve fitting; Fresnel-integrals; interpolation; splines

Introduction

The characteristic property of curves known as *Cornu-spirals* or *clothoids* is that their curvature $x(s)$ is a linear function of the arc length, $x(s) = x_0 + \lambda s$. Straight lines ($x_0 = 0, \lambda = 0$) and circles ($\lambda = 0$) may be considered as limiting cases. We are interested in constructing C^2 -curves in the plane R^2 which are composed of finitely many Cornu-spirals; that is, C^2 -curves whose curvature is a continuous piecewise linear function of their arc lengths. We will call such curves *clothoidal splines*. Typical elementary problems encountered in such an effort are to construct a clothoid joining a given straight line and a given circle, or joining two circles. Composite curves of this type have been used by engineers, for instance, for the construction of highway sections, some of which are specified to be straight lines and circles. A more complex problem is to construct a clothoidal spline Z through a sequence of finitely many points $(x_i, y_i) \in R^2$, $i = 0, 1, \dots, n+1$ such that the integral

$$K = \int_Z x(s)^2 ds$$

along the curve is minimal. This problem can be considered as an approximation to the "true" problem of curve fitting in R^2 , namely that of finding a curve $Z(\cdot)$ minimizing this integral among all C^2 -curves passing through the given points. The latter problem has been studied by several authors (Lee, Forsythe [7],¹ Mehlum [8]), and its exact solution leads to a multipoint boundary value problem for elliptic functions (Reinsch [14]). Mehlum [8] also proposed to approximate its solution by solving the corresponding multipoint boundary value problem for clothoidal spline functions, however the resulting clothoidal spline does in general not minimize the integral K among all interpolating clothoidal splines (see also Pal and Nutbourne [10] for a related use of clothoidal splines in computer aided geometric design).

There is also the problem of smoothing: for given points (x_i, y_i) , $i = 0, 1, \dots, n+1$, the problem is to find a clothoidal spline Z in such a way that its deviation (in the least squares sense) from the given points is not greater than a prescribed tolerance and the integral K along Z is minimal (compare Reinsch [13] for the related problem for spline functions).

*NBS Guest Worker with the Operations Research Division, Center for Applied Mathematics, National Engineering Laboratory.

¹Figures in brackets indicate literature references at the end of this paper.

Cornu-spirals can be easily computed in terms of Fresnel integrals, though admittedly not as easily as the cubic polynomials generally used for spline functions. In contrast to the latter, however, clothoidal splines are represented in terms of the natural parameter of plane curves; namely, the curvature as function of arc length. Furthermore, we hope that they do not exhibit the drawbacks observed with other schemes for curve fitting which have been observed in practice, namely, a tendency toward oscillations.

In the first section we list some elementary properties of Cornu-spirals and Fresnel integrals, mainly taken from Abramowitz and Stegun [1]. The second section deals with simple interpolation problems for a single Cornu-spiral. Section 3 is devoted to interpolation with clothoidal spirals; section 4 to the problem of smoothing.

1. Elementary properties of Cornu-spirals

By definition, a Cornu-spiral or clothoid is a curve,

$$Z(s) = \begin{bmatrix} x(s) \\ y(s) \end{bmatrix}, s \in R,$$

whose curvature $x(s) = x_0 + \lambda s$ is a linear function of arc length s . If its tangent vector is

$$\dot{Z}(s) = \begin{bmatrix} \cos \phi(s) \\ \sin \phi(s) \end{bmatrix},$$

then

$$x(s) = \dot{\phi}(s),$$

so that

$$\phi(s) = \phi_0 + \int_0^s x(\tau) d\tau = \phi_0 + x_0 s + \frac{\lambda}{2} s^2, \quad (1.1)$$

$$Z(s) = Z_0 + \int_0^s \begin{bmatrix} \cos \phi(t) \\ \sin \phi(t) \end{bmatrix} dt.$$

According to the sign of λ , Z is called positively or negatively oriented. In the sequel, we restrict ourselves to the case of $\lambda > 0$. Similar results will hold for $\lambda < 0$.

Using the Fresnel integrals,

$$C(z) := \int_0^z \cos \frac{\pi t^2}{2} dt, \quad S(z) := \int_0^z \sin \frac{\pi t^2}{2} dt, \quad F(z) := \begin{bmatrix} C(z) \\ S(z) \end{bmatrix},$$

$Z(s)$ can be expressed in closed form by [see [1], formulas (7.4.38), (7.4.39)]

$$Z(s) = Z_0 + \sqrt{\pi/\lambda} V \left(\phi_0 - \frac{x_0^2}{2\lambda} \right) \left\{ F \left(\frac{x_0 + \lambda s}{\sqrt{\pi\lambda}} \right) - F \left(\frac{x_0}{\sqrt{\pi\lambda}} \right) \right\}, \text{ if } \lambda > 0, \quad (1.2)$$

where $V(a)$ is the orthogonal matrix,

$$V(\alpha) := \begin{bmatrix} \cos \alpha & -\sin \alpha \\ \sin \alpha & \cos \alpha \end{bmatrix}.$$

Note that $F(s)$ also describes a Cornu-spiral with arc length s , curvature $x(s) = \pi s$ and phase angle $\phi(s) = (\pi/2)s^2$. The Fresnel integrals have the following properties [see [1], (7.3.17), (7.3.20)] which we list without proof:

$$\begin{aligned} F(z) &= -F(-z) \\ \lim_{z \rightarrow +\infty} F(z) &= \frac{1}{2} \begin{bmatrix} 1 \\ 1 \end{bmatrix}, \quad \lim_{z \rightarrow -\infty} F(z) = -\frac{1}{2} \begin{bmatrix} 1 \\ 1 \end{bmatrix}. \end{aligned} \quad (1.3)$$

Moreover, $F(z)$ can be expressed in the following way [see [1], (7.3.9), (7.3.10)];

$$F(z) = \frac{1}{2} \begin{bmatrix} 1 \\ 1 \end{bmatrix} - V\left(\frac{\pi}{2} z^2\right) h(z) , \quad (1.4)$$

where the component functions $g(z)$ and $f(z)$ of

$$h(z) = \begin{bmatrix} g(z) \\ f(z) \end{bmatrix}$$

satisfy [see [1], (7.3.5), (7.3.6), (7.3.21), (7.3.27)-(7.3.31)],

- (a) $h(0) = \frac{1}{2} \begin{bmatrix} 1 \\ 1 \end{bmatrix}, \quad \lim_{z \rightarrow +\infty} h(z) = 0$
- (b) $g(z)$ and $f(z)$ are strictly monotonically decreasing for $z \in [0, +\infty]$
- (c) $f'(z) = -\pi z g(z), \quad g'(z) = \pi z f(z) - 1, \quad \text{for } z \in R$
- (d) For $z > 0$ the following estimates hold for $g(z)$ and $f(z)$:

$$\begin{aligned} \frac{1}{\pi^2 z^3} \left(1 - \frac{15}{(\pi z^2)^2} \right) &< g(z) < \frac{1}{\pi^2 z^3} \\ \frac{1}{\pi z} \left(1 - \frac{3}{(\pi z^2)^2} \right) &< f(z) < \frac{1}{\pi z} \\ \frac{-3}{\pi^3 z^5} < f(z) - \frac{1}{\pi z} &< -\frac{3}{\pi^3 z^5} \left(1 - \frac{35}{(\pi z^2)^2} \right) \end{aligned}$$

Approximations of $f(z)$, $g(z)$ suitable for the calculation of $F(z)$ are given in [1], (7.3.32), (7.3.33), and in Boersma [2].

As a simple consequence of (1.5d) we note the following estimates for the euclidean norms of the vectors $h(z)$ and

$$h(z) := \begin{bmatrix} g(z) \\ f(z) - 1/(\pi z) \end{bmatrix}$$

to be used later on:

$$\begin{aligned}
 \text{(a)} \quad 1 - \frac{15}{(\pi z^2)^2} &\leq \|h(z)\| \left((1/\pi z) \sqrt{1 + \frac{1}{(\pi z^2)^2}} \right)^{-1} \leq 1 \text{ for } z > 0, \\
 \text{(b)} \quad 1 - \frac{35}{(\pi z^2)^2} &\leq \|\bar{h}(z)\| \left((1/\pi^2 z^3) \sqrt{1 + \frac{9}{(\pi z^2)^2}} \right)^{-1} \leq 1 \text{ for } z > 0, \\
 \text{(c)} \quad \lim_{z \rightarrow +\infty} z h(z) &= \begin{bmatrix} 0 \\ 0 \end{bmatrix}, \quad \lim_{z \rightarrow +\infty} \pi \bar{h}(z) = \begin{bmatrix} 0 \\ 1 \end{bmatrix}.
 \end{aligned} \tag{1.6}$$

By (1.5a), (1.5b), $\|h(z)\|$ decreases strictly monotonically toward 0 for $z \rightarrow +\infty$. The same holds for $\bar{h}(z)$:

$$\|\bar{h}(z)\| \text{ decreases strictly monotonically toward 0 as } z \rightarrow +\infty. \tag{1.7}$$

The following is a consequence of (1.6) and (1.5):

$$\frac{1}{2} \frac{d}{dz} \|\bar{h}(z)\|^2 = \frac{1}{\pi z^2} (f(z) - \frac{1}{\pi z}) < 0 \quad \text{for } z > 0.$$

It follows from (1.3), (1.4) that $F(z)$ has the form shown in figure 1.

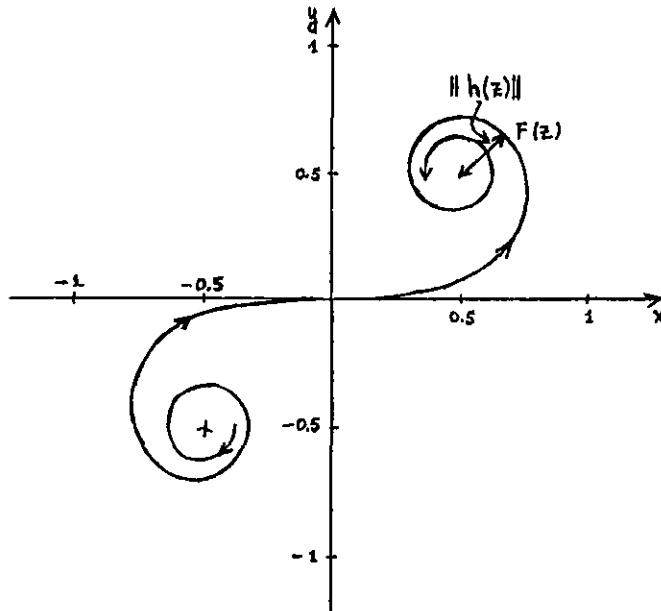


FIGURE 1. Positively Oriented Cornu-Spiral with $Z_0 = X_0 = 0$ and $\lambda = \pi$

For $z \geq 0$ the vector

$$h(z) = \|h(z)\| \cdot \begin{bmatrix} \cos \sigma(z) \\ \sin \sigma(z) \end{bmatrix} > 0, \quad \sigma(z) := \arctan(f(z)/g(z))$$

stays in the interior of the first quadrant of R^2

$$0 < \sigma(z) < \frac{\pi}{2}, \quad \sigma(0) = \frac{\pi}{4}, \quad \sigma(+\infty) = \pi/2.$$

Moreover, the vector

$$r(z) := F(z) - \frac{1}{2} \begin{bmatrix} 1 \\ 1 \end{bmatrix} = -V \left(\frac{\pi}{2} \bigcirc z^2 \right) h(z) =: ||h(z)|| \cdot \begin{bmatrix} \cos \varrho(z) \\ \sin \varrho(z) \end{bmatrix}$$

where

$$\varrho(z) := \sigma(z) + \frac{\pi}{2} z^2 + \pi, \quad \frac{\pi}{2} z^2 + \pi < \varrho(z) < \frac{\pi}{2} z^2 + \frac{3}{2}\pi$$

rotates counterclockwise for $z \geq 0$ as z tends to $+\infty$. This follows from (1.5):

$$\dot{\varrho}(z) = \dot{\sigma}(z) + \pi z = \frac{d}{dz} \arctan(f(z)/g(z)) + \pi z = \frac{f(z)}{f(z)^2 + g(z)^2} > 0 \text{ for } z \geq 0$$

Therefore, the curve $F(z)$ crosses any fixed ray

$$d_\alpha := \left\{ \frac{1}{2} \begin{bmatrix} 1 \\ 1 \end{bmatrix} + \sigma \begin{bmatrix} \cos \alpha \\ \sin \alpha \end{bmatrix} \middle| \sigma \geq 0 \right\}$$

infinitely often at abscissae $0 \leq z_1 < z_2 < \dots$, for which

$$\lim_{i \rightarrow \infty} z_i = +\infty$$

$$(z_i)^2 + 4n-1 \leq (z_{i+n})^2 \leq (z_i)^2 + 4n+1, \quad i \geq 1, n \geq 1 \quad (1.8)$$

$$4n-1 \leq (z_n)^2 \leq 4n+1$$

These estimates easily imply the following bounds

$$\frac{4n-1}{z_i} \left(1 + \sqrt{1 + \frac{4n-1}{(z_i)^2}} \right)^{-1} \leq z_{i+n} - z_i \leq \frac{4n+1}{z_i} \left(1 + \sqrt{1 + \frac{4n+1}{(z_i)^2}} \right)^{-1}, \quad i, n \geq 1$$

$$\sqrt{4n-1} \leq z_n \leq \sqrt{4n+1}, \quad (1.9)$$

which we note for later reference.

Upon inserting (1.4) into (1.2), we get the following representation of $Z(s)$ in terms of the vector h :

$$Z(s) = Z(0) - \sqrt{\frac{\pi}{\lambda}} \left(V(\phi(s))h \left(\frac{x(s)}{\sqrt{\pi\lambda}} \right) - V(\phi_0)h \left(\frac{x_0}{\sqrt{\pi\lambda}} \right) \right) \quad (1.10)$$

where (see (1.1))

$$x(s) := x_0 + \lambda s, \quad \phi(s) := \phi_0 + x_0 s + \frac{\lambda}{2}s^2.$$

Note that because of $\lambda > 0$ and (1.5) (a), (1.3)

$$\begin{aligned}
(a) \quad Z(+\infty) &= Z(0) + \sqrt{\frac{\pi}{\lambda}} V(\phi_0) h \left(\frac{x_0}{\sqrt{\pi\lambda}} \right) \\
(b) \quad Z(-\infty) &= Z(+\infty) - \sqrt{\frac{\pi}{\lambda}} V \left(\phi_0 - \frac{x_0^2}{2\lambda} \right) \cdot \begin{bmatrix} 1 \\ 1 \end{bmatrix} \\
(c) \quad Z(s) - Z(+\infty) &= -\sqrt{\frac{\pi}{\lambda}} V(\phi(s)) h \left(\frac{x(s)}{\sqrt{\pi\lambda}} \right)
\end{aligned} \tag{1.11}$$

The evolute of Z , that is the locus of all centers of curvature $M(s)$ of $Z(s)$ for $s \in R$, is given by

$$M(s) = Z(s) + \frac{1}{x(s)} \begin{bmatrix} -\sin \phi(s) \\ \cos \phi(s) \end{bmatrix} = Z(s) + \frac{1}{x(s)} V(\phi(s)) \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{1.12}$$

$$= Z(0) - \sqrt{\frac{\pi}{\lambda}} \left(V(\phi(s)) \bar{h} \left(\frac{x(s)}{\sqrt{\pi\lambda}} \right) - V(\phi_0) h \left(\frac{x_0}{\sqrt{\pi\lambda}} \right) \right)$$

because $\bar{h}(z) = h(z) - \begin{bmatrix} 0 \\ nz \end{bmatrix}$. Again, the evolute M is a spiral type of curve with the following properties:

- (a) $M(+\infty) = Z(+\infty)$
- (b) $M(-\infty) = Z(-\infty)$

$$\begin{aligned}
(c) \quad M(s) - M(+\infty) &= -\sqrt{\frac{\pi}{\lambda}} V(\phi(s)) \bar{h} \left(\frac{x(s)}{\sqrt{\pi\lambda}} \right) \\
(d) \quad M(s_1) &\neq M(s_2) \text{ for } s_1 \neq s_2
\end{aligned} \tag{1.13}$$

(a) follows directly from (1.7) and (1.11), (b) and (c) follow from (1.11), and (d) from (1.7], since $V(\phi(s))$ is an orthogonal matrix. Furthermore,

if $x(\bar{s}) > 0, \lambda > 0$, then for every $s > \bar{s}$

$$||M(\bar{s}) - M(s)|| < \frac{1}{x(\bar{s})} - \frac{1}{x(s)} , \tag{1.14}$$

$$||M(\bar{s}) - Z(s)|| < \frac{1}{x(\bar{s})} ,$$

that is, for $s > \bar{s}$ the osculating circle of Z at s and $Z(s)$ are contained in the interior of the osculating circle of Z at \bar{s} .

Indeed, according to a well-known result of differential geometry (see, e.g., [15]), the arclength $\sigma(s)$ of the evolute $M(s)$ of any curve $Z(s)$ is given relative to the curvature $x(s)$ of $Z(s)$ by

$$\dot{\sigma}(s) = - \frac{d}{ds} x(s)^{-1}$$

so that in our case for $s > \bar{s}$

$$\sigma(s) - \sigma(\bar{s}) = \frac{1}{x(\bar{s})} - \frac{1}{x(s)}.$$

Since $M(\tau)$, $\tau \in [\bar{s}, s]$ is not a straight line, we have the additional inequality

$$||M(s) - M(\bar{s})|| < \sigma(s) - \sigma(\bar{s}) = x(\bar{s})^{-1} - x(s)^{-1}$$

which proves the first part of (1.14). The second part follows from the first, as

$$||Z(s) - M(s)|| = x(s)^{-1}$$

2. Interpolation properties of Cornu spirals

In this section we study some simple interpolation problems for Cornu spirals. In stating the results we make use of oriented circles

$$K(a, r) := \left\{ s + r \begin{bmatrix} \cos \phi \\ \sin \phi \end{bmatrix} \mid 0 \leq \phi \leq 2\pi \right\},$$

whose orientation is determined by the sign of the radius $r \neq 0$, and of oriented lines

$$g = g(b, \alpha) := \left\{ b + \sigma \begin{bmatrix} \cos \alpha \\ \sin \alpha \end{bmatrix} \mid \sigma \in R \right\},$$

whose orientation is determined by the direction of the vector $(\cos \alpha, \sin \alpha)^T$. We say that the orientations of an oriented line g and of an oriented circle $K(a, r)$ not meeting g are *coherent*, if $K(a, r)$ lies in the same halfplane determined by g which contains the point

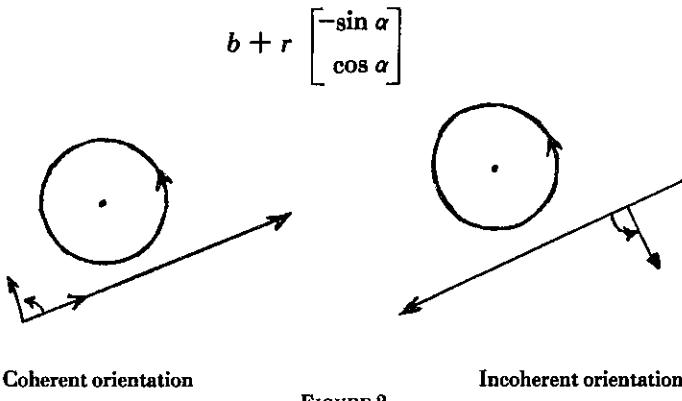


FIGURE 2

A first simple result refers to the problem of joining a line to a circle by a Cornu spiral.

(2.1) THEOREM:

1. For any given oriented circle $K(a, r)$, $r \neq 0$, not meeting a coherently oriented line $g(b, \alpha)$ there exists exactly one oriented Cornu-spiral $Z(s)$ which joins g to $K(a, r)$ (in this order) such that the resulting composite curve is a C^2 curve with a coherent orientation.

2. If g meets K or the orientation of g and K are not coherent, then there is no such interpolating Cornu-spiral.

Of course, a similar result holds for joining an oriented circle K to an oriented line (in this order) by an oriented Cornu-spiral which we do not state explicitly.

PROOF: 1. Without loss of generality we may assume that $r=1/x > 0$ and g is the x -axis in R^2 with its usual orientation. Since $K(a, r)$ is coherently oriented with g , the center $a = (x_0, y_0)^T$ of K is such that $\bar{y} := y_0/r = y_0x > 1$.

Any positively oriented Cornu-spiral touching the x -axis at $(0,0)^T$ with $s = 0$ (i.e., $\phi_0 = 0$, $Z(0) = 0$) with a curvature $x(0) = x_0 = 0$ has the form (see (1.2)).

$$Z(s) = \sqrt{\frac{\pi}{\lambda}} F \left(\sqrt{\frac{\lambda}{\pi}} s \right) =: \begin{bmatrix} x(s) \\ y(s) \end{bmatrix}$$

with some $\lambda > 0$. In order to solve the problem it suffices to determine $s > 0$ and $\lambda > 0$ such that Z has at s the curvature x and $(x_0, y_0)^T$ as center of curvature (see fig. 3).

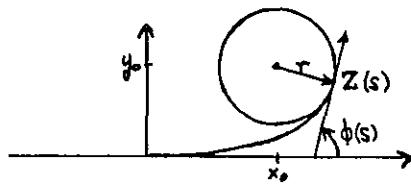


FIGURE 3

This leads to the conditions

$$\begin{aligned} x(s) &= \lambda s = x \quad \rightarrow \quad \lambda = x/s , \\ \phi(s) &= \frac{\lambda}{2} s^2 = xs/2 , \\ \cos \phi(s) &= (y_0 - y(s)) x = \bar{y} - x \sqrt{\frac{\pi}{\lambda}} S \left(\sqrt{\frac{\lambda}{\pi}} s \right) \end{aligned}$$

Hence s must satisfy the equation

$$\cos \frac{xs}{2} + \sqrt{\frac{\pi x}{\lambda}} S \left(\sqrt{\frac{\pi}{\lambda}} s \right) = \bar{y} \quad ,$$

or the variable

$$\Psi := \sqrt{\frac{xs}{2}} \quad ,$$

must solve

$$\cos \Psi^2 + \Psi \sqrt{2\pi} S \left(\sqrt{\frac{2}{\pi}} \Psi \right) = \bar{y} \quad .$$

Now the function

$$\begin{aligned} p(\Psi) &:= \cos \Psi^2 + \Psi \sqrt{2\pi} S \left(\sqrt{\frac{2}{\pi}} \Psi \right) \\ &= \cos \Psi^2 + 2\Psi \int_0^\Psi \sin t^2 dt \end{aligned}$$

is strictly monotonically increasing for $\Psi \geq 0$ because

$$p'(\Psi) = 2 \int_0^\Psi \sin t^2 dt > 0 \text{ for } \Psi > 0.$$

Since $\bar{y} > 1$, $p(0) = 1$ and $\lim_{\tau \rightarrow \infty} p(\tau) = +\infty$, there exists therefore a unique solution $\bar{\Psi} > 0$ of (2.2),

which can be found by Newton's method. In terms of $\bar{\Psi}$, the solution of the problem is

$$s = 2\bar{\Psi}^2/\kappa, \quad \lambda = \kappa/s$$

$$Z(s) = \sqrt{\frac{\pi}{\lambda}} F\left(\sqrt{\frac{\lambda}{\pi}} s\right), \quad x_0 = x(s) - \frac{1}{\kappa} \sin \bar{\Psi}^2$$

The proof of (2) is straightforward.

We now turn to the problem of joining two oriented circles,

$$K_i(a_i, 1/x_i), \quad i = 1, 2, \dots,$$

by an oriented Cornu spiral.

We first show an auxiliary result for the family of Cornu spirals $Z_\lambda(s)$, $\lambda > 0$ with

$$x_0 = 0, \quad \phi_0 = 0, \quad Z_\lambda(0) = 0$$

$$x(s) = \lambda s, \quad \phi(s) = \frac{\lambda}{2} s^2$$

given by [see (1.10), (1.5a)]

$$Z_\lambda(s) = -\sqrt{\frac{\pi}{\lambda}} \left(V\left(\frac{\lambda s^2}{2}\right) h\left(\frac{\lambda s}{\pi}\right) - \frac{1}{2} \begin{bmatrix} 1 \\ 1 \end{bmatrix} \right)$$

For their center of curvature $M_\lambda(s)$ taken at arclength $s = \bar{x}/\lambda$ for which $x(s) = \bar{x}$, the following holds:

$$M_\lambda(\bar{x}/\lambda) = -\sqrt{\frac{\pi}{\lambda}} \left(V\left(\frac{\bar{x}^2}{2\lambda}\right) \bar{h}\left(\frac{\bar{x}}{\sqrt{\pi\lambda}}\right) - \frac{1}{2} \begin{bmatrix} 1 \\ 1 \end{bmatrix} \right)$$

so that because of (1.6) (c), (1.11) and (1.13)

- (a) $\lim_{\lambda \downarrow 0} M_\lambda(\bar{x}/\lambda) - \sqrt{\frac{\pi}{\lambda}} \begin{bmatrix} 0.5 \\ 0.5 \end{bmatrix} = 0 \quad \text{if } \bar{x} > 0$
- (b) $\lim_{\lambda \downarrow 0} M_\lambda(\bar{x}/\lambda) + \sqrt{\frac{\pi}{\lambda}} \begin{bmatrix} 0.5 \\ 0.5 \end{bmatrix} = 0 \quad \text{if } \bar{x} < 0$
- (c) $\lim_{\lambda \rightarrow +\infty} M_\lambda(\bar{x}/\lambda) = \begin{bmatrix} 0 \\ 1/\bar{x} \end{bmatrix}.$

As an easy consequence, we get

(2.4) THEOREM: Let $K_i(a_i, 1/x_i)$, $i = 1, 2$ be two oriented circles.

1. If K_1 and K_2 are coherently oriented, i.e. if $x_1 \cdot x_2 > 0$, then there exists an oriented Cornu spiral joining K_1 to K_2 (in this order) and having both K_1 and K_2 as osculating circle if and only if their centers a_i are different and one of the circles contains the other in its interior.
2. If $x_1 \cdot x_2 < 0$, then there exists an oriented Cornu spiral joining K_1 and K_2 (in this order) and having both K_1 and K_2 as osculating circles if and only if neither circle contains the other, i.e. $\|a_1 - a_2\| > |K_1|^{-1} + |K_2|^{-1}$.

PROOF: (1) Assume $x_2 > x_1 > 0$ without loss of generality and let K_1 contain K_2 in its interior; that is,

$$0 < \|a_1 - a_2\| < 1/x_1 - 1/x_2. \quad (2.5)$$

Then by (2.3) (a), (c)

$$\lim_{\lambda \downarrow 0} \| M_\lambda(x_1/\lambda) - M_\lambda(x_2/\lambda) \| = 0$$

$$\lim_{\lambda \rightarrow +\infty} \| M_\lambda(x_1/\lambda) - M_\lambda(x_2/\lambda) \| = 1/x_1 - 1/x_2 .$$

Since $M_\lambda(x/\lambda)$ depends continuously on $\lambda > 0$, there is a $\lambda' > 0$ such that

$$\| M_{\lambda'}(x_1/\lambda') - M_{\lambda'}(x_2/\lambda') \| = \| a_1 - a_2 \| ,$$

that is the Cornu spiral Z_λ , has two osculating circles of radii $1/x_1$ and $1/x_2$ respectively, whose centers $M_{\lambda'}(x_i/\lambda')$, $i = 1, 2$ have the desired distance. This proves the "if" part of (1). To prove the "only if" part, note that by (1.13)(d), the centers of curvature of any Cornu spiral are different for different arclengths, so that $a_1 \neq a_2$ is a necessary condition for the existence of a Cornu spiral joining two different circles K_1, K_2 . The rest follows from (1.14).

(2.) Assume $x_1 > 0 > x_2$ and $\| a_1 - a_2 \| > 1/x_1 - 1/x_2$. Then, because of (2.3)

$$\lim_{\lambda \rightarrow +\infty} \| M_\lambda(x_1/\lambda) - M_\lambda(x_2/\lambda) \| = 1/x_1 - 1/x_2$$

$$\lim_{\lambda \downarrow 0} \| M_\lambda(x_1/\lambda) - M_\lambda(x_2/\lambda) \| = +\infty$$

Hence by a continuity argument there exists $\lambda' > 0$ such that

$$\| M_{\lambda'}(x_1/\lambda') - M_{\lambda'}(x_2/\lambda') \| = \| a_1 - a_2 \|$$

which proves the "if" part of (2). The "only if" part is trivial. We next turn to the following problems:

(2.6) PROBLEM: For a given oriented circle K and two points $P_0 \in K$ and $P_1 \in K$ find an oriented Cornu-spiral connecting P_0 to P_1 (in this order) which has K as osculating circle at P_0 (see figs. 4 (A), (B)).

(2.6) is equivalent to the problem of connecting a point $P_1 \in K$ to a point $P_0 \in K$ (in this order) on an oriented circle K by an oriented Cornu spiral which has K as osculating circle at P_0 . Using suitable reflections and changes of orientation [compare fig. 4 (B), (C)], (2.6) is seen to be equivalent to the following, which involves only positive orientations:

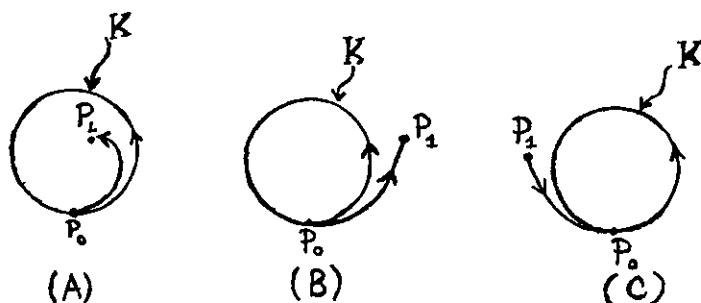


FIGURE 4

(2.6') PROBLEM: For a given positively oriented circle $K = K(M_0, 1/x)$, $x > 0$, and two points $P_0 \in K$ and $P_1 \in K$ find a positively oriented Cornu-spiral with K as osculating circle at P_0 , which leads from P_0 to P_1 , if P_1 is inside, K and leads from P_1 to P_0 if P_1 is outside K .

Clearly, (2.6') depends only on x and the relative positions of P_0 and P_1 so that we may assume without loss of generality

$$M_0 = \begin{bmatrix} 0 \\ 0 \end{bmatrix}, \quad P_0 = \begin{bmatrix} 0 \\ -1/x \end{bmatrix}, \quad P_1 = r \begin{bmatrix} \sin \alpha \\ -\cos \alpha \end{bmatrix}, \quad r \geq 0 ,$$

(see Fig. 5).

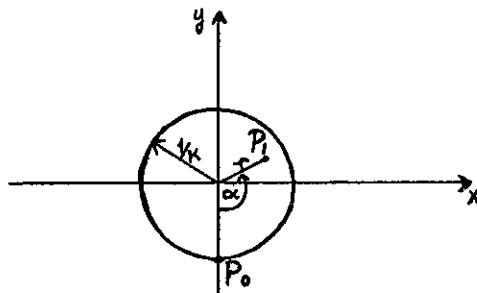


FIGURE 5

By (1.10) the class of positively oriented Cornu spirals Z with

$$Z(0) = P_0 = \begin{bmatrix} 0 \\ -1/x \end{bmatrix}, \quad x(0) = x, \quad \phi(0) = 0$$

is given by

$$\begin{aligned} C_\lambda(s) &= \begin{bmatrix} 0 \\ -1/x \end{bmatrix} + \sqrt{\frac{\pi}{\lambda}} \underbrace{h\left(\frac{x}{\sqrt{\pi\lambda}}\right)}_{h(x/\sqrt{\pi\lambda})} - \sqrt{\frac{\pi}{\lambda}} V(\phi_\lambda(s)) h'(x_\lambda(s)/\sqrt{\pi\lambda}) \\ &= \sqrt{\frac{\pi}{\lambda}} \underbrace{h(x/\sqrt{\pi\lambda})}_{h(x/\sqrt{\pi\lambda})} - V(\phi_\lambda(s)) h'(x_\lambda(s)/\sqrt{\pi\lambda}) \end{aligned}$$

where

$$x_\lambda(s) := x + \lambda s, \quad \phi_\lambda(s) := xs + (\lambda/2)s^2.$$

Essentially, we will show [Theorem (2.25)] that for $r \neq 1/x$, i.e. $P_1 \notin K$, there are countably many numbers $\lambda_1 > \lambda_2 > \dots > 0$ and arclengths s_i , $i \geq 1$, such that $C_{\lambda_i}(s_i) = P_1$ for all $i \geq 1$. To prove this, we need some auxiliary results. From (1.5) (a) and (1.14) follow

$$C_\lambda(+\infty) = \sqrt{\frac{\pi}{\lambda}} h(x/\sqrt{\pi\lambda}), \quad \|C_\lambda(+\infty)\| < 1/x . \quad (2.8)$$

We show next:

(2.9) For any fixed bounded interval $I = [s_1, s_2]$ such that for all $\lambda > 0$ and all $s \in I$, $x(s) = x + \lambda s > 0$ there holds

$$\limsup_{\lambda \downarrow 0} \sup_{s \in I} \|C_\lambda(s)\| = 1/x . \quad (2.9)$$

PROOF. It follows from (2.7):

$$C_\lambda(s) = \sqrt{\frac{\pi}{\lambda}} \left(\bar{h}(x/\sqrt{\pi\lambda}) - V(\phi_\lambda(s)) \bar{h}\left(\frac{x_\lambda(s)}{\pi\lambda}\right) \right) - V(\phi_\lambda(s)) \begin{bmatrix} 0 \\ 1/x_\lambda(s) \end{bmatrix}.$$

By (1.6)(c), the first two terms tend to 0 uniformly in $s \in I$ as $\lambda \downarrow 0$. Hence,

$$\limsup_{\lambda \downarrow 0} \sup_{s \in I} \|C_\lambda(s)\| = \limsup_{\lambda \downarrow 0} \sup_{s \in I} 1/x_\lambda(s) = 1/x, \text{ QED.}$$

With the abbreviations

$$\begin{aligned} \bar{h}_\lambda &:= \sqrt{\frac{\pi}{\lambda}} = \bar{h}(x/\sqrt{\pi\lambda}), \quad h_\lambda(s) := \sqrt{\frac{\pi}{\lambda}} h(x_\lambda(s)/\pi\lambda) \\ \bar{r}_\lambda &:= \|\bar{h}_\lambda\|, \quad r_\lambda(s) := \|h_\lambda(s)\|, \end{aligned}$$

we have from (2.7)

$$C_\lambda(s) = \bar{h} - V(\phi_\lambda(s)) h_\lambda(s) \tag{2.10}$$

and from (1.6), (2.8), the estimates

$$\begin{aligned} \frac{\lambda}{x^3} \left(1 - \frac{35\lambda^2}{x^4}\right) &\leq \bar{r}_\lambda / \sqrt{1 + \frac{9\lambda^2}{x^4}} \leq \lambda/x^3, \quad \bar{r}_\lambda < 1/x \\ \frac{1}{x_\lambda(s)} \left(1 - \frac{15\lambda^2}{x_\lambda(s)^4}\right) &\leq r_\lambda(s) / \sqrt{1 + \frac{\lambda^2}{x_\lambda(s)^4}} \leq \frac{1}{x_\lambda(s)} \end{aligned} \tag{2.11}$$

for all s with $x_\lambda(s) = x + \lambda s > 0$.

Two cases are possible with respect to the location of the target point

$$P_1 = r \begin{bmatrix} \sin \alpha \\ -\cos \alpha \end{bmatrix}$$

which will be treated somewhat differently.

Case (1): $0 \leq r < 1/x$, P_1 lies in the interior of K

Case (2): $r > 1/x$, P_1 lies outside of K .

In Case (1) there is a sufficiently small $\bar{\lambda} > 0$ such that

$$C_\lambda(+\infty) = \bar{h}_\lambda \neq P_1 \text{ for all } 0 < \lambda \leq \bar{\lambda} \tag{2.12}$$

Note this is exactly true if $r = 0, P_1 = 0$, for then by (2.8),

$$C_\lambda(+\infty) = \bar{h}_\lambda \neq 0 \text{ for all } \lambda > 0.$$

If $r > 0$, a suitable $\bar{\lambda} > 0$ can be found because of (2.11). With $\bar{\lambda} > 0$ satisfying (2.12), consider the rays

$$d_\lambda := \{\bar{h}_\lambda + \sigma(P_1 - \bar{h}_\lambda) \mid \sigma \geq 0\}, \quad 0 < \lambda \leq \bar{\lambda}$$

extending from \bar{h}_λ towards P_1 (see fig. 6).

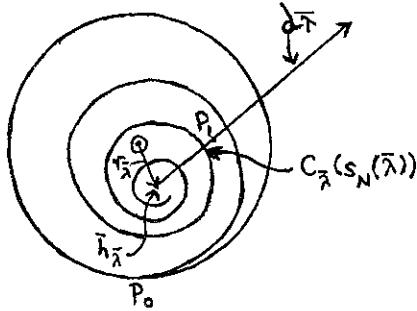


FIGURE 6

Because of (2.10) and using the same reasoning as with (1.8), every Cornu spiral $C_\lambda(s)$, $0 < \lambda \leq \bar{\lambda}$ cuts d_λ infinitely often at abscissae $0 \leq s_1(\lambda) < s_2(\lambda) < \dots$, which satisfy estimates of the form [cf. (1.8)].

$$\begin{aligned} \phi_\lambda(s_n(\lambda)) + 3\pi/2 &\leq \phi_\lambda(s_{n+1}(\lambda)) \\ 2(n-1)\pi \leq 2(n - \frac{1}{4})\pi &\leq \phi_\lambda(s_n(\lambda)) \leq 2(n + \frac{1}{4})\pi \leq 2(n+1)\pi \end{aligned} \quad (2.14)$$

for $n \geq 1$, so that

$$\begin{aligned} s_{n+1}(\lambda) - s_n(\lambda) &\geq \frac{3\pi}{x + \lambda s_n(\lambda)} \left(1 + 1 + \sqrt{\frac{3\pi\lambda}{[x + \lambda s_n(\lambda)]^2}} \right) \\ \bar{s}_{n-1}(\lambda) \leq s_n(\lambda) &\leq \bar{s}_{n+1}(\lambda) \end{aligned} \quad (2.15)$$

where

$$\bar{s}_m(\lambda) := \frac{4m\pi}{x} \left(1 + \sqrt{1 + \frac{4m\pi\lambda}{x^2}} \right)$$

is the solution of the quadratic equation,

$$\phi_\lambda(s) \equiv xs + \frac{\lambda}{2}s^2 = 2m\pi .$$

As a consequence,

$$\lim_{n \rightarrow \infty} s_n(\lambda) = +\infty, \lim_{n \rightarrow \infty} C_\lambda(s_n(\bar{\lambda})) = \bar{h}_\lambda ,$$

and therefore there exists an N such that for all $n \geq N$ (see fig. 6),

$$C_\lambda(s_n(\bar{\lambda})) \in [\bar{h}_\lambda, P_1] := \{ \bar{h}_\lambda + \sigma(P_1 - \bar{h}_\lambda) \mid 0 \leq \sigma \leq 1 \} ,$$

that is, C_λ intersects d_λ between \bar{h}_λ and P_1 at the abscissae $s_n(\bar{\lambda})$, $n \leq N$. Consider any fixed $n \leq N$. By (2.14), $s_n(\lambda)$ is bounded

$$m_n \leq s_n(\lambda) \leq M_n \quad \text{for all } 0 < \lambda \leq \bar{\lambda} \quad (2.16)$$

by some positive constants m_n, M_n . Hence by (2.15), also the differences

$$s_{n+1}(\lambda) - s_n(\lambda) \geq \bar{m}_n > 0 \text{ for all } 0 < \lambda \leq \bar{\lambda} \quad (2.17)$$

are bounded below by a positive $\bar{m}_n > 0$. Moreover, for each $n \geq N$, $s_n(\lambda)$ is a continuous function of λ , hence also $C_\lambda(s_n(\lambda))$, for $0 < \lambda \leq \bar{\lambda}$. Since $s_n(\lambda)$ is bounded above (2.16), (2.9) gives for every fixed n

$$\lim_{\lambda \downarrow 0} \|C_\lambda(s_n(\lambda))\| = 1/x$$

that is, the points $P_{\lambda,n} := C_\lambda(s_n(\lambda)) \in d_\lambda$ tend to the boundary of the circle K as λ tends to 0. Therefore, by the continuity of $P_{\lambda,n}$ and because of

$$P_{\lambda}, \in \varepsilon [\frac{\bar{h}}{\lambda}, P_1]$$

there is a λ_n , $0 < \lambda_n \leq \bar{\lambda}$ such that $P_{\lambda_n, n} = P_1$.

Because of (2.17),

$$\|C_{\lambda_n}(s_{n+1}(\lambda_n)) - \bar{h}_{\lambda_n}\| = r_{\lambda_n}[s_{n+1}(\lambda_n)] < r_{\lambda_n}[s_n(\lambda_n)] = \|P_1 - \bar{h}_{\lambda_n}\| ,$$

so that

$$P_1 \neq C_{\lambda_n}(s_{n+1}(\lambda_n)) \in [\bar{h}_{\lambda_n}, P_1] ,$$

and therefore $\lambda_{n+1} < \lambda_n$.

This proves that in case (1) there are indeed countably many positively oriented different Cornu-spirals C_{λ_n} , $n \geq 1$, and abscissae s'_n , namely

$$s'_n := s_n(\lambda_n) ,$$

having K as osculating circle at $s = 0$ and passing through P_1 ,

$$C_{\lambda_n}(s'_n) = P_1 , \text{ for all } n \geq 1.$$

In case (2), $r > 1/x$, a similar reasoning applies: Here we consider the Cornu-spiral $C_\lambda(s)$ for $0 \geq s > -x/\lambda$, that is for all $s \leq 0$ for which

$$x_\lambda(s) = x + \lambda s > 0$$

is still positive. We will show that:

(2.18) To every integer $n \geq 1$ there exists a $\bar{\lambda} > 0$ and an integer $N \geq 1$ such that for every $0 < \lambda \leq \bar{\lambda}$ the Cornu-spiral $C_\lambda(s)$, $0 \geq s \geq -x/\lambda$, cuts d_λ at abscissae $0 \geq s_{-1}(\lambda) > s_{-2}(\lambda) \dots > s_{-N-n}(\lambda)$ such that

$$(a) s_{-N}(\lambda) > -x/\bar{\lambda} > -x/\lambda ,$$

$$(b) s_{-i}(\lambda) - s_{-i-1}(\lambda) \geq m_i > 0 \text{ for } i = 1, 2, \dots, N+n-1, 0 < \lambda \leq \bar{\lambda} , \quad (2.19)$$

$$(c) r_{\bar{\lambda}}[s_{-N-1}(\bar{\lambda})] \geq r + \frac{1}{x} .$$

(c) means that for $\lambda = \bar{\lambda}$, $C_\lambda(s)$ has at least n cutting points, namely

$$C_{\bar{\lambda}}(s_{-N-i}(\bar{\lambda})) \in \{ \bar{h}_{\bar{\lambda}} + \sigma(P_1 - \bar{h}_{\bar{\lambda}}) \mid \sigma \geq 1 \}, \quad i = 1, 2, \dots, n$$

with $d_{\bar{\lambda}}$ which lie beyond P_1 .

Once (2.18) is proved, then as in case (1), a simple limiting argument $\lambda \downarrow 0$ gives the existence of n values $\lambda_i, \bar{\lambda} \geq \lambda_1 > \lambda_2 > \dots > \lambda_n > 0$ such that

$$C_{\lambda_i}(s_{-N-i}(\lambda_i)) = P_1,$$

since for $\lambda \downarrow 0$ by (2.9) each $C_{\lambda_i}(s_{-N-i}(\lambda)), i \geq 1$, tends to the circle K and so, by the continuity of $s_{-N-i}(\lambda)$ has to pass the point P_1 for a certain parameter value λ_i .

Since by (2.18) n is arbitrary, this gives the existence of countably many Cornu-spirals satisfying the interpolation requirement.

For the proof of (2.18) let γ be defined by $\gamma/x := r + 1/x$, so that $\gamma > 2$. Let $n \geq 1$ be an arbitrary positive integer. Choose any numbers α and β such that

$$\begin{aligned} 0 < \alpha < 1, \quad \sqrt{1-\alpha} &\leq 1/(2\gamma) \\ \alpha\beta < 1, \quad \beta &> 1. \end{aligned} \tag{2.20}$$

Choose a natural number N so large that

$$\begin{aligned} N + n + 1 &\leq \beta N \\ \frac{\alpha^2}{N^2\pi^2(1-\alpha)^2} &\leq \frac{1}{2} \end{aligned} \tag{2.21}$$

and set

$$\bar{\lambda} := \frac{\alpha x^2}{4N\pi}.$$

Consider the solution $\bar{s}_{-m}, N \leq m \leq \beta N$ of the quadratic equation

$$\phi_{\bar{\lambda}}(s) \equiv xs + \frac{\bar{\lambda}}{2}s^2 = -2mn\pi$$

given by

$$\bar{s}_{-m} = \frac{-4mn\pi}{x} \left(1 + \sqrt{1 - \frac{4m\pi\bar{\lambda}}{x^2}} \right)^{-1}.$$

Since by (2.20)

$$0 < \alpha \leq \frac{4m\pi\bar{\lambda}}{x^2} = \alpha \frac{m}{N} \leq \alpha\beta < 1$$

every such \bar{s}_{-m} is real. Moreover,

$$\bar{\lambda} \bar{s}_{-N} = -\alpha x / (1 + 1 - \alpha) = -x \cdot (1 - 1 - \alpha)$$

$$\bar{\lambda} \bar{s}_{-\beta N} = -x (1 - 1 - \beta\alpha)$$

so that by (2.20)

$$x_{\bar{\lambda}}(\bar{s}_{-N}) = x + \bar{s}_{-N} = x \sqrt{1-\alpha} > x_{\bar{\lambda}}(\bar{s}_{-\beta N}) = x \sqrt{1-\beta}\alpha > 0 \quad (2.23)$$

Since by (2.21)

$$\frac{15\bar{\lambda}^2}{x_{\bar{\lambda}}(\bar{s}_{-N})^4} = \frac{15\alpha^2}{16N^2\pi^2(1-\alpha)^2} \leq \frac{1}{2}$$

we get from (2.11) and (2.20) the estimate

$$r_{\bar{\lambda}}(\bar{s}_{-N}) \geq \frac{0.5}{x_{\bar{\lambda}}(\bar{s}_{-N})} = \frac{0.5}{x\sqrt{1-\alpha}} \geq \frac{\gamma}{x} = r + \frac{1}{x}. \quad (2.24)$$

Since by (2.21)

$$\phi_{\bar{\lambda}}(\bar{s}_{-\beta N}) = -2\beta N\pi < -2(N+n+1)\pi ,$$

$C_{\bar{\lambda}}(\bar{s})$ cuts $d_{\bar{\lambda}}$ at least $N+n$ times within the interval $[\bar{s}_{-\beta N}, 0]$ at abscissae

$$0 > s_{-1}(\bar{\lambda}) > s_{-2}(\bar{\lambda}) > \dots > s_{-N-n}(\bar{\lambda}) ,$$

satisfying the estimates

$$-2(i-1)\pi \geq \phi_{\bar{\lambda}}(s_{-i}(\bar{\lambda})) \geq -2(i+1)\pi \quad \text{for } i = 1, 2, \dots, N+n$$

so that

$$\bar{s}_{-i+1} \geq s_{-i}(\bar{\lambda}) \geq \bar{s}_{-i-1} .$$

In particular, we have $0 \geq \bar{s}_{-N} \geq s_{-N-1}(\bar{\lambda})$, so that because of (2.24) and the monotonicity of $r_{\bar{\lambda}}(s)$, we get (2.19)(c). (2.19)(a) follows from $s_{-N-n}(\bar{\lambda}) \geq \bar{s}_{-N-n-1}$, (2.21) implying $\bar{s}_{-N-n-1} \geq \bar{s}_{-\beta N}$ and (2.23). (2.19)(b) is proved as in case (1). All in all, we have shown the following:

(2.25) THEOREM: *For all oriented circles K and two points $P_0 \in K$ and $P_1 \in K$ there are countably many different Cornu-spirals connecting P_0 to P_1 (in this order) and all have K as osculating circle at P_0 .*

3. Interpolation by Clothoidal Splines

A clothoidal spline is a C^2 -curve in R^2 whose curvature $x(s)$ is a continuous piecewise linear function of arclength s . More precisely, such a curve $Z(s)$ is given by a finite collection of parameters

$$0 = s_0 < s_1 < \dots < s_{n+1}$$

$$(Z_i, \phi_i, x_i, \lambda_i), \quad Z_i \in R^2, \quad i = 0, 1, \dots, n$$

such that for each $i = 0, 1, \dots, n$, $Z^i(s) := Z(s)|[s_i, s_{i+1}]$ is a Cornu-spiral with curvature $x^i(s)$ and phase $\phi^i(s)$ given by

$$\begin{aligned}
x^i(s) &:= x_i + \lambda_i(s-s_i) \\
\phi^i(s) &:= \phi_i + x_i(s-s_i) + \frac{\lambda_i}{2}(s-s_i)^2 \\
Z^i(s) &:= Z_i + \int_{s_i}^s \begin{bmatrix} \cos \\ \sin \end{bmatrix} (\phi^i(t)) dt
\end{aligned} \tag{3.1}$$

so that $Z(s)$ is a c^2 -curve; that is, the $Z^i(\cdot)$, $\phi^i(\cdot)$, $x^i(\cdot)$ satisfy the following continuity conditions for all $i = 0, 1, \dots, n-1$:

$$\begin{aligned}
Z^i(s_{i+1}) - Z_i + 1 &\equiv Z_i + \int_0^{\tau_i} \begin{bmatrix} \cos \\ \sin \end{bmatrix} (\phi^i(s_i + \tau)) d\tau - Z_{i+1} = 0 \\
\phi^i(s_{i+1}) - \phi_{i+1} &\equiv \phi_i + x_i + x_i \tau_i + \frac{\lambda_i}{2} \tau_i^2 - \phi_{i+1} = 0 \\
x^i(s_{i+1}) - x_{i+1} &\equiv x_i + \lambda_i \tau_i - x_{i+1} = 0
\end{aligned} \tag{3.2}$$

with $\tau_i := s_{i+1} - s_i$. Of course, the parameters s_i are determined by the τ_i , $s_{i+1} = \tau_0 + \tau_1 + \dots + \tau_i$ so that instead of the s_i , we may take the $\tau_i > 0$ as parameters. Note that we do not require $\lambda_i \neq 0$, so that $Z(s)$ may contain linear or circular segments.

In this section we study the interpolation problem of finding a clothoidal spline passing through a finite number of given points. In this form, the problem is not very meaningful, since by Theorem (2.25) it has arbitrarily many different solutions. More interesting is the problem of finding an interpolating clothoidal spline with minimal $\int x(s)^2 ds$, in analogy to cubic spline interpolation.

(3.3) PROBLEM: *For a given family $\{Z_i\}_{i=0,1,\dots,n+1}$ of different points $Z_i \in \mathbb{R}^2$ find parameters $P_i^T = (\phi_i, x_i, \lambda_i, \tau_i)$, $i = 0, 1, \dots, n$ with $\tau_i > 0$ such that these parameters together with the Z_i determine a clothoidal spline $Z(s)$ by (3.1) satisfying (3.2) and $Z(s_{n+1}) = Z_{n+1}$ so that*

$$\int_0^{s_{n+1}} x(s)^2 ds = \sum_{i=0}^n \int_{s_i}^{s_{i+1}} x^i(s)^2 ds$$

is minimal.

With the notation

$$\begin{aligned}
a_i^T &:= (\phi_i, x_i), b_i^T := (\lambda_i, \tau_i) \\
P^T &:= (P_0^T, P_1^T, \dots, P_n^T), P_i^T := (a_i^T, b_i^T), i = 0, 1, \dots, n
\end{aligned} \tag{3.4}$$

the objective function to be minimized is the function

$$F(P) := \sum_{i=0}^n \int_0^{\tau_i} (x_i + \lambda_i \tau)^2 d\tau$$

which is separable in variables P_i .

The transpose $F'(P)$ of its gradient and its Hessian $F''(P)$ are

$$F'(P) = (u_0, v_0, u_1, v_1, \dots, u_n, v_n)$$

$$F''(P) = \begin{bmatrix} F_0 & & & 0 \\ F_1 & & & \\ & \ddots & & \\ & & \ddots & \\ 0 & & & F_n \end{bmatrix} \quad (3.5)$$

with the \mathbb{R}^2 row vectors

$$\begin{aligned} u_i &:= [0, 2x_i\tau_i + \lambda_i\tau_i^2] \\ v_i &:= [\tau_i^2(x_i + \frac{2}{3}\lambda_i\tau_i)(K_i + \lambda_i\tau_i)^2] \end{aligned} \quad (3.6)$$

and the 4×4 square matrices

$$F_i := 2 \begin{bmatrix} 0, 0 & | & 0, 0 \\ 0, \tau_i & | & \frac{1}{2}\tau_i^2, x_i + \lambda_i\tau_i \\ \hline 0, \frac{1}{2}\tau_i^2 & | & \frac{1}{3}\tau_i^3, (x_i + \lambda_i\tau_i)\tau_i \\ 0, x_i + \lambda_i\tau_i & | & (x_i + \lambda_i\tau_i)\tau_i, (x_i + \lambda_i\tau_i)\lambda_i \end{bmatrix} \quad (3.7)$$

Also, the conditions (3.2) to be satisfied by P are highly structured. They have a staircase-like form

$$G(P) \equiv G(a_0, b_0, \dots, a_n, b_n) \equiv$$

$$\begin{bmatrix} J(a_0, b_0) + Z_0 - Z_1, \\ K(a_0, b_0), -a_1 \\ , J(a_1, b_1) + Z_1 - Z_2, \\ , K(a_1, b_1), -a_2 \\ . \\ . \\ . \\ , J(a_{n-1}, b_{n-1}) + Z_{n-1} - Z_n, \\ , K(a_{n-1}, b_{n-1}), -a_n \\ , J(a_n, b_n) + Z_n - Z_{n+1} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ . \\ . \\ . \\ 0 \\ 0 \end{bmatrix}$$

where

$$J(a, b) := \int_0^{\tau} \begin{bmatrix} \cos \\ \sin \end{bmatrix} (\phi + x\tau + \frac{\lambda}{2}\tau^2) d\tau, \quad a := \begin{bmatrix} \phi \\ x \end{bmatrix}, b := \begin{bmatrix} \lambda \\ \tau \end{bmatrix} \quad (3.9)$$

$$K(a, b) := \begin{bmatrix} \phi + x\tau + \frac{\lambda}{2}\tau^2 \\ x + \lambda\tau \end{bmatrix}$$

Note that the integral in $J(a, b)$ is easily computed in terms of Fresnel integrals (see 1.2) for $\lambda_i \neq 0$ and elementary integration rules for $\lambda_i = 0$. The Jacobian G' of G has a similar structure

$$G'(P) \equiv G'(a_0, b_0, \dots, a_n, b_n) \equiv$$

$$\equiv \begin{bmatrix} A_0, B_0, & & & 0 \\ C_0, D_0, -I & & & \\ & A_1, B_1 & & \\ & C_1, D_1, -I & & \\ & & \ddots & \\ & & & A_{n-1}, B_{n-1} \\ & & & C_{n-1}, D_{n-1}, -I \\ 0 & & & A_n, & B_n \end{bmatrix} \quad (3.10)$$

with partial derivative 2×2 matrices

$$\begin{aligned} A_i &:= D_{(\phi, x)} J(\phi, x, \lambda, \tau)|_{P_i} \\ B_i &:= D_{(\lambda, \tau)} J(\phi, x, \lambda, \tau)|_{P_i} \\ C_i &:= \begin{bmatrix} 1 & \tau_i \\ 0 & 1 \end{bmatrix}, \quad D_i := \begin{bmatrix} \tau_i^2/2 & x_i + \lambda_i \tau_i \\ \tau_i & \lambda_i \end{bmatrix} \end{aligned} \quad (3.11)$$

In terms of the notation just introduced, (3.3) is equivalent to the minimization problem,

$$\text{Minimize } F(P) \text{ subject to } G(P) = 0 \quad (3.12)$$

Let

$$L(P, \Lambda) := F(P) + \Lambda^T G(P)$$

be the Lagrangean of (3.12) and suppose that (3.12) satisfies the usual first order necessary and second order sufficient conditions at the optimal point \bar{P} (which we assume to exist):

1. *The Jacobian $G'(\bar{P})$ of G at \bar{P} has full row rank and there exists a Λ such that $(\bar{P}, \bar{\Lambda})$ is a stationary point of L :*

$$\phi(\bar{P}, \bar{\Lambda}) = 0, \quad \text{with } \phi(P, \Lambda) := \begin{bmatrix} \Delta_p L(P, \Lambda) \\ G(P) \end{bmatrix} = L'(P, \Lambda)^T \quad (3.13)$$

2. *For the Hessian $L_{pp}(\bar{P}, \bar{\Lambda})$ of L with respect to P*

$$P^T L_{pp}(\bar{P}, \bar{\Lambda}) P > 0$$

holds for all $P \neq 0$ satisfying $G'(\bar{P})P = 0$.

Then \bar{P} and $\bar{\Lambda}$ can be found as the solution of the nonlinear equations (3.13). The Jacobian ϕ' of ϕ is a highly structured matrix of the form

$$\phi'(P, \Lambda) = \begin{bmatrix} L_{pp}(P, \Lambda) & , & G'(P)^T \\ G'(P) & , & 0 \end{bmatrix} \quad (3.14)$$

where G' is given by (3.10). It is seen from (3.5), (3.10) that L_{pp} has the same block-structure as F'' (3.5). In solving (3.13), Newton's method can be applied to generate iterates $(P^{(k)}, \Lambda^{(k)})$, $k = 0, 1, \dots$ by solving at each iterate $(P^{(k)}, \Lambda^{(k)})$ the linear equations

$$\phi'(P^{(k)}, \Lambda^{(k)}) \begin{bmatrix} \delta P^{(k)} \\ \delta \Lambda^{(k)} \end{bmatrix} = -\phi(P^{(k)}, \Lambda^{(k)}) \quad (3.15)$$

for the Newton direction $\begin{bmatrix} \delta P^{(k)} \\ \delta \Lambda^{(k)} \end{bmatrix}$, with ϕ' given by (3.14).

Since computing the Hessian $L_{pp}(P^{(k)}, \Lambda^{(k)})$ may be too costly, we may replace L_{pp} within ϕ' by a sufficiently close approximation $H^{(k)}$ as it is done in the minimization algorithms of Han [4, 5] and Powell [11, 12]. One may choose as $H^{(k)}$, e.g. a matrix of the same block structure as L_{pp} , namely (compare 3.5)

$$H^{(k)} = \begin{bmatrix} H_0^{(k)} & & & & \\ & H_1^{(k)} & & & \\ & & \ddots & & \\ & & & \ddots & \\ 0 & & & & H_n^{(k)} \end{bmatrix} \quad (3.16)$$

with 4×4 blocks $H_i^{(k)}$, $i = 0, 1, \dots, n$. One then solves (3.15) with L_{pp} replaced by $H^{(k)}$, namely

$$\begin{bmatrix} H^{(k)} & , & G'(P^{(k)})^T \\ G'(P^{(k)}) & , & 0 \end{bmatrix} \begin{bmatrix} \delta P^{(k)} \\ \delta \Lambda^{(k)} \end{bmatrix} = -\phi(P^{(k)}, \Lambda^{(k)}) \quad (3.17)$$

and computes a new iterate of the form

$$\begin{bmatrix} P^{(k+1)} \\ \Lambda^{(k+1)} \end{bmatrix} = \begin{bmatrix} P^{(k)} \\ \Lambda^{(k)} \end{bmatrix} + \sigma_k \cdot \begin{bmatrix} \delta P^{(k)} \\ \delta \Lambda^{(k)} \end{bmatrix}$$

by choosing a step size σ_k , $0 < \sigma_k \leq 1$, for example as in Han [5], by minimizing a certain penalty function along the ray

$$\left\{ \begin{bmatrix} P^{(k)} \\ \Lambda^{(k)} \end{bmatrix} + \sigma \begin{bmatrix} \delta P^{(k)} \\ \delta \Lambda^{(k)} \end{bmatrix} \mid \sigma \geq 0 \right\} .$$

After having computed the new iterate $(P^{(k+1)}, \Lambda^{(k+1)})$, one may use a rank-2 update formula, say the PSB-update formula, on each 4×4 block $H_i^{(k)}$ in order to generate another matrix $H_i^{(k+1)}$ for each $i = 0, 1, \dots, n$, and thereby $H^{(k+1)}$, having the same structure (3.16) as $H^{(k)}$ and satisfying the usual Quasi-Newton equation:

$$H_i^{(k+1)}(P_i^{(k+1)} - P_i^{(k)}) = \nabla_{P_i} L(P^{(k+1)}, \Lambda^{(k+1)}) - \nabla_{P_i} L(P^{(k)}, \Lambda^{(k)}) \quad (3.18)$$

When solving (3.17), the structure of $H^{(k)}$ (3.16) and $G'(P_k)$ (3.10) can be exploited to reduce the number of operations drastically. For ease of notation, let us drop the superscripts and arguments in (3.17) and write briefly

$$\begin{bmatrix} c \\ d \end{bmatrix}$$

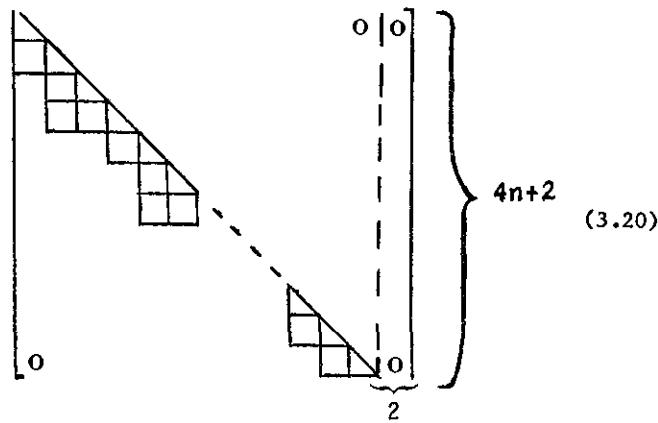
for the right hand side $-\phi(P^{(k)}, \Lambda^{(k)})$ of (3.17). The problem then is to solve an equation of the form

$$\begin{bmatrix} H & , G'^T \\ G' & , 0 \end{bmatrix} \begin{bmatrix} \delta P \\ \delta \Lambda \end{bmatrix} = \begin{bmatrix} c \\ d \end{bmatrix} \quad (3.19)$$

where H and G' have the block structure (3.16) and (3.10), respectively.

We first reduce G' by a series of Givens reflexions Ω_j , $\Omega_j^H = \Omega_j$, $\Omega_j^2 = I$, to a lower triangular matrix of the form [compare its structure with (3.10)]:

$$G'^{-1} \cdot \Omega_1 \cdot \Omega_2 \cdots \cdot \Omega_N = (L, 0) \equiv$$



where all blocks indicated have size 2×2 and L is a $(4n+2) \times (4n+2)$ -lower triangular band matrix. Again, because of the band-structure of (3.10), the number $N = O(n)$ of Givens reflexions needed is

linear in n , so that the unitary matrix

$$\Omega := \Omega_1 \cdot \Omega_2 \cdot \dots \cdot \Omega_N \quad (3.21)$$

need not be computed explicitly, but can be stored in product form. Partition the matrix

$$\Omega = (\bar{\Omega}, \tilde{\bar{\Omega}})$$

where

$$\bar{\Omega} = \Omega \begin{bmatrix} 0 & 0 \\ \vdots & \vdots \\ \vdots & \vdots \\ 1 & 0 \\ 0 & 1 \end{bmatrix} = \Omega_1 \cdot \Omega_2 \cdot \dots \cdot \Omega_N \begin{bmatrix} 0 & 0 \\ \vdots & \vdots \\ \vdots & \vdots \\ 1 & 0 \\ 0 & 1 \end{bmatrix}$$

are the last two columns of Ω , which are computed using the product form of (3.21), $\bar{\Omega}$ is not needed explicitly. Introduce new variables

$$t = \begin{bmatrix} t_1 \\ t_2 \end{bmatrix}$$

via $\delta P = \Omega t = \bar{\Omega}t_1 + \tilde{\bar{\Omega}}t_2$.

Then because of

$$G' \bar{\Omega} = L, G' \tilde{\bar{\Omega}} = 0$$

the second set of equations (3.19)

$$G' \delta P = Lt_1 = d \rightarrow t_1$$

can be solved for t_1 in $O(n)$ steps using the structure of L (3.20), and the vector

$$P^1 := \bar{\Omega}t_1 = \Omega_1 \Omega_2 \dots \Omega_N \begin{bmatrix} t_1 \\ 0 \\ 0 \end{bmatrix}$$

is computed using (3.21).

Now we turn to the first set of equations (3.19)

$$H\delta P + G'\mathbf{T}\delta \Lambda = c \quad (3.22)$$

Multiplying these equations by $\tilde{\bar{\Omega}}^T$ and introducing t_1 and t_2 instead of δP , we get because of $\tilde{\bar{\Omega}}^T G'^T = 0$

$$\tilde{\bar{\Omega}}^T H \bar{\Omega} t_1 + \tilde{\bar{\Omega}}^T H \tilde{\bar{\Omega}} t_2 = \tilde{\bar{\Omega}}^T c$$

or

$$(\tilde{\bar{\Omega}}^T H \bar{\Omega}) t_2 = \tilde{\bar{\Omega}}^T c - \tilde{\bar{\Omega}}^T H P^1 \rightarrow t_2 \quad (3.23)$$

Again, the 2×2 matrix $\bar{\Omega}^T H \bar{\Omega}$ and the vectors $\bar{\Omega}^T H P^1$ can be computed with $O(n)$ operations using the block structure of H (3.16). t_2 is obtained by solving the two linear equations (3.23) and δP is calculated by

$$P^2 := \bar{\Omega} t_2, \quad \delta P := P^1 + P^2.$$

Finally, we multiply (3.22) by $\bar{\Omega}^T$ in order to get $\delta \Lambda$. Observing (3.20) we obtain a triangular system of linear equations

$$L^T t \delta \Lambda = \bar{\Omega}^T c - \bar{\Omega}^T H \delta P$$

the right hand side of which can be easily computed with $O(n)$ operations using the structure of H and the product form of $\bar{\Omega}^T$:

$$\bar{\Omega}^T = \begin{bmatrix} 1 & & 0 & 0 & 0 \\ & \ddots & & & \\ & & \ddots & & \\ 0 & & & 1 & 0 & 0 \end{bmatrix} \quad \Omega_N \Omega_{N-1} \dots \Omega_1$$

All in all, we can compute the solution of (3.19) with $O(n)$ arithmetic operations, so that the Han-Powell method is quite effective in our case. The method has been realized and successively tested by Huckle [6]. With respect to a convergence analysis of the above method (the method converges locally superlinearly under some mild assumptions) we refer to the literature Han [4,5], Powell [12], Tapia [16].

4. Smoothing by Clothoidal Splines

We consider the following generalization of (3.3) (compare Reinsch [13]):

PROBLEM: For a given family $\{\bar{Z}_i\}_{i=0,1,\dots,n+1}$ of different points

$$\bar{Z}_i = \begin{bmatrix} \bar{x}_i \\ \bar{y}_i \end{bmatrix} \in \mathbb{R}^2$$

and numbers $S \geq 0, \Delta x_i > 0, \Delta y_i > 0, i = 0, 1, \dots, n+1$, find parameters

$$\left\{ (\phi_i, x_i, \lambda_i, \tau_i) \right\}_{i=0,1,\dots,n}, \left\{ Z_i \right\}_{i=0,1,\dots,n+1}, z, Z_i = \begin{bmatrix} x_i \\ y_i \end{bmatrix} \in \mathbb{R}^2, \quad (4.1)$$

which determine a clothoidal spline $Z(s)$ via (3.1) satisfying the conditions

$$\text{a)} \quad (3.2) \text{ and } Z(s_{n+1}) = Z_{n+1} \quad (4.2)$$

$$\text{b)} \quad \sum_{i=0}^{n+1} \left(\left(\frac{x_i - \bar{x}_i}{\Delta x_i} \right)^2 + \left(\frac{y_i - \bar{y}_i}{\Delta y_i} \right)^2 \right) + z^2 = S$$

(z is a slack variable) such that $\int_0^{s_{n+1}} \lambda(s)^2 ds$ is minimal.

$$L_{PP}(P, \Lambda) = \begin{bmatrix} L_0 & & & 0 \\ & L_1 & & \\ & & \ddots & \\ & & & L_n \\ 0 & & & L_{n+1} \end{bmatrix} \quad (4.10)$$

where the L_i , $i \leq n$, are symmetric 4 by 4 matrices and L_{n+1} is the $(2n+5)$ by $(2n+5)$ diagonal matrix.

$$L_{n+1} := \Lambda_z \cdot \text{diag}(\Delta x_0, \Delta y_0, \dots, \Delta x_{n+1}, 1)^{-2}, \quad (4.11)$$

where Λ_z is the last component of Λ .

As in the previous section, one has to solve (4.8) by Newton's method (compare (3.15) – (3.17) where at each iteration point $[P^{(k)}, \Lambda^{(k)}]$ the Hessian L_{PP} is approximated by a positive definite matrix $H^{(k)}$ having the same structure as L_{PP} (4.10),

$$H^{(k)} = \begin{bmatrix} H_0^{(k)} & & & 0 \\ & H_1^{(k)} & & \\ & & \ddots & \\ & & & H_n^{(k)} \\ 0 & & & H_{n+1}^{(k)} \end{bmatrix} \quad (4.12)$$

with certain 4 by 4 matrices $H_i^{(k)}$ for $i \leq n$ and the diagonal matrix (see 4.11)

$$H_{n+1}^{(k)} = \Lambda_z^{(k)} \cdot \text{diag}(\Delta x_0, \Delta y_0, \dots, \Delta x_{n+1}, \Delta y_{n+1}, 1)^{-2}. \quad (4.13)$$

After having computed $P^{(k+1)}, \Lambda^{(k+1)}$ (see previous section) $H^{(k+1)}$ is obtained from $H^{(k)}$ by updating each $H_i^{(k)}$, $i \leq n$, individually by some update method (e.g., the PSB-method) which guarantees the same quasi-Newton relation (3.18) as in section 4; $H_{(n+1)}^{(k+1)}$ is computed by (4.13).

Of course, for large numbers n the efficiency of the algorithm outlined crucially depends on the number of operations needed to perform one Newton step $[P^{(k)}, \Lambda^{(k)}] \rightarrow [P^{(k+1)}, \Lambda^{(k+1)}]$, that is to solve a linear system of equations [see (3.17), (3.19)] of the form

$$\begin{bmatrix} H & , G^T \\ G' & , 0 \end{bmatrix} \begin{bmatrix} \delta P \\ \delta \Lambda \end{bmatrix} = \begin{bmatrix} c \\ d \end{bmatrix} \quad (4.14)$$

for $\delta P, \delta \Lambda$, where H and G' are given matrices with the structure (4.12) and (4.9), respectively. An algorithm of the type considered at the end of the previous section leads to difficulties inasmuch as it would take $O(n_3)$ operations to solve (4.14) because it requires the computation and storage of a large dense matrix of the order $O(n)$.

Another numerically stable way to solve the linear system (4.14), which exploits the symmetry of the matrix

$$\begin{bmatrix} H & , G^T \\ G' & , 0 \end{bmatrix} \quad (4.15)$$

would be to use the Bunch-Parlett decomposition of (4.15) (see Bunch, Parlett [4]). However, this method requires a pivot selection in each basic elimination step, which, though preserving the symmetry, will in general destroy the specific block structure of the matrix in (4.15). This method, therefore, also requires $O(n^3)$ operations to solve (4.14). A cheaper method for solving (4.14) might be a variant of the conjugate gradient algorithm for solving linear equations

$$Ax = b$$

with a symmetric nonsingular, but perhaps indefinite matrix A , which is described in Paige and Saunders [9]. This method can take the block structure (4.12), (4.9) of H and G' into account and therefore requires only $O(n^2)$ operations and $O(n)$ storage to solve (4.14).

It is interesting to note in this context that the system (4.14) can be solved with only $O(n)$ operations, if the block-diagonal matrix $L_{PP}(\bar{P}, \bar{\Lambda})$ (4.10) would be positive definite at the solution $(\bar{P}, \bar{\Lambda})$ of (4.7). In this case, it can be shown that the matrices $H^{(k)}$ (4.12) generated by the usual update techniques (PSP-, DFP-, or BFGS-methods) will be positive definite, at least locally, if the starting values $[P^{(0)}, \Lambda^{(0)}$, and $H^{(0)}$] are sufficiently close to $(\bar{P}, \bar{\Lambda})$ and $L_{PP}(\bar{P}, \bar{\Lambda})$, respectively.

If H is positive definite, then a numerically stable method of solving (4.14) requiring only $O(n)$ operations runs as follows:

In a first step compute the Cholesky decomposition of

$$H = R^T R$$

which requires $O(n)$ operations and gives an upper triangular R of the form [compare (4.12)]

$$R = \begin{bmatrix} R_0 & & & 0 \\ & R_1 & & \\ & & \ddots & \\ & & & R_n \\ 0 & & & R_{n+1} \end{bmatrix} \quad (4.16)$$

with 4×4 upper triangular R_i for $i \leq n$ and diagonal R_{n+1} . Premultiplying (4.14) by

$$\begin{bmatrix} R^{-T} & , & 0 \\ -G'R^{-1}R^{-T} & , & I \end{bmatrix}$$

gives the equivalent system

$$\begin{bmatrix} R & , (G'R^{-1})^T \\ 0 & , -(G'R^{-1})(G'R^{-1})^T \end{bmatrix} \begin{bmatrix} \delta P \\ \delta \Lambda \end{bmatrix} = \begin{bmatrix} R^{-T}c \\ d - G'R^{-1}R^{-T}c \end{bmatrix} \quad (4.17)$$

So the next step is to compute

$$c' := R^{-T}c, A := G'R^{-1}$$

which again requires only $O(n)$ operations because of the simple structure of R (4.16) and G' (4.9). Note, moreover, that the product matrix $A = G'R^{-1}$ has a form very similar to (4.9), namely (illustration for $n=2$):

$$A = \begin{bmatrix} x & x & x & x \\ x & x & x & x \\ x & x & x & x & o \\ x & x & x & x & x \\ x & x & x & x & x \\ x & x & x & x & x \\ x & x & x & x & x & o \\ x & x & x & x & x & x \\ x & x & x & x & x & x \\ 0 & & & & & 0 \\ 0 & & & & & 0 \end{bmatrix} \quad (4.18)$$

We next reduce A to "lower triangular" form by multiplying A from the right by suitable Givens reflexions $\Omega_1, \Omega_2, \dots, \Omega_N = O(n)$ matrices Ω_i and only $O(n)$ operations are needed and the structure of (4.16) is essentially preserved and fill in will occur at most $O(n)$ places. Each will annihilate a particular above diagonal element of A ; the resulting matrix is of the form

$$A\Omega_1\Omega_2\dots\Omega_N = (L, O) \quad (4.19)$$

where "O" denotes a $(4n+3)$ by $(2n+6)$ zero matrix and L is a $(4n+3)$ by $(4n+3)$ lower triangular matrix with the structure

$$L = \begin{bmatrix} \text{Lower triangular} & & O \\ & \ddots & \\ & & \text{Lower triangular} \\ 0 & \dots & 0 \end{bmatrix} \quad \left. \begin{array}{c} \} 2 \\ \} 1 \end{array} \right.$$

Note that the dense $(6n+9)$ by $(6n+9)$ product matrix $\Omega = \Omega_1\Omega_2\dots\Omega_N$ need not be computed. Its storage in product form requires only $O(n)$ places. Concurrently with the elimination process for finding L , we can compute the vector

$$c'' := \Omega_N\dots\Omega_2\Omega_1 c'$$

Now it is easy to solve (4.17) for δP and $\delta \Lambda$. The second equation (4.17) gives by (4.19) at once

$$AA^T\delta\Lambda = LL^T\delta\Lambda = -d + Ac' = -d + (L, 0)c'' \quad (4.20)$$

so that

$$\delta\Lambda = -L^{-T}L^{-1}d + (L^{-T}, 0)c'' \quad (4.21)$$

i.e. $\delta\Lambda$ can be found by solving three linear equations with triangular matrices. The first equation (4.17) now gives by (4.21)

$$\begin{aligned}
R\delta P &= R^{-T}c - A^T\delta\Lambda \\
&= c' - \Omega \begin{bmatrix} L^T \\ 0 \end{bmatrix} \delta\Lambda \\
&= c' - \Omega \begin{bmatrix} -L^{-1}d + (I, 0)c'' \\ 0 \end{bmatrix}
\end{aligned} \tag{4.22}$$

Unfortunately enough, the computation of

$$c''' := \Omega \begin{bmatrix} L^{-1}d - (I, 0)c'' \\ 0 \end{bmatrix} = \Omega_1 \Omega_2, \dots, \Omega_N \begin{bmatrix} L^{-1}d - (I, 0)c'' \\ 0 \end{bmatrix}$$

requires the storage of all Ω_i (this was not needed in computing c''). Note that $L^{-1}d$ has already been obtained during the calculation of $\delta\Lambda$ (4.21). Finally, by (4.22), δP is obtained by solving one more triangular system of linear equations

$$R\delta P = c' - c''' \rightarrow \delta P , \tag{4.23}$$

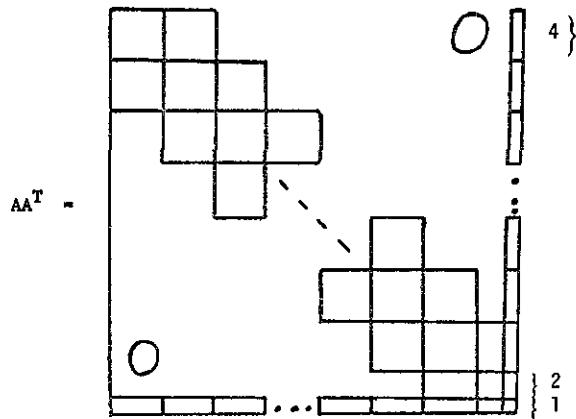
again requiring only $O(n)$ operations.

At the expense of numerical stability one may get around the elimination process to find L and the storage of the orthogonal matrices Ω_i in the following way:

Having computed the Cholesky decomposition of $H = R^T R$, the matrix $A = G^T R^{-1}$, the product $A A^T$ and its Cholesky decomposition $A A^T = L L^T$, computing $\delta\Lambda$ and δP from (4.20), (4.22) is straightforward:

$$\begin{aligned}
L L^T \delta\Lambda &= -d + A c' \rightarrow \delta\Lambda \rightarrow A^T \delta\Lambda \\
R\delta P &= c' - A^T \delta\Lambda \rightarrow \delta P
\end{aligned} \tag{4.24}$$

Note in this context that the product $A A^T$ has a simple sparse structure needing only $O(n)$ places for storage:



Both algorithms require only $O(n)$ operations for solving (4.14) in each Newton step, but the former will be numerically more stable, as it avoids the calculation of $A A^T$ and cancels products such as $L L^{-1}$, $R R^{-1}$, which arise inherently during the solution of (4.24), as often as possible.

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5. References

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