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# The Thermal Conductivity of Oxygen*

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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).

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

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

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

$T_{\mathrm{ref}}$ is the reference temperature, the temperature of the cell;

$q$ is the applied power;

$\lambda$ is the thermal conductivity of the fluid, a function of both temperature and density;

$K$ is the thermal diffusivity of the fluid, i.e., $K = \lambda/\varrho C_p$. $K$ is normally taken at the temperature $T_{\mathrm{ref}}$ 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 $\gamma$ is Euler's constant, $\gamma = 0.5772...$

The relation given by eq (1) implies a straight line for a plot of $\Delta T$ 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 $\Delta T$ and $ln(t)$ is linear. This range of validity is determined from 250 measured $\Delta$T-t pairs by selecting a beginning time $t_1$ and an ending time $t_2$. The slope of the $\Delta T$ 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 $\lambda$ is given by

$$T = T_{\mathrm{ref}} + \frac{1}{2}\left[\Delta T(t_1) + \Delta T(t_2)\right] \qquad (2)$$

The density assigned to the measurement of $\lambda$ 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 $\Delta T_w$. A number of corrections account for the departure of the real instrument from the ideal model:

$$\Delta T = \Delta T_w - \Sigma\, \delta T_i \qquad (3)$$

These corrections $\delta T_i$ have been fully described elsewhere [9]; the most important at lower times is $\delta T_1$, 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 Ω at 76 K to 90 Ω at 298 K. A short or compensating wire is approximately 5 cm in length and its resistance varies from 10 to 45 Ω. 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 $\Delta T$-$ln(t)$ 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 $\Delta T$ vs

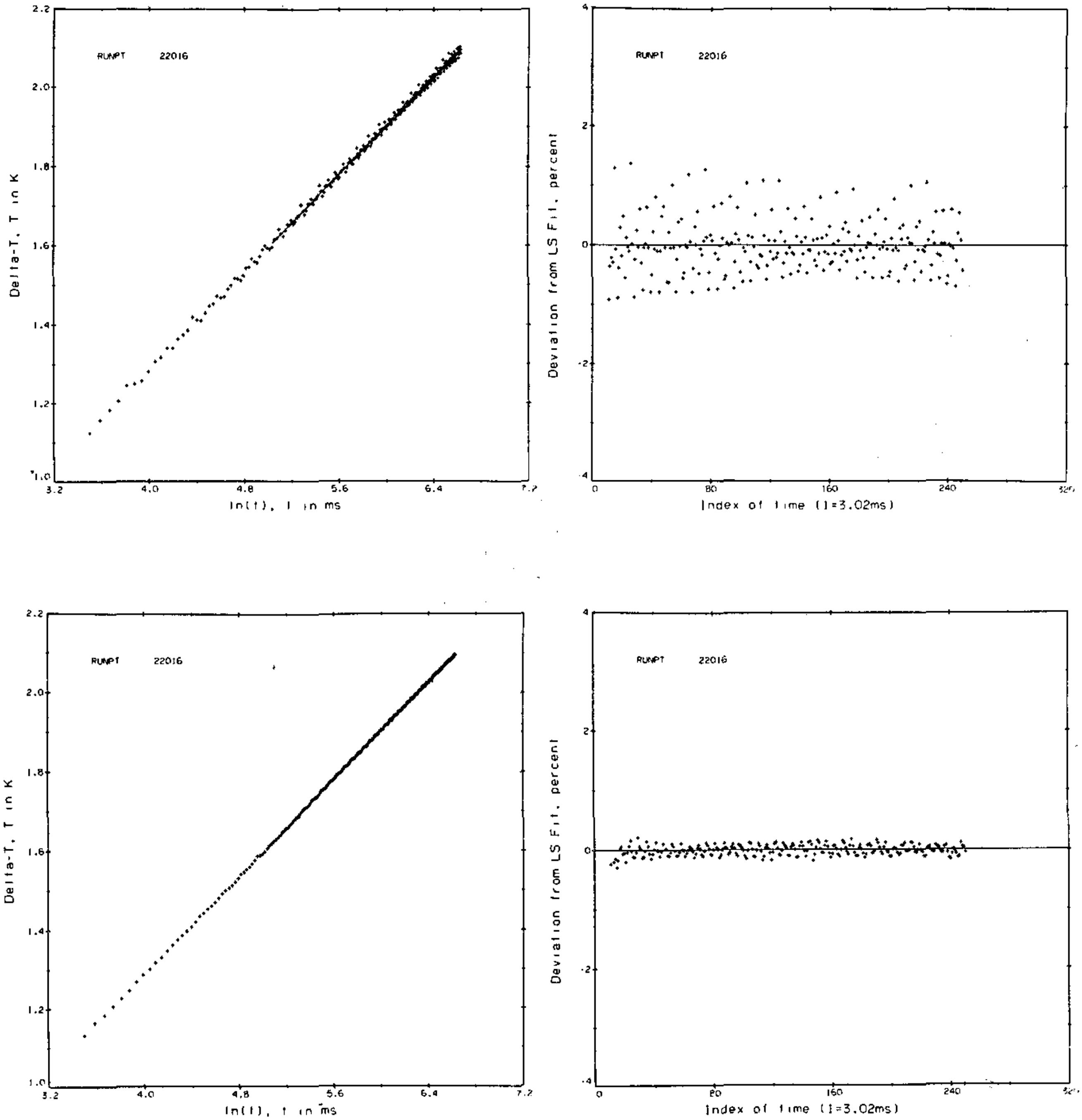

FIGURE 1. Effect of the digital filtering technique for point 22016.

*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, $\Delta T$-*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 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 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.

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. |

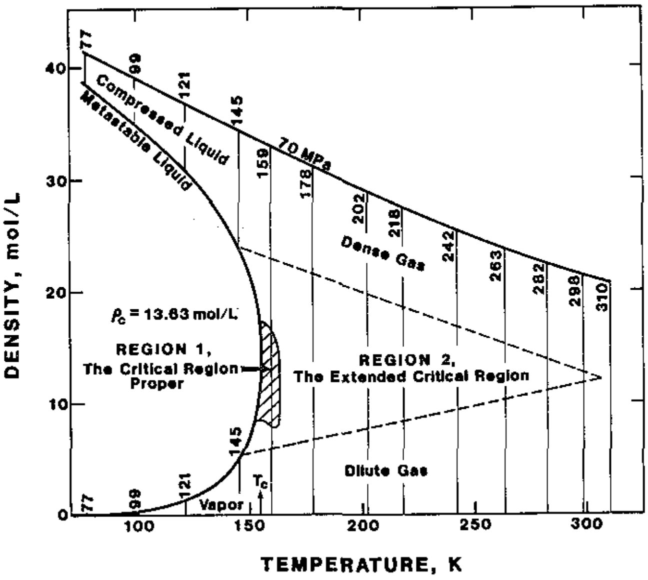

FIGURE 2. Region of the PVT surface covered by the present thermal conductivity measurements.

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

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

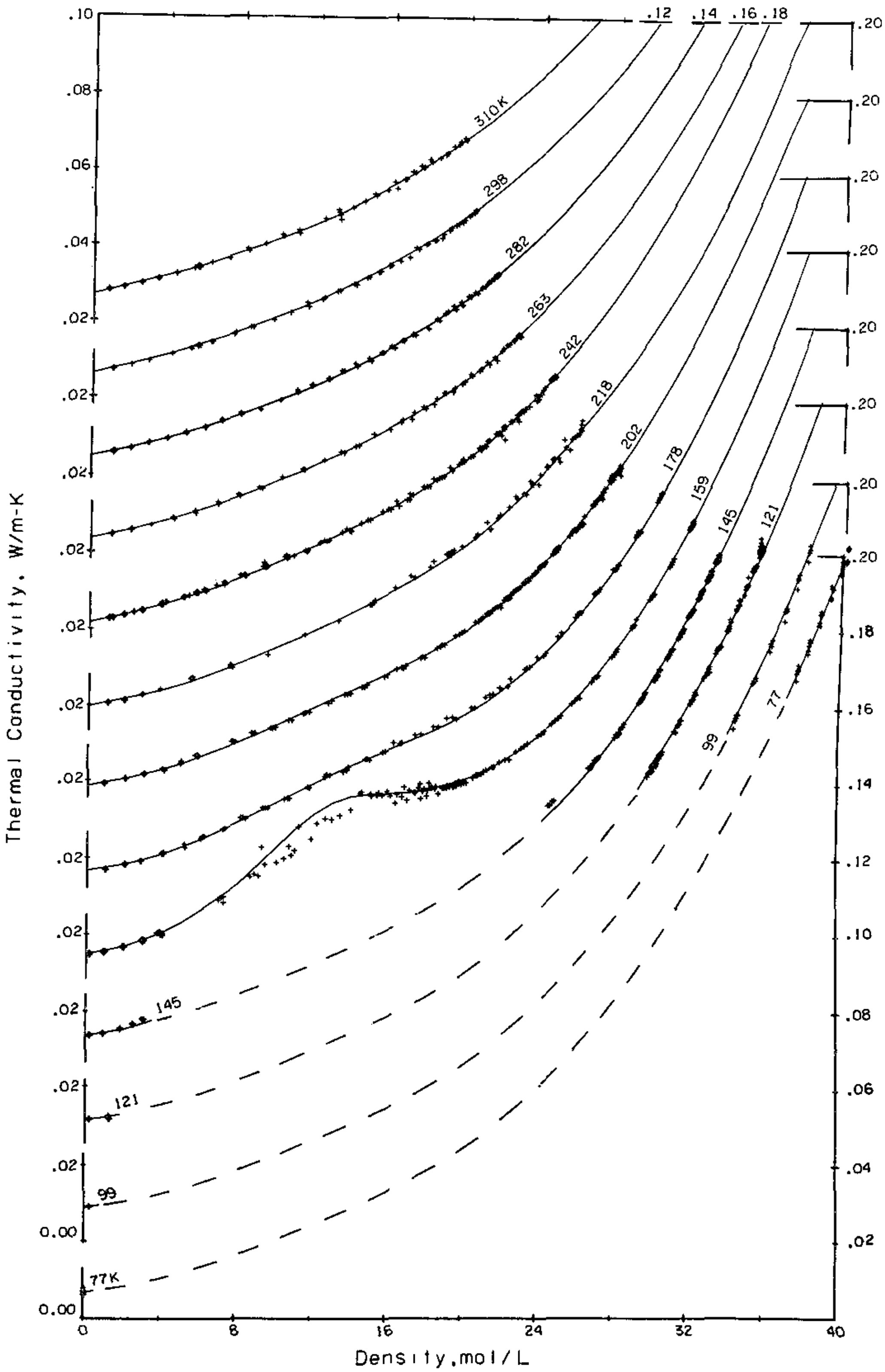

**Figure 3.** Overview of the thermal conductivity measurements on oxygen. Each isotherm is on a separate scale. The scales are offset from each other by 0.02 W/m·K for better visibility.

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 $\Delta T$ 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 $N_2$ 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 12.6 mol/L, or 0.92 $\varrho_c$. The power level varies by a factor of 2, and experimental temperature and experimental density are perforce 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 $\Delta T$ 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

$$\lambda(\varrho,T) = \lambda_0\ (T) + \lambda_{\mathrm{excess}}(\varrho,T) + \Delta\lambda_{\mathrm{critical}}(\varrho,T) \quad (4)$$

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

$$\lambda_0(T) = [A_1T^{-1} + A_2T^{-2/3} + A_3T^{-1/3} + A_4 + A_5T^{1/3} + A_6T^{2/3} + A_7T + A_8T^{4/3} + A_9T^{5/3}]/1000. \quad (5)$$

with $\lambda_0$ 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 polynominal. 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 $\lambda_0$ 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:

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

where the parameters $\alpha$, $\beta$, $\gamma$, $\delta$ are functions of temperature as follows:

$$\alpha = B_1T$$
$$\beta = B_2 + B_3T + B_4T^2$$
$$\gamma = B_5 + B_6T + B_7T^2$$
$$\delta = B_8 + B_9T + B_{10}/T^2.$$

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 $\alpha\varrho$ is necessary if the exponential part of the term is to fit the isotherms adequately. At the same time, $\alpha \varrho$ 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 $\theta$ used in the analysis of propane [14] to account for the high density behavior of the excess thermal conductivity was also considered here. The $\theta$ is a function of density with different contributions above and

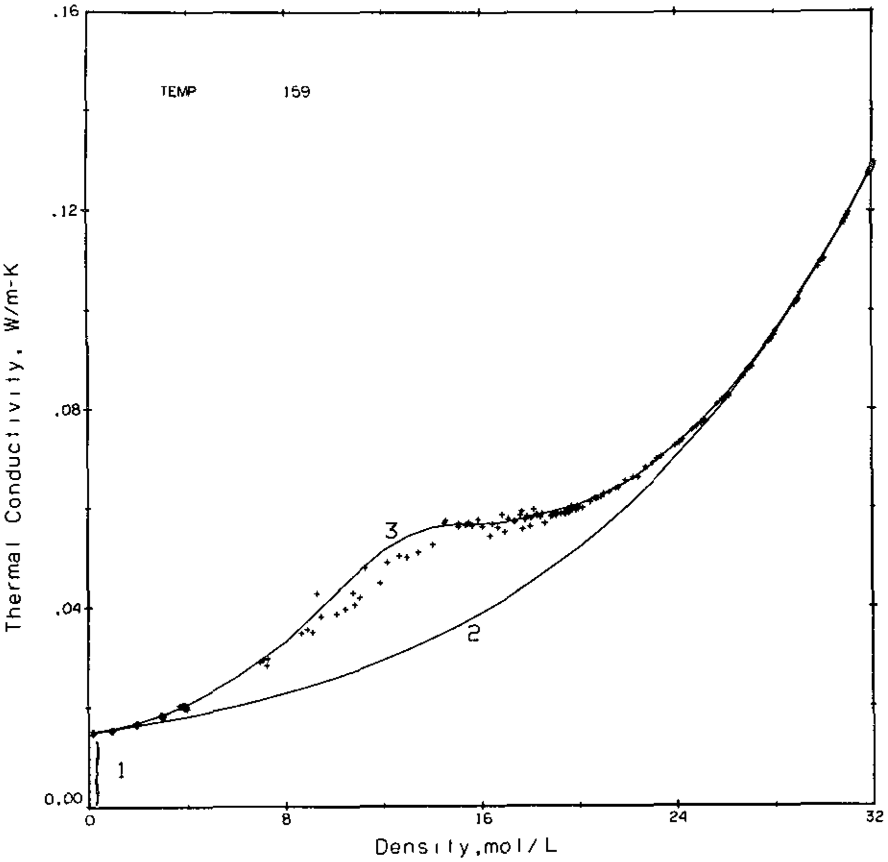

FIGURE 4. Isotherm analysis illustrated for a temperature of 159 K. + experimental points as adjusted to 159 K in table 2; 1 the dilute gas term, $\lambda_o$; 2 the background term, $\lambda_o + \lambda_{excess}$; 3 the calculated thermal conductivity, $\lambda_o + \lambda_{excess} + \Delta\lambda_{critical}$.

TABLE 3. *Extrapolated and calculated values of $\lambda_o$*

| Temperature K | $\lambda_o$ | | differences | | number of terms in series | cut off density mol/L |
|---|---|---|---|---|---|---|
| | extrapolated ± 2σ W/m·K | calculated, eq (5) W/m·K | W/m·K | percent | | |
| 145. | 0.01358 ± 0.00019 | 0.01340 | 0.00018 | 1.31 | 3 | 8.5 |
| 159. | .01467 ± .00021 | .01472 | -.00005 | -.34 | 3 | 8.5 |
| 178. | .01636 ± .00060 | .01644 | -.00008 | -.51 | 4 | 10.5 |
| 202. | .01845 ± .00036 | .01851 | -.00006 | -.31 | 3 | 8.5 |
| 218. | .01977 ± .00086 | .01984 | -.00006 | -.32 | 4 | 10.5 |
| 242. | .02161 ± .00042 | .02177 | -.00016 | -.73 | 4 | 10.5 |
| 263. | .02349 ± .00084 | .02341 | .00008 | .34 | 4 | 10.5 |
| 282. | .02497 ± .00037 | .02487 | .00010 | .39 | 3 | 8.5 |
| 298. | .02599 ± .00028 | .02609 | -.00010 | -.37 | 3 | 8.5 |
| 310. | .02725 ± .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 $\lambda$-$\varrho$ 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 $\delta$ the parameters are well behaved and vary slowly with temperature. Their dependence on temperature is shown in figure 5.

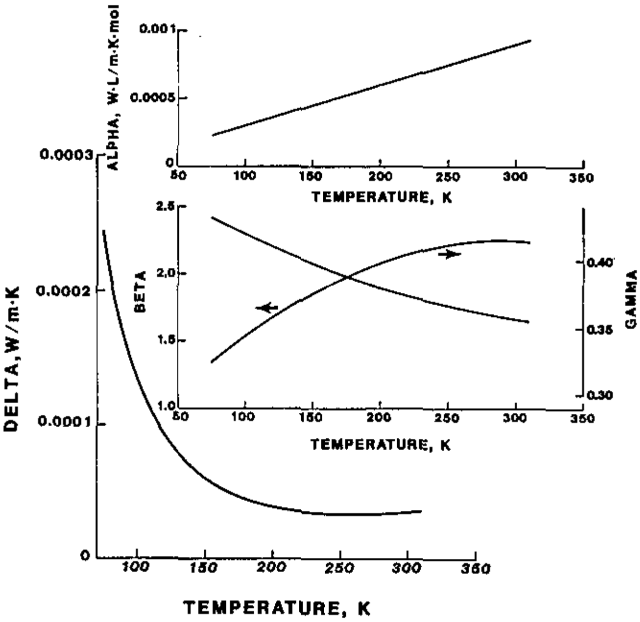

FIGURE 5. Parameters $\alpha$-$\delta$ of the excess thermal conductivity as a function of temperature.

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 substracting terms 1 and 2 from the experimental values. For this analysis we will consider two separate regions which are shown in $\varrho$-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

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

For oxygen $T_c = 154.581$ K and $\varrho_c = 13.63$ mol/L. Therefore, the region of concern is bounded approximately by $150. \leqslant T \leqslant 160.$ K and $10. \leqslant \varrho \leqslant 17.$ 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 calcultions. The use of a PVT surface by Weber [18], i.e., a polynomial representation of isotherms, with

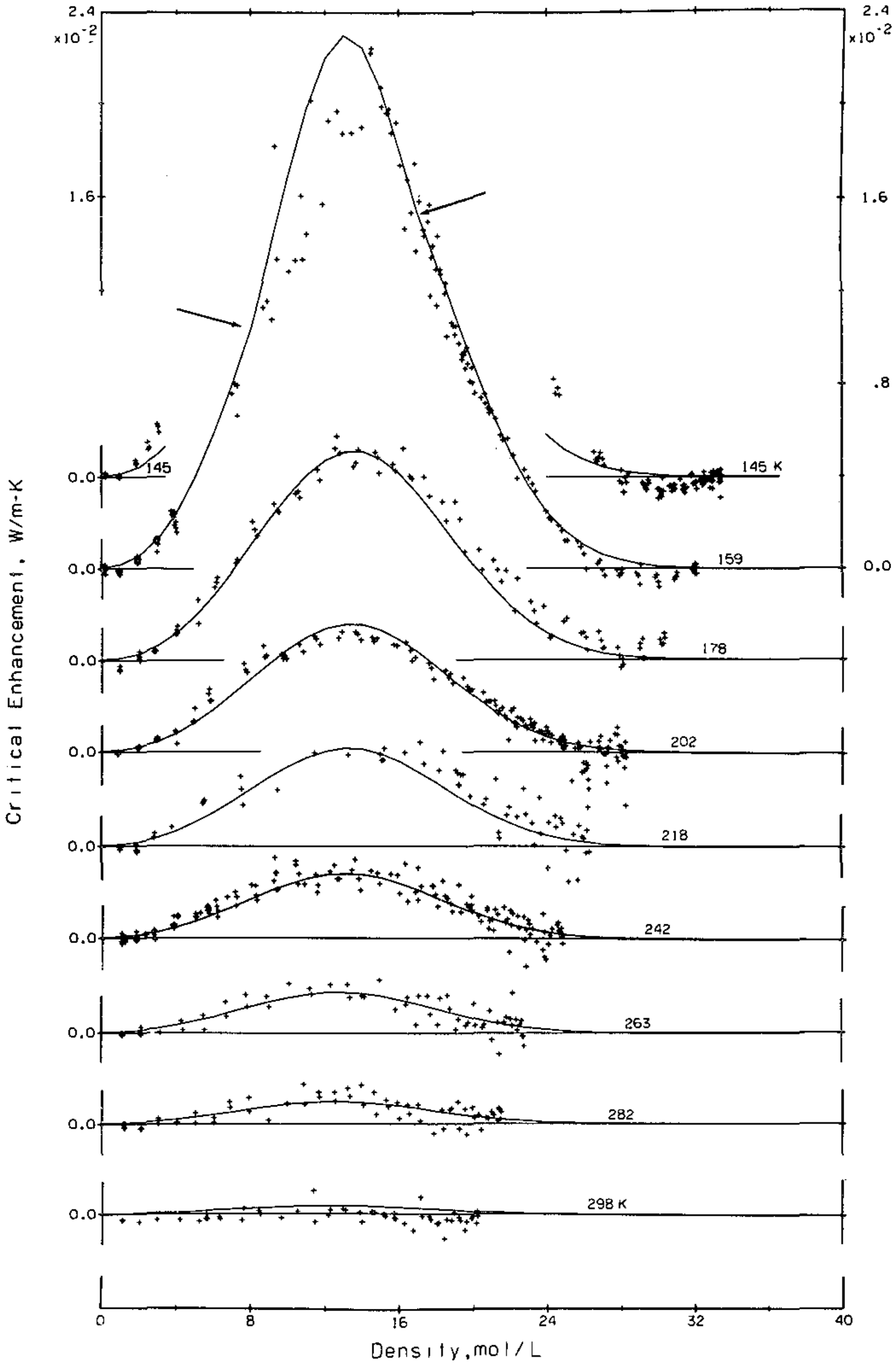

FIGURE 6. Term 3, the critical enhancement or anomalous increase along isotherms. Each isotherm is on a separate scale. The spacing between isotherms is 0.004 W/m • K. For the 159K isotherm the arrows indicate the switch from region 1 to region 2 in the computation.

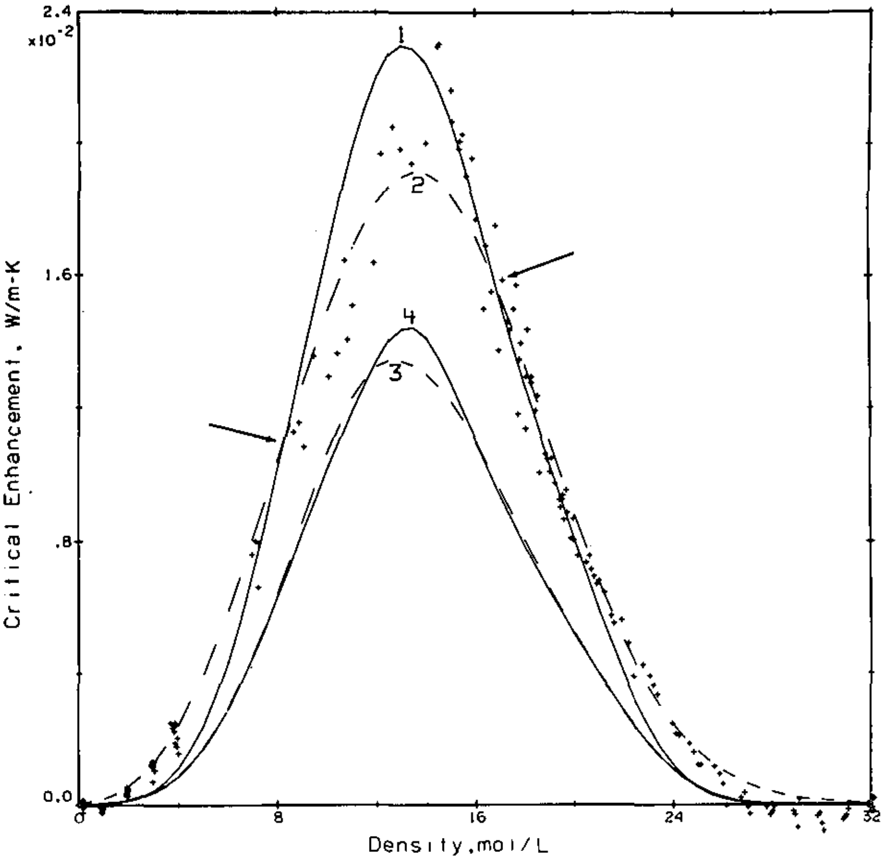

FIGURE 7. Comparison of experimental and calculated $\Delta\lambda_c$ at 159 K. + experimental points as adjusted to 159 K in table 2; 1 $\Delta\lambda_c$ calculated according to [17]; 2 $\Delta\lambda_c$ calculated from eqs (9-13) this paper; 3 $\Delta\lambda_c$ calculated according to [5]; 4 $\Delta\lambda_c$ 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 $\Delta\lambda_c(\varrho,T)$ 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, $\varrho_{\text{center}}$, which is a function of temperature. Close to critical $\varrho_{\text{center}}$ is nearly equal to the critical density, but at higher temperatures $\varrho_{\text{center}}$ changes to lower densities as will be seen in figure 6. A third aspect is that the data proved to be slightly asymmetric about $\varrho_{\text{center}}$.

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 $\varrho_c$, whereas what is needed is a maximum at a density less than $\varrho_c$. A plot of the densities at which we require the maxima to occur, i.e., $\varrho_{center}$, 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 $\varrho_{center}$ multiplied by an amplitude

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

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

$$\text{AMPL} = C_1/(T + C_2) + C_3 + C_4T \tag{10}$$

$$\varrho_{center} = \varrho_c + C_5(T - T_c)^{1.5} \tag{11}$$

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 $\varrho_{center}$ as follows:

$$x = C_6(\varrho - \varrho_{center}) \quad \text{for} \quad \varrho > \varrho_{center} \tag{12}$$

and

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

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.

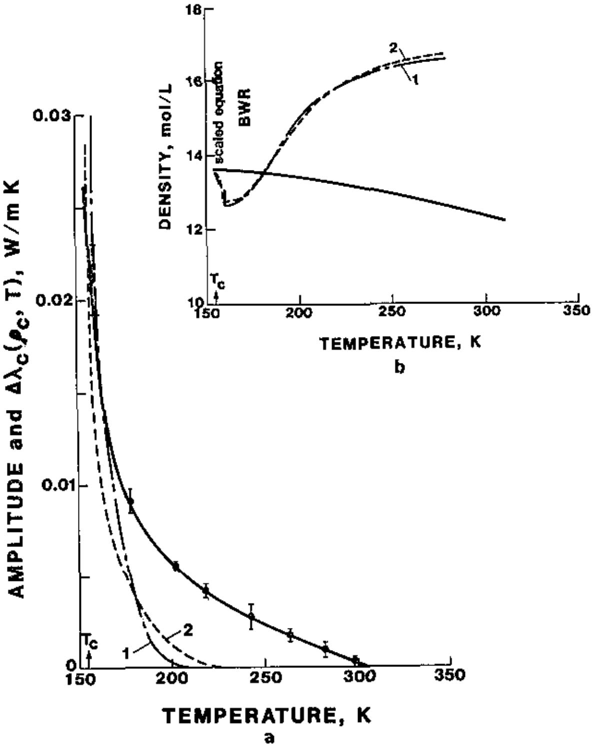

FIGURE 8. Amplitudes and densities at maximum $\Delta\lambda_c$ as a function of temperature.

Amplitudes

———————— eq (10) this paper, with the range of experimental values I taken from figure 6;

— — - — - — 1 $\Delta\lambda_c(\varrho_c, T)$ scaled equation only [17];

............ 2 $\Delta\lambda_c(\varrho_c, T)$ scaled equation and BWR [5].

Densities at maximum $\Delta\lambda_c$

———————— eq (11) this paper, i.e., $\varrho_{center}$;

— — - — - — 1 scaled equation and BWR according to [17];

............ 2 scaled equation and BWR according to [5].

## 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 $\lambda$ 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 $\lambda$. 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 $\Lambda$ adopted to be 1.02 for $CO_2$ 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 $\Delta\lambda_c(\varrho_c,T)$ 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 $\Delta\lambda_c(\varrho_c,T)$ and $\Delta\lambda_c(\varrho_{center},T)$ are equal for regions 1 and 2. The crossover is shown in figure 8a where one of the dashed lines represents the extrapolation of $\Delta\lambda_c(\varrho_c,T)$ from [17] for the scaled equation mode and the other represents the extrapolation of $\Delta\lambda_c$ $(\varrho_c,T)$ [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 1σ 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 $\varrho_c$ in figure 8.

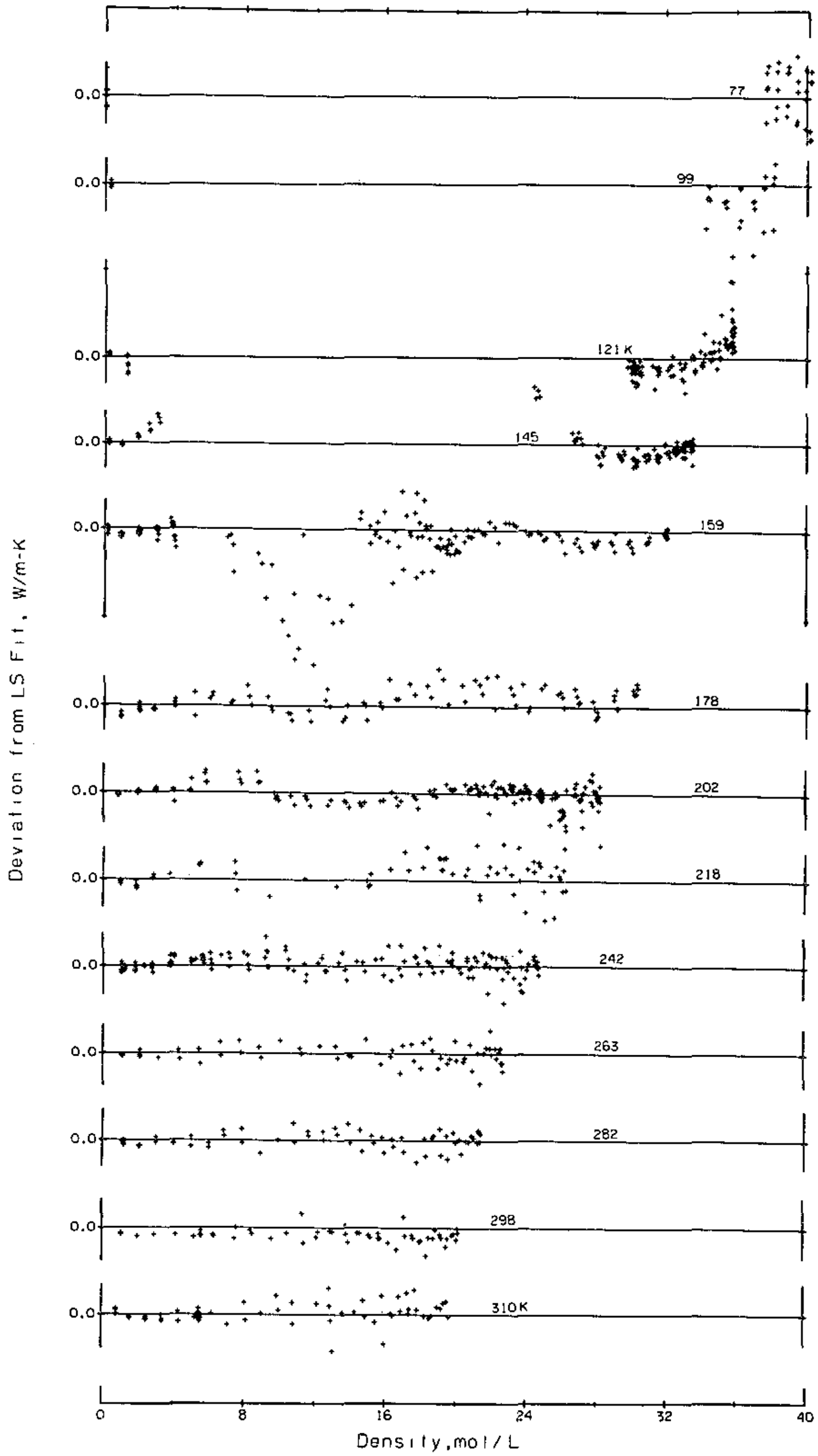

**FIGURE 9.** Deviations between experimental values and the correlating surface along isotherms. Each isotherm is on a separate scale. The spacing between isotherms or isotherms and tick marks is 0.004 W/m·K.

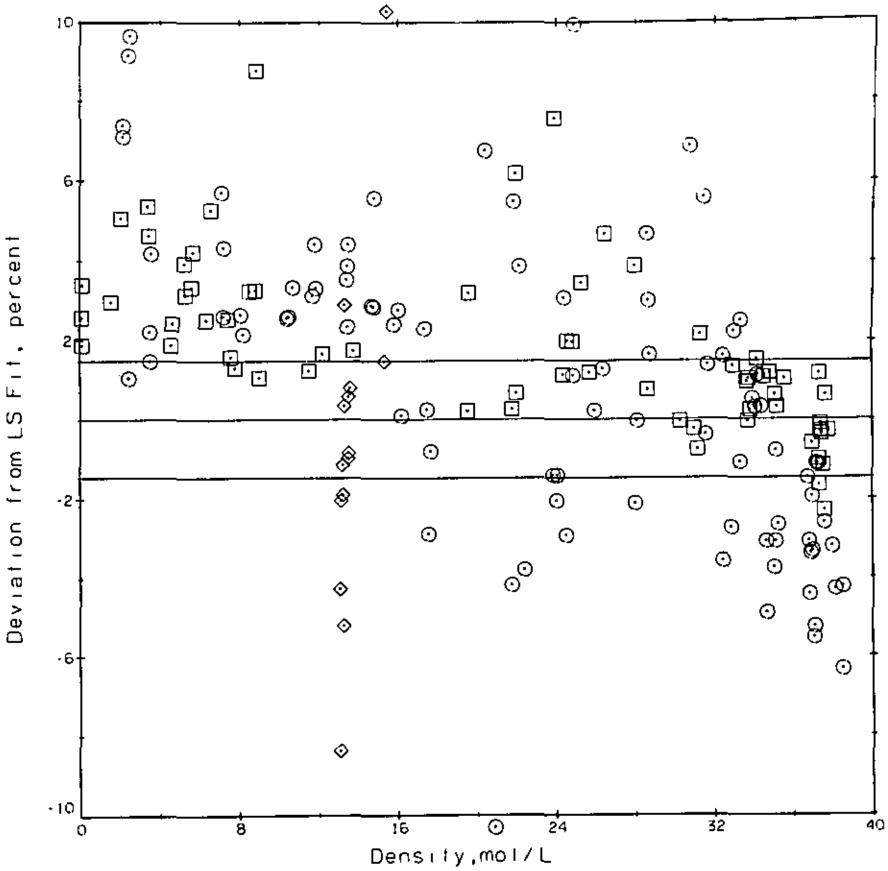

FIGURE 10. Deviations between experimental values of other authors and the correlating surface.
⊡Ref. 3 ⊙Ref. 4 ◇Ref. 23
The horizontal band shows the ± 1.5 percent fit of the correlating surface to the present 1126 points.

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 at 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

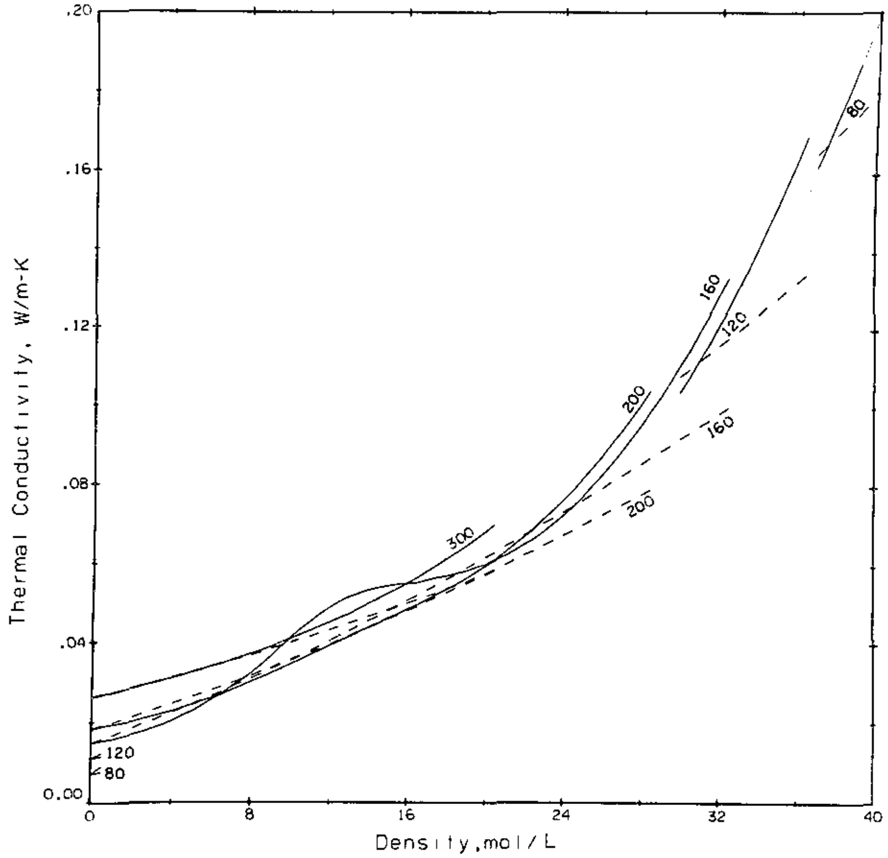

FIGURE 11. Comparison of the correlation by Hanley, et al. [5] - - - - - and the present correlation ______ for isotherms of 80, 120, 160, 200, and 300 K.

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

```
      FUNCTION DILTR(TEMP)
C     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)
C     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
```

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


      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/CM-S,BK J/K
C     1.02 REPLACED BY 1.04, PARAMETER VARIATION FOR WEBER DATA
      DATA (TC=154.581),(DC=13.63),(BK=1.38054E-23),(PC=49.77054)
     1 ,(ZZ=5.9783E-10)
      DATA (E=0.287),(G=1.190),(B=0.355),(DD=2.36),(XZ=0.183),(DE=4.352)
      DEN=RHO
      T=TEMP
      DELD=ABS(DEN-DC)/DC
      DELT=ABS(T-TC)/TC
      DFACT=EXP(-(39.8*DELT**2+5.45*DELD**4))
      RSTAR=DEN/DC
      VIS=VISC(DEN,T)*(1.0E-06)
      CALL DPDT(DPT,DEN,T)
C     IF(DELD.LE.0.25.AND.DELT.LT.0.03) GO TO 8
C     CALL DPDD(DPD,DEN,T)
C     CHISTAR=PC*DEN/(DC**2*DPD)
C     GO TO 12
    8 IF(DELD.EQ.0.) GO TO 3
      X=DELT/DELD**(1.0/B)
      Y=(X+XZ)/XZ
      TOP=DELD**(-G/B)*((1.+E)/(1.+E*Y**(2.*B)))**((G-1.)/(2.*B))
      DIV=DD*(DE+(Y-1.)*(DE-1./B+E*Y**(2.*B))/(1.+E*Y**(2.*B)))
      CHISTAR=TOP/DIV
   12 CHI=CHISTAR**0.468067
      UPPER=1.04*BK/PC*(T*DPT/RSTAR)**2*CHI*DFACT*1.01325E+6
      SENG81=UPPER/(ZZ*6.*3.14159*VIS)
      RETURN
    3 BGAM=XZ**G/DD*((1.+E)/E)**((G-1.)/(2.*B))
      CHISTAR=BGAM*(DELT)**(-G)
      GO TO 12
      END
```

## Table 2. The Thermal Conductivity of Oxygen

| Run Pt. | Pressure MPa | Temperature K | Density mol/L | Power W/m | Experimental Thermal Conductivity W/m.K | STAT | Adjusted Thermal at a nominal Temperature of 77.K W/m.K | Conductivity Deviation from Correlation percent |
|---|---|---|---|---|---|---|---|---|
| 23001 | 64.519 | 76.866 | 40.2622 | .20587 | .20186 | .006 | .20192 | .38 |
| 23002 | 64.517 | 77.034 | 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 | -8.42 |
| 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 | -7.90 |
| 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 W/m.K | STAT | Adjusted Thermal at a nominal Temperature of 99.K W/m.K | Conductivity Deviation from Correlation percent |
|---|---|---|---|---|---|---|---|---|
| 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 | -1.93 |
| 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 | .080 | .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 at a nominal Temperature of 121.K W/m.K | Conductivity Deviation from Correlation percent |
|---|---|---|---|---|---|---|---|---|
| 17001 | 66.830 | 120.725 | 35.8415 | .16153 | .16230 | .010 | .16238 | .23 |
| 17002 | 66.827 | 121.079 | 35.8058 | .19941 | .16308 | .007 | .16306 | .90 |
| 17003 | 66.823 | 121.014 | 35.8121 | .24084 | .16310 | .006 | .16310 | .88 |
| 17004 | 66.821 | 121.104 | 35.8031 | .28636 | .16281 | .005 | .16278 | .75 |
| 17005 | 66.819 | 121.326 | 35.7806 | .33606 | .16196 | .004 | .16187 | .36 |
| 17006 | 66.818 | 121.476 | 35.7656 | .38985 | .16233 | .003 | .16219 | .67 |
| 17007 | 66.817 | 121.588 | 35.7543 | .44748 | .16177 | .002 | .16160 | .39 |
| 17008 | 66.810 | 121.880 | 35.7246 | .50957 | .16168 | .002 | .16143 | .50 |
| 17009 | 66.812 | 122.030 | 35.7096 | .57552 | .16133 | .002 | .16103 | .37 |
| 17010 | 66.807 | 122.074 | 35.7050 | .64516 | .16099 | .001 | .16068 | .18 |
| 17011 | 66.803 | 122.475 | 35.6646 | .72021 | .16161 | .002 | .16119 | .79 |
| 17012 | 66.804 | 122.764 | 35.6356 | .80010 | .16080 | .001 | .16030 | .45 |
| 17013 | 66.802 | 121.785 | 35.7337 | .44805 | .16229 | .002 | .16206 | .82 |
| 17014 | 66.800 | 121.854 | 35.7267 | .44817 | .16261 | .003 | .16236 | 1.06 |
| 17015 | 66.794 | 121.952 | 35.7166 | .44831 | .16436 | .003 | .16409 | 2.17 |
| 17016 | 66.793 | 121.960 | 35.7157 | .44836 | .16190 | .006 | .16162 | .68 |
| 17017 | 66.791 | 122.039 | 35.7076 | .44856 | .16546 | .004 | .16516 | 2.87 |
| 17018 | 66.790 | 122.446 | 35.6668 | .64652 | .16221 | .003 | .16180 | 1.15 |
| 17019 | 66.786 | 122.482 | 35.6630 | .64675 | .16264 | .002 | .16222 | 1.43 |
| 17020 | 66.785 | 122.621 | 35.6490 | .64715 | .16378 | .002 | .16332 | 2.20 |
| 17021 | 59.914 | 120.808 | 35.4695 | .16156 | .15808 | .010 | .15813 | .32 |
| 17022 | 59.916 | 121.015 | 35.4480 | .24080 | .15794 | .006 | .15794 | .35 |
| 17023 | 59.919 | 121.241 | 35.4246 | .33602 | .15779 | .004 | .15772 | .39 |
| 17024 | 59.920 | 121.699 | 35.3770 | .44768 | .15763 | .003 | .15743 | .56 |
| 17025 | 59.926 | 122.098 | 35.3357 | .57576 | .15708 | .002 | .15678 | .45 |
| 17026 | 59.932 | 122.555 | 35.2884 | .72069 | .15694 | .001 | .15651 | .63 |
| 17027 | 52.721 | 120.785 | 35.0664 | .16150 | .15498 | .010 | .15504 | 1.32 |
| 17028 | 52.728 | 121.026 | 35.0406 | .24075 | .15279 | .006 | .15278 | .05 |
| 17029 | 52.730 | 121.300 | 35.0110 | .33594 | .15245 | .004 | .15237 | -.00 |
| 17030 | 52.735 | 121.661 | 34.9720 | .44761 | .15287 | .003 | .15269 | .50 |
| 17031 | 52.743 | 122.104 | 34.9243 | .57572 | .15210 | .002 | .15180 | .27 |
| 17032 | 52.747 | 122.608 | 34.8697 | .72075 | .15076 | .001 | .15033 | -.30 |
| 17033 | 45.937 | 120.724 | 34.6609 | .16145 | .14872 | .006 | .14879 | .22 |
| 17034 | 45.943 | 120.949 | 34.6357 | .24068 | .14897 | .004 | .14898 | .54 |
| 17035 | 45.949 | 121.287 | 34.5976 | .33592 | .14784 | .002 | .14776 | .00 |
| 17036 | 45.955 | 121.709 | 34.5500 | .44770 | .14773 | .002 | .14754 | .21 |
| 17037 | 45.963 | 122.148 | 34.5005 | .57585 | .14692 | .001 | .14662 | -.05 |
| 17038 | 45.970 | 122.767 | 34.4304 | .72143 | .14668 | .001 | .14623 | .20 |
| 17039 | 38.451 | 120.792 | 34.1569 | .16162 | .14314 | .009 | .14319 | .14 |
| 17040 | 38.458 | 121.094 | 34.1211 | .24097 | .14381 | .006 | .14379 | .82 |
| 17041 | 38.465 | 121.429 | 34.0812 | .33628 | .14215 | .003 | .14204 | -.10 |
| 17042 | 38.471 | 121.781 | 34.0391 | .44803 | .14157 | .003 | .14137 | -.26 |
| 17043 | 38.478 | 122.245 | 33.9837 | .57643 | .14117 | .001 | .14086 | -.21 |
| 17044 | 38.484 | 122.833 | 33.9132 | .72205 | .14119 | .001 | .14074 | .23 |
| 17045 | 31.221 | 120.887 | 33.6143 | .16169 | .13674 | .009 | .13677 | -.39 |
| 17046 | 31.229 | 121.094 | 33.5883 | .24102 | .13643 | .005 | .13641 | -.46 |
| 17047 | 31.237 | 121.473 | 33.5402 | .33660 | .13670 | .003 | .13659 | .04 |
| 17048 | 31.250 | 121.857 | 33.4918 | .44840 | .13629 | .002 | .13608 | .03 |
| 17049 | 31.257 | 122.391 | 33.4236 | .57699 | .13586 | .001 | .13553 | .13 |
| 17050 | 31.263 | 122.870 | 33.3623 | .72253 | .13520 | .001 | .13476 | .02 |
| 17051 | 24.034 | 120.891 | 33.0206 | .16174 | .12972 | .009 | .12975 | -1.20 |
| 17052 | 24.041 | 120.755 | 33.0400 | .12800 | .13126 | .014 | .13132 | -.14 |
| 17053 | 24.053 | 121.100 | 32.9932 | .24111 | .13073 | .005 | .13071 | -.25 |
| 17054 | 24.060 | 121.427 | 32.9485 | .33659 | .12970 | .003 | .12960 | -.77 |
| 17055 | 24.071 | 121.932 | 32.8793 | .44864 | .12924 | .002 | .12903 | -.69 |
| 17056 | 24.082 | 122.394 | 32.8160 | .57724 | .12915 | .002 | .12883 | -.36 |
| 17057 | 24.095 | 122.959 | 32.7382 | .72293 | .12881 | .001 | .12837 | -.13 |
| 17058 | 16.732 | 120.750 | 32.3484 | .12802 | .12402 | .011 | .12408 | -.59 |
| 17059 | 16.739 | 120.956 | 32.3177 | .19941 | .12463 | .006 | .12464 | .10 |
| 17060 | 16.744 | 121.329 | 32.2611 | .28692 | .12377 | .003 | .12370 | -.23 |
| 17061 | 16.754 | 121.763 | 32.1956 | .39079 | .12279 | .002 | .12262 | -.61 |
| 17062 | 16.761 | 122.190 | 32.1307 | .51103 | .12267 | .001 | .12241 | -.29 |
| 17063 | 16.770 | 122.789 | 32.0393 | .64842 | .12182 | .001 | .12144 | -.40 |
| 17064 | 9.823 | 120.750 | 31.5707 | .12802 | .11705 | .010 | .11710 | -.47 |
| 17065 | 9.829 | 121.049 | 31.5199 | .19945 | .11682 | .005 | .11681 | -.33 |
| 17066 | 9.837 | 121.359 | 31.4671 | .28696 | .11608 | .003 | .11601 | -.62 |
| 17067 | 9.847 | 121.841 | 31.3848 | .39100 | .11576 | .002 | .11559 | -.36 |
| 17068 | 9.854 | 122.331 | 31.3002 | .51164 | .11415 | .002 | .11388 | -1.21 |
| 17069 | 9.864 | 122.964 | 31.1906 | .64895 | .11439 | .001 | .11399 | -.27 |
| 17070 | 2.634 | 120.844 | 30.5303 | .12808 | .10792 | .010 | .10795 | -.67 |
| 17071 | 2.641 | 121.060 | 30.4867 | .19952 | .10772 | .005 | .10771 | -.56 |
| 17072 | 2.644 | 121.440 | 30.4080 | .28707 | .10710 | .003 | .10702 | -.60 |
| 17073 | 2.646 | 121.992 | 30.2919 | .39122 | .10650 | .002 | .10631 | -.37 |
| 17074 | 2.657 | 122.405 | 30.2063 | .51180 | .10582 | .001 | .10555 | -.43 |
| 17075 | 2.664 | 123.103 | 30.0579 | .64974 | .10489 | .001 | .10450 | -.29 |
| 17076 | 2.856 | 120.805 | 30.5747 | .12812 | .10864 | .007 | .10868 | -.33 |
| 17077 | 2.857 | 121.098 | 30.5146 | .19960 | .10784 | .003 | .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 | -.99 |
| 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 | Power W/m | Experimental Thermal Conductivity W/m.K | STAT | Adjusted Thermal Conductivity at a nominal Temperature of 145.K W/m.K | Deviation from Correlation percent |
|---|---|---|---|---|---|---|---|---|
| 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 | 40.494 | 145.921 | 31.2765 | .79802 | .11961 | .001 | .11945 | -.13 |
| 16042 | 40.503 | 143.246 | 31.6032 | .15772 | .12178 | .009 | .12209 | -.40 |
| 16043 | 40.511 | 145.136 | 31.3739 | .62915 | .11993 | .001 | .11991 | -.48 |
| 16044 | 40.516 | 143.615 | 31.5595 | .24570 | .12143 | .005 | .12168 | -.41 |
| 16045 | 40.523 | 144.558 | 31.4454 | .48113 | .12063 | .002 | .12071 | -.35 |
| 16046 | 40.526 | 143.931 | 31.5221 | .35327 | .12091 | .003 | .12110 | -.61 |
| 16047 | 40.530 | 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 | -.5 |
| 16052 | 34.518 | 145.202 | 30.7617 | .62918 | .11463 | .001 | .11460 | -.3 |
| 16053 | 34.528 | 145.585 | 30.7127 | .71107 | .11426 | .001 | .11416 | -.4 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 16054 | 28.783 | 143.335 | 30.3661 | .15778 | .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 | Adjusted Thermal Conductivity at a nominal Temperature of 159.K W/m.K | Deviation from Correlation percent |
|---|---|---|---|---|---|---|---|---|
| 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 | .33585 | .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 | 161.652 | 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 | 24.8298 | .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 | -3.38 |
| 21168 | 6.283 | 158.471 | 17.6972 | .07057 | .05605 | .015 | .05562 | -3.84 |
| 21169 | 6.283 | 158.717 | 17.3311 | .10108 | .05750 | .010 | .05726 | -.20 |
| 21171 | 6.144 | 158.459 | 16.9412 | .04561 | .05568 | .028 | .05518 | -3.24 |
| 21172 | 6.145 | 158.601 | 16.6821 | .07060 | .05654 | .016 | .05603 | -1.38 |
| 21173 | 6.145 | 158.721 | 16.4510 | .10107 | .05715 | .010 | .05676 | -.05 |
| 21175 | 6.043 | 158.386 | 16.3470 | .04559 | .05530 | .029 | .05436 | -4.46 |
| 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 W/m.K | Deviation from Correlation 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 | .016 | .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 | Density mol/L | Power W/m | Experimental Thermal Conductivity W/m.K | STAT | Adjusted Thermal Conductivity at a nominal Temperature of 202.K W/m.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 | 22.3532 | .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 | 201.878 | 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 | 28.2809 | .09196 | .10074 | .089 | .10097 | -2.33 |
| 20002 | 67.991 | 200.402 | 28.2618 | .13157 | .10267 | .052 | .10287 | -.30 |
| 20003 | 67.985 | 200.625 | 28.2410 | .17840 | .10323 | .030 | .10341 | .36 |
| 20004 | 67.990 | 200.891 | 28.2176 | .23233 | .10260 | .021 | .10274 | -.12 |
| 20005 | 67.990 | 201.167 | 28.1928 | .29346 | .10184 | .014 | .10195 | -.72 |
| 20006 | 67.990 | 201.553 | 28.1579 | .36171 | .10210 | .010 | .10216 | -.26 |
| 20007 | 67.991 | 201.807 | 28.1352 | .43725 | .10201 | .008 | .10203 | -.22 |
| 20008 | 67.985 | 202.281 | 28.0919 | .52019 | .10199 | .005 | .10195 | .01 |
| 20009 | 67.983 | 202.696 | 28.0544 | .60980 | .10163 | .005 | .10154 | -.13 |
| 20010 | 67.982 | 203.132 | 28.0152 | .70751 | .10171 | .004 | .10157 | .17 |
| 20011 | 59.170 | 200.693 | 27.2716 | .17842 | .09610 | .028 | .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 | 21.8302 | .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 | -.76 |
| 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 | .17865 | .04313 | .013 | .04314 | -1.04 |
| 20065 | 14.724 | 202.127 | 13.6071 | .23305 | .04298 | .009 | .04298 | -.78 |
| 20067 | 13.748 | 200.754 | 12.8843 | .09211 | .04129 | .032 | .04132 | -.78 |
| 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 218.K W/m.K | Deviation from Correlation 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 | .19460 | .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 W/m.K | Deviation from Correlation 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 | 22.4559 | .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 | 21.2580 | .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 | .06118 | .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 | -.53 |
| 10049 | 15.678 | 243.813 | 9.3038 | .21919 | .03655 | .018 | .03642 | 1.81 |
| 10050 | 15.678 | 244.825 | 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 | 2.7442 | .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 | -.48 |
| 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 at a nominal Temperature of 263.K W/m.K | Conductivity Deviation from Correlation 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 | 262.556 | 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 | 4.3487 | .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 | Experimental Thermal Conductivity W/m.K | STAT | Adjusted Thermal Conductivity at a nominal Temperature of 282.K W/m.K | Deviation from Correlation percent |
|---|---|---|---|---|---|---|---|---|
| 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 | 15.9910 | .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 | .04554 | .019 | .04551 | .04 |
| 12039 | 28.060 | 283.325 | 12.4874 | .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 | Power W/m | Experimental Thermal Conductivity W/m.K | STAT | Adjusted Thermal Conductivity at a nominal Temperature of 298.K W/m.K | Deviation from Correlation percent |
|---|---|---|---|---|---|---|---|---|
| 6001 | 64.203 | 297.095 | 20.2487 | .35206 | .06909 | .003 | .06914 | -.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 | -1.33 |
| 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 W/m.K | STAT | Adjusted Thermal at a nominal Temperature of 310.K W/m.K | Conductivity Deviation from Correlation percent |
|---|---|---|---|---|---|---|---|---|
| 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 |

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# Measurements of the Octanol/Water Partition Coefficient by Chromatographic Methods

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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 bioaccumulation, 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),

$$\Pi_x = \log K^x_{o/w} - \log K^h_{o/w} \qquad (1)$$

where $K^x_{o/w}$ and $K^h_{o/w}$ 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-

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[1] Figures in brackets indicated 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),

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

where $\gamma_{\phi}^{w}$ and $\gamma_{\phi}^{o}$ are the activity coefficients *at infinite dilution*, based on volume fraction, for the solute in water and *n*-octanol, respectively. The quantity, $\gamma_{\phi}^{w}$, is calculated from the solute aqueous solubility, $C_w$, and the solute molar volume, $V$[7], and $\gamma_{\phi}^{o}$ 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 $\gamma_{\phi}^{w}$ and $\gamma_{\phi}^{o}$, 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.

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

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

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

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 $K_{a/o}$

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

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,

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

where $x$ represents mole fraction, $\phi$ the volume fraction, $W$ the weight fraction, and $C/C^\circ$ 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

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

substitution for $P$ in eq (5) yields

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

where $\gamma_{\phi}^{w}$ 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,

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

where $\gamma_{\phi}^{w}$ is the activity coefficient in water saturaterd with n-octanol. Provided there is no significant excess volume of mixing in either solvent, the normal solution,

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

It remains only to emphasize again that $\gamma_{\phi}^{o}$ and $\gamma_{\phi}^{w}$ are values. An immediate and obvious attraction of eq (10) is the absence of explicit solvent parameters, which is not the case if $\gamma_x$ 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

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

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

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

where $\varrho$ is the solvent density, eq (11) yields

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

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

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

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

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

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

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

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

## 4. Results

The solute activity coefficients in octanol, $\gamma_\phi^o$ and in water $\gamma_\phi^w$ listed in columns 1 and 2 of table 1 were obtained from an earlier publication of Wasik *et al* (12). $\gamma_\phi^o$ 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. $\gamma_\phi^w$ values were calculated from solubility data using the following equation

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

where $\phi_w$ 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 $\gamma_\phi^o$ (GLC) | Log $\gamma_\phi^w$ (Generator column /HPLC or GC) | Log $K_{o/w}$ Calculated[a] | 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 |

[a] 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*,

$$\begin{aligned} H = \log K_{o/w} &= \log \gamma_\phi^w - 0.510 \\ &= \log \gamma_\phi^w - k \end{aligned} \qquad (17)$$

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 | Inter-cept | Coefficient of Correlation (r) |
|---|---|---|---|---|
| $\log K_{o/w} = A \log P^{\circ} + B$ | | | | |
| | 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) $\gamma_{\phi}^{w}$ 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 $\gamma_{\phi}^{o}$: (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 $\gamma_{\phi}^{o}$ 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 $\gamma_{\phi}^{ow} \cong \gamma_{\phi}^{o}$ and $\gamma_{\phi}^{wo} \cong \gamma_{\phi}^{w}$ where $\gamma_{\phi}^{w}$ and $\gamma_{\phi}^{o}$ 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 $\gamma_{\phi}^{o}$ 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 $\log P^{\circ}$, i.e.

$$\log K_{o/w} = k_1 n_c + k_2 \tag{18}$$

$$\log K_{o/w} = k_3 T_b + k_4 \tag{19}$$

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

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Clothoids, i.e. curves $Z(s)$ in $R^2$ whose curvatures $\kappa(s)$ 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 $Z_i \varepsilon R^2 . i = 0,1,..., n+1$, which minimizes the integral $\int_Z \kappa(s)^2 ds$.

This algorithm is superlinearly convergent and needs only $0(n)$ 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 $\kappa(s)$ is a linear function of the arc length, $\kappa(s) = \kappa_0 + \lambda s$. Straight lines ($\kappa_0 = 0, \lambda = 0$) 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 $(x_i, y_i) \varepsilon R^2, i = 0, 1, \dots, n + 1$ such that the integral

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

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).

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[1] Figures 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-spriral. 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,

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

whose curvature $\kappa(s) = \kappa_0 + \lambda s$ is a linear function of arc length $s$. If its tangent vector is

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

then

$$\kappa(s) \quad = \dot{\phi}(s) ,$$

so that

$$\begin{aligned} \phi(s) \quad &= \phi_0 + \int_0^s \kappa(\tau) d\tau = \phi_0 + \kappa_0 s + \frac{\lambda}{2} s^2 , \\ Z(s) \quad &= Z_0 + \int_0^s \begin{bmatrix} \cos \phi(t) \\ \sin \phi(t) \end{bmatrix} dt . \end{aligned} \tag{1.1}$$

According to the sign of $\lambda$, $Z$ 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,

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

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

$$Z(s) = Z_0 + \sqrt{\pi/\lambda}\, V\left(\phi_0 - \frac{\kappa_0^2}{2\lambda}\right)\left\{ F\left(\frac{\kappa_0 + \lambda s}{\sqrt{\pi\lambda}}\right) - F\left(\frac{\kappa_0}{\sqrt{\pi\lambda}}\right)\right\}, \text{if } \lambda > 0, \tag{1.2}$$

where $V(\alpha)$ 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 $\kappa(s) = \pi s$ 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:

$$F(z) = -F(-z)$$

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

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

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

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) $h(0) = \frac{1}{2}\begin{bmatrix} 1 \\ 1 \end{bmatrix}, \quad \lim_{z \to +\infty} h(z) = 0$

(b) $g(z)$ and $f(z)$ are strictly monotonically decreasing for $z \,\varepsilon\, [0, +\infty]$

(c) $f'(z) = -\pi z g(z)\,, \; g'(z) = \pi z f(z) - 1,$ for $z \,\varepsilon\, R$ (1.5)

(d) For $z > 0$ the following estimates hold for $g(z)$ and $f(z)$:

$$\frac{1}{\pi^2 z^3}\left(1 - \frac{15}{(\pi z^2)^2}\right) < g(z) < \frac{1}{\pi^2 z^3}$$

$$\frac{1}{\pi z}\left(1 - \frac{3}{(\pi z^2)^2}\right) < f(z) < \frac{1}{\pi z}$$

$$\frac{-3}{\pi^3 z^5} < f(z) - \frac{1}{\pi z} < -\frac{3}{\pi^3 z^5}\left(1 - \frac{35}{(\pi z^2)^2}\right)$$

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

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

to be used later on:

$$\text{(a)}\ 1 - \frac{15}{(\pi z^2)^2} \leqslant ||h(z)|| \left( (1/\pi z) \sqrt{1 + \frac{1}{(\pi z^2)^2}} \right)^{-1} \leqslant 1 \text{ for } z > 0\,,$$

$$\text{(b)}\ 1 - \frac{35}{(\pi z^2)^2} \leqslant ||\bar{h}(z)|| \left( (1/\pi^2 z^3 \sqrt{1 + \frac{9}{(\pi z^2)^2}} \right)^{-1} \leqslant 1 \text{ for } z > 0\,, \tag{1.6}$$

$$\text{(c)}\ \lim_{z \to +\infty} z\bar{h}(z) = \begin{bmatrix} 0 \\ 0 \end{bmatrix}, \lim_{z \to +\infty} \pi z h(z) = \begin{bmatrix} 0 \\ 1 \end{bmatrix}.$$

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

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

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.

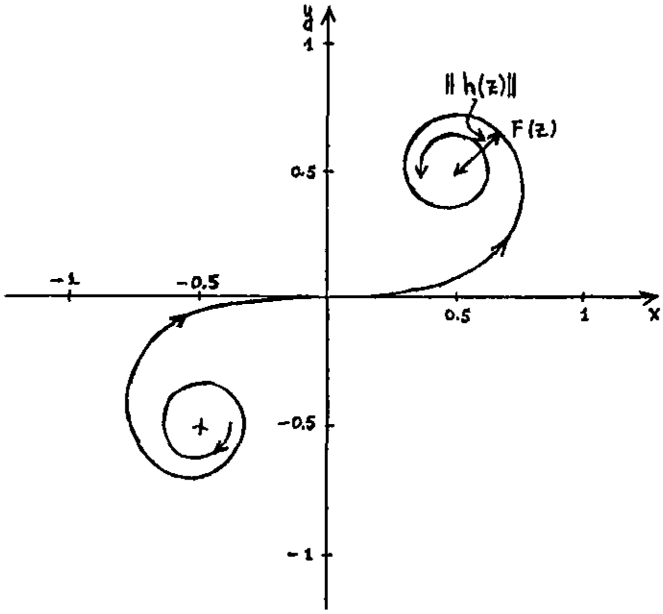


FIGURE 1. Positively Oriented Cornu-Spiral with $Z_o = X_o = o$ and $\lambda = \pi$

For $z \geqslant 0$ the vector

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

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

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

Moreover, the vector

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

where

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

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

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

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

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

infinitely often at abscissae $0 \leqslant z_1 < z_2 < \ldots$, for which

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

$$(z_i)^2 + 4n-1 \leqslant (z_{i+n})^2 \leqslant (z_i)^2 + 4n+1 \quad , \quad i \geqslant 1, n \geqslant 1 \tag{1.8}$$

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

These estimates easily imply the following bounds

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

$$\sqrt{4\mathrm{n}-1} \leqslant z_n \leqslant \sqrt{4n+1} \quad , \tag{1.9}$$

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 $h$:

$$Z(s) = Z(0) - \sqrt{\frac{\pi}{\lambda}}\left(V(\phi(s))h\left(\frac{x(s)}{\sqrt{\pi\lambda}}\right) - V(\phi_o)h\left(\frac{x_o}{\sqrt{\pi\lambda}}\right)\right) \tag{1.10}$$

where (see (1.1))

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

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

$$\begin{aligned} &\text{(a)}\ Z(+\infty) = Z(0) + \sqrt{\frac{\pi}{\lambda}}V(\phi_0)h\left(\frac{\varkappa_0}{\sqrt{\pi\lambda}}\right) \\ &\text{(b)}\ Z(-\infty) = Z(+\infty) - \sqrt{\frac{\pi}{\lambda}}V\left(\phi_0 - \frac{\varkappa^2{}_0}{2\lambda}\right)\cdot\begin{bmatrix}1\\1\end{bmatrix} \\ &\text{(c)}\ Z(s) - Z(+\infty) = -\sqrt{\frac{\pi}{\lambda}}V(\phi(s))h\left(\frac{\varkappa(s)}{\sqrt{\pi\lambda}}\right) \end{aligned} \tag{1.11}$$

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

$$\begin{aligned} M(s) &= Z(s) + \frac{1}{\varkappa(s)}\begin{bmatrix}-\sin\phi(s)\\ \cos\phi(s)\end{bmatrix} = Z(s) + \frac{1}{\varkappa(s)}V(\phi)s))\begin{bmatrix}0\\1\end{bmatrix} \\ &= Z(0) - \sqrt{\frac{\pi}{\lambda}}\left(V(\phi(s))\bar{h}\left(\frac{\varkappa(s)}{\sqrt{\pi\lambda}}\right) - V(\phi_0)h\left(\frac{\varkappa_0}{\sqrt{\pi\lambda}}\right)\right) \end{aligned} \tag{1.12}$$

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

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

(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,

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

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

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

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 $\varkappa(s)$ of $Z(s)$ by

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

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

$$\sigma(s) - \sigma(\overline{s}) \;=\; \frac{1}{\kappa(\overline{s})} - \frac{1}{\kappa(s)} \;.$$

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

$$||M(s) - M(\overline{s})|| < \sigma(s) - \sigma(\overline{s}) = \kappa(\overline{s})^{-1} - \kappa(s)^{-1}$$

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

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

## 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

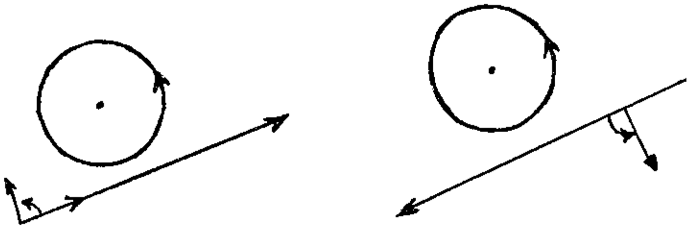
$$K(a,r) \;:=\; \left\{ s + r \begin{bmatrix} \cos\phi \\ \sin\phi \end{bmatrix} \middle|\, 0 \leqslant \phi \leqslant 2\pi \right\} \;,$$

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

$$g = g(b,\alpha) \;:=\; \left\{ b + \sigma \begin{bmatrix} \cos\alpha \\ \sin\alpha \end{bmatrix} \middle|\, \sigma \,\varepsilon\, R \right\} \;,$$

whose orientation is deterined 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

$$b + r \begin{bmatrix} -\sin\alpha \\ \cos\alpha \end{bmatrix}$$



Coherent orientation

Incoherent orientation

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 ≠ 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 $r=1/\varkappa > 0$ 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 $\overline{y} := y_0/r = y_0\varkappa > 1$.

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 $\varkappa(0) = \varkappa_0 = 0$ 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 $\varkappa$ and $(x_0,y_0)^T$ as center of curvature (see fig. 3).

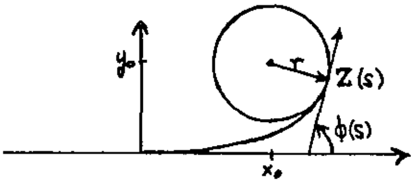


FIGURE 3

This leads to the conditions

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

Hence $s$ must satisfy the equation

$$\cos\frac{\varkappa s}{2} + \sqrt{\pi s \varkappa}\;S\left(\sqrt{\frac{\varkappa s}{\pi}}\right) = \overline{y} \quad ,$$

or the variable

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

must solve

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

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* $\Psi \geqslant 0$ *because*

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

Since $\overline{y} > 1$, $p(0) = 1$ and $\lim_{\tau\to\infty} p(\tau) = +\infty$, there exists therefore a unique solution $\overline{\Psi} > 0$ of (2.2), which can be found by Newton's method. In terms of $\overline{\Psi}$, the solution of the problem is

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

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

The proof of (2) is straightforward.

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

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

by an oriented Cornu spiral.

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

$$\kappa_0 = 0\,, \quad \phi_0 = 0\,, \quad Z_\lambda\,(0) = 0$$

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

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

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

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

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

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

$$\begin{array}{ll}
\text{(a)} & \lim\limits_{\lambda\downarrow 0} M_\lambda\,(\overline{\kappa}/\lambda) - \sqrt{\frac{\pi}{\lambda}}\begin{bmatrix}0.5\\0.5\end{bmatrix} = 0 \quad \text{if } \overline{\kappa} > 0 \\
\text{(b)} & \lim\limits_{\lambda\downarrow 0} M_\lambda\,(\overline{\kappa}/\lambda) + \sqrt{\frac{\pi}{\lambda}}\begin{bmatrix}0.5\\0.5\end{bmatrix} = 0 \ \text{ if } \overline{\kappa} < 0 \\
\text{(c)} & \lim\limits_{\lambda\to+\infty} M_\lambda\,(\overline{\kappa}/\lambda) \ = \ \begin{bmatrix}0\\1/\overline{\kappa}\end{bmatrix}.
\end{array} \tag{2.3}$$

As an easy consequence, we get

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

1. *If* $K_i$ and $K_2$ *are coherently oriented*, i.e. *if* $\kappa_i \cdot \kappa_2 > 0$, *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* $\kappa_1 \cdot \kappa_2 < 0$, *then there exists an oriented Cornu spiral joining* $\underline{K}_1$ and $\underline{K}_2$ *(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.* $//a_1 - a_2|| > K_1||^{-7} + ||K_2||^{-7}$.

**PROOF:** (1) Assume $\kappa_2 > \kappa_1 > 0$ without loss of generality and let $K_1$ contain $K_2$ in its interior; that is,

$$0 < \,||\, a_1 - a_2 \,||\, < 1/\kappa_1 - 1/\kappa_2 \quad . \tag{2.5}$$

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

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

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

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 $Z_{\lambda}$, 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)

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

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

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* $P_0 \varepsilon K$ and $P_1 \varepsilon K$ *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 $P_1 \varepsilon K$ to a point $P_0 \varepsilon K$ (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:

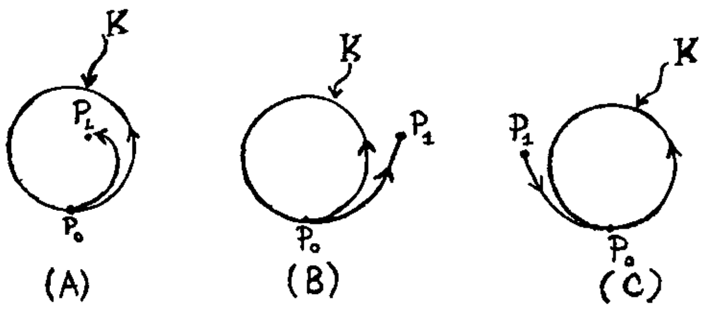


FIGURE 4

(2.6′) **Problem:** *For a given positively oriented circle* K = K($M_0$, $1/\varkappa$), $\varkappa > 0$, *and two points* $P_0 \varepsilon$ K *and* $P_1 \varepsilon$ 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* $P_1$, *if* $P_1$ *is outside* K.

Clearly, (2.6′) depends only on $\varkappa$ and the relative positions of $P_0$ and $P_1$ so that we may assume without loss of generality

$$M_0 = \begin{bmatrix} 0 \\ 0 \end{bmatrix}, \ \underline{P}_0 = \begin{bmatrix} 0 \\ -1/\varkappa \end{bmatrix}, \ \underline{P}_1 = \ r \begin{bmatrix} \sin\alpha \\ -\cos\alpha \end{bmatrix}, \ r \geqslant 0 \ ,$$

(see Fig. 5).

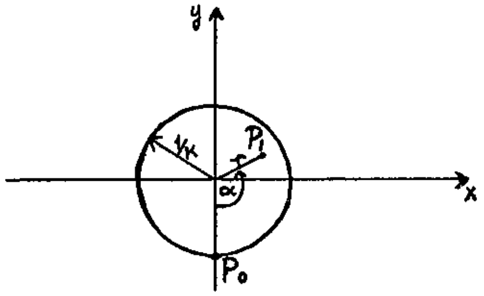


FIGURE 5

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

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

is given by

$$\begin{aligned} C_\lambda(s) &= \begin{bmatrix} 0 \\ -1/\varkappa \end{bmatrix} + \sqrt{\frac{\pi}{\lambda}}\,\underline{\mathrm{h}}\left(\frac{\varkappa}{\sqrt{\pi\lambda}}\right) - \underset{\smile}{\overset{\frown}{\sqrt{\frac{\pi}{\lambda}}}} \ V(\phi_\lambda(s))\,h(\varkappa_\lambda(s)/\sqrt{\pi\lambda}\,) \\ &= \sqrt{\frac{\pi}{\lambda}}(\overline{h}\ (\varkappa/\sqrt{\pi\lambda}) \ - \ V(\phi_\lambda(s))\,h(\varkappa_\lambda(s)/\sqrt{\pi\lambda})) \end{aligned}$$

where

$$\varkappa_\lambda(s) := \varkappa + \lambda s \ , \ \phi_\lambda(s) := \varkappa s + (\lambda/2)s^2.$$

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

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

We show next:

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

$$\limsup_{\lambda\downarrow 0 \ \ s\varepsilon I} \ \| \ \underset{\smile}{\overset{\frown}{C_\lambda}}(s) \ \| = 1/\varkappa \ . \tag{2.9}$$

PROOF. It follows from (2.7):

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

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

$$\limsup_{\lambda \downarrow 0 \quad s \varepsilon I} \|C_\lambda(s)\| = \limsup_{\lambda \downarrow 0 \quad s \varepsilon I} 1/\varkappa_\lambda(s) = 1/\varkappa \text{ , QED.}$$

With the abbreviations

$$\bar{h}_\lambda := \sqrt{\frac{\pi}{\lambda}} = \bar{h}\ (\varkappa/\sqrt{\pi\lambda}) \ , \ h_\lambda(s) := \sqrt{\frac{\pi}{\lambda}}\ h(\varkappa_\lambda(s)/\ \pi\lambda)$$

$$\bar{r}_\lambda := \|\ \bar{h}_\lambda\ \| \ , \ r_\lambda(s) := \|\ h_\lambda(s)\ \| \ ,$$

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

$$\frac{\lambda}{\varkappa^3} \left(1 - \frac{35\lambda^2}{\varkappa^4}\right) \leqslant \bar{r}_\lambda \ / \sqrt{1 + \frac{9_\lambda{}^2}{\varkappa^4}} \leqslant \lambda/\varkappa^3 \ , \ \ \bar{r}_\lambda < 1/\varkappa$$

$$\frac{1}{\varkappa_\lambda(s)} \left(1 - \frac{15\lambda^2}{\varkappa_\lambda(s)^4}\right) \leqslant r_\lambda(s) \ / \sqrt{1 + \frac{\lambda^2}{\varkappa_\lambda(s)^4}} \leqslant \frac{1}{\varkappa_\lambda(s)} \tag{2.11}$$

for all $s$ with $\varkappa_\lambda(s) = \varkappa + \lambda s > 0$.

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

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

which will be treated somewhat differently.

Case (1): $0 \leqslant r < 1/\varkappa$ , $P_1$ lies in the interior of $K$
Case (2): $r > 1/\varkappa$ , $P_1$ lies outside of $K$.

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

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

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

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

extending from $\bar{h}_\lambda$ towards $P_1$ (see fig. 6).

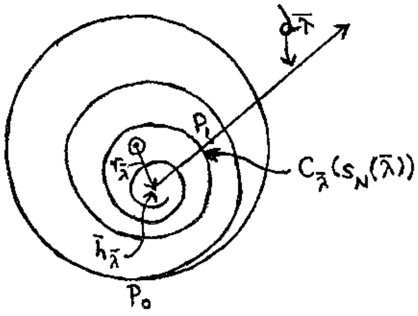


FIGURE 6

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

$$\begin{gathered}\phi_\lambda(s_n(\lambda)) + 3\pi/2 \quad \leqslant \quad \phi_\lambda(s_{n+1}(\lambda)) \\ 2(n-1)\pi \leqslant 2(n - \frac{1}{4})\,\pi \leqslant \phi_\lambda(s_n(\lambda)) \leqslant 2(n + \frac{1}{4})\pi \leqslant 2(n+1)\pi\end{gathered} \tag{2.14}$$

for $n \geqslant 1$ , so that

$$\begin{gathered}s_{n+1}(\lambda) - s_n(\lambda) \quad \geqslant \frac{3\pi}{\varkappa+\lambda s_n(\lambda)}\left(1 + \quad 1 + \sqrt{\frac{3\pi\lambda}{[\varkappa+\lambda s_n(\lambda)]^2}}\right) \\ \bar s_{n-1}(\lambda) \leqslant s_n(\lambda) \leqslant \bar s_{n+1}(\lambda) ,\end{gathered} \tag{2.15}$$

where

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

is the solution of the quadratic equation,

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

As a consequence,

$$\lim_{n\to\infty} s_n(\lambda) \quad = \quad +\infty, \lim_{n\to\infty} C_{\bar\lambda}(s_n(\bar\lambda)) \quad = \quad \bar h_{\bar\lambda} \quad ,$$

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

$$C_{\bar\lambda}(s_n(\bar\lambda)) \quad \varepsilon \quad [\bar{\mathrm{h}}_{\bar\lambda}, P_1] := \{\bar h_{\bar\lambda} + \sigma (P_1 - \bar{\mathrm{h}}_{\bar\lambda}) \mid \leqslant \sigma \leqslant 1\} \ ,$$

that is, $C_{\bar\lambda}$ intersects $d_{\bar\lambda}$ between $\bar h_{\bar\lambda}$ and $P_1$ at the abscissae $s_n(\bar\lambda)$ , $n \leqslant N$. Consider any fixed $n \leqslant N$. By (2.14), $s_n(\lambda)$ is bounded

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

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

$$s_{n+1}(\lambda) - s_n(\lambda) \geqslant \overline{m}_n > 0 \text{ for all } 0 < \lambda \leqslant \overline{\lambda} \tag{2.17}$$

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

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

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

$$\underline{P}_{\overline{\lambda}}, \underline{n} \; \varepsilon \; [\underline{\overline{h}}_{\overline{\lambda}}, \underline{P}_1]$$

there is a $\lambda_n$, $0 < \lambda_n \leqslant \overline{\lambda}$ such that $P_{\lambda_n, n} = P_1$.

Because of (2.17),

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

so that

$$P_1 \neq C_{\lambda_n}(s_{n+1}(\lambda_n)) \quad \varepsilon \quad [\overline{h}_{\lambda_n}, P_1] \quad ,$$

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

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

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

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

$$C_{\lambda_n}(s_n') = P_1 , \quad \text{for all } n \geqslant 1.$$

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

$$\kappa_\lambda(s) = \kappa + \lambda s > 0$$

is still positive. We will show that:

(2.18) *To every integer* n $\geqslant 1$ *there exists a* $\overline{\lambda} > 0$ *and an integer* N $\geqslant 1$ *such that for every* $0 < \lambda \leqslant \overline{\lambda}$ *the Cornu-spiral* $C_\lambda(s)$ , $0 \geqslant s \geqslant -\kappa/\lambda$, *cuts* $d_\lambda$ *at abscissae* $0 \geqslant s_{-1}(\lambda) > s_{-2}(\lambda) \ldots > s_{-N-n}(\lambda)$ *such that*

$$\begin{aligned} &\text{(a)} \;\; s_{-N}(\lambda) > -\kappa/\overline{\lambda} > -\kappa/\lambda \quad , \\ &\text{(b)} \;\; s_{-i}(\lambda) - s_{-i-1}(\lambda) \geqslant m_i > 0 \;\; \textit{for} \;\; i = 1, 2, \ldots, N+n-1, \;\; 0 < \lambda \leqslant \overline{\lambda}, \\ &\text{(c)} \;\; r_{\overline{\lambda}}[s_{-N-1}(\overline{\lambda})] \geqslant r + \frac{1}{\kappa} \quad . \end{aligned} \tag{2.19}$$

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

$$C_{\bar{\lambda}}\, |s_{-N-i}(\bar{\lambda})| \;\; \varepsilon \;\; \{\bar{h}_{\bar{\lambda}} + \sigma(\mathrm{P}_1 - \bar{h}_{\bar{\lambda}})| \;\; \sigma \geqslant 1\}, \quad i = 1, 2, \ldots, n$$

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 $\lambda_i, \bar{\lambda} \geqslant \lambda_1 > \lambda_2 > \ldots > \lambda_n > 0$ such that

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

since for $\lambda \downarrow 0$ by (2.9) each $C_{\lambda_i}(s_{-N-i}(\lambda))$, $i \geqslant 1$, 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 $\lambda_i$.

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 $\gamma$ be defined by $\gamma/x := r + 1/x$, so that $\gamma > 2$. Let $n \geqslant 1$ be an arbitrary positive integer. Choose any numbers $\alpha$ and $\beta$ such that

$$\begin{gathered} 0 < \alpha < 1 \;\;,\;\; \sqrt{1-\alpha} \leqslant 1/(2\gamma) \\ \alpha\beta < 1 \;\;,\;\; \beta > 1\,. \end{gathered} \tag{2.20}$$

Choose a natural number $N$ so large that

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

and set

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

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

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

given by

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

Since by (2.20)

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

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

$$\begin{aligned} \bar{\lambda}\,\bar{s}_{-N} &= -\alpha x/(1 + \quad 1-\alpha) = -x \cdot (1 - \quad 1-\alpha) \\ \bar{\lambda}\,\bar{s}_{-\beta N} &= -x\,(1 - \quad 1-\beta\alpha) \end{aligned}$$

so that by (2.20)

$$\varkappa_{\bar\lambda}(\bar s_{-N}) = \varkappa + \bar\lambda \bar s_{-N} = \varkappa\sqrt{1-\alpha} > \varkappa_{\bar\lambda}(\bar s_{-\beta N}) = \varkappa\sqrt{1-\beta\alpha} > 0 \tag{2.23}$$

Since by (2.21)

$$\frac{15\bar\lambda^2}{\varkappa_{\bar\lambda}(\bar s_{-N})^4} = \frac{15\alpha^2}{16N^2\pi^2(1-\alpha)^2} \leqslant \frac{1}{2}$$

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

$$r_{\bar\lambda}(\bar s_{-N}) \geqslant \frac{0.5}{\varkappa_{\bar\lambda}(\bar s_{-N})} = \frac{0.5}{\varkappa\sqrt{1-\alpha}} \geqslant \frac{\gamma}{\varkappa} = r + \frac{1}{\varkappa}\ . \tag{2.24}$$

Since by (2.21)

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

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

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

satisfying the estimates

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

so that

$$\bar s_{-i+1} \geqslant s_{-i}(\bar\lambda) \geqslant \bar s_{-i-1} \quad .$$

In particular, we have $0 \geqslant \bar s_{-N} \geqslant s_{-N-1}(\bar\lambda)$, so that because of (2.24) and the monotonicity of $r_{\bar\lambda}(s)$, we get (2.19)(c). (2.19)(a) follows from $s_{-N-n}(\bar\lambda) \geqslant \bar s_{-N-n-1}$, (2.21) implying $\bar s_{-N-n-1} \geqslant \bar s_{-\beta N}$ 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* $P_0 \varepsilon$ K *and* $P_1 \varepsilon$ 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 $\varkappa(s)$ is a continuous piecewise linear function of arclength $s$. More precisely, such a curve $Z(s)$ is given by a finite collection of parameters

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

$$(Z_i, \phi_i, \varkappa_i, \lambda_i)\,,\ Z_i \varepsilon R^2\,,\ i = 0,\ 1, \ldots, n$$

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

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

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

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

with $\tau_i := s_{i+1} - s_i$. Of course, the parameters $s_i$ are determined by the $\tau_i$, $s_{i+1} = \tau_0 + \tau_1 + \ldots + \tau_i$ 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 $\int \kappa(s)^2 ds$, in analogy to cubic spline interpolation.

(3.3) PROBLEM: *For a given family* $\{Z_i\}_{i=0,1,\ldots,n+1}$ *of different points* $Z_i \in R^2$ *find parameters* $P_i^T = (\phi_i, \kappa_i, \lambda_i, \tau_i)$, $i = 0, 1, \ldots, n$ *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*

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

*is minimal.*

With the notation

$$a_i^T := (\phi_i, \kappa_i)\,,\, b_i^T := (\lambda_i, \tau_i)$$

$$P^T := (P_0^T, P_1^T, \ldots, P_n^T)\,,\, P_i^T := (\kappa_i, \kappa_i, \lambda_i, \tau_i)\,,\, i = 0,1, \ldots, n \tag{3.4}$$

the objective function to be minimized is the function

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

which is separable in variables $P_i$.

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

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

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

with the $R^2$ row vectors

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

and the 4 x 4 square matrices

$$F_i := 2 \left[\begin{array}{cc|cc} 0 \ , & 0 & 0 & , \ 0 \\ 0 \ , & \tau_i & \frac{1}{2}\tau_i^2 & , \ x_i + \lambda_i\tau_i \\ \hline 0 \ , & \frac{1}{2}\tau_i^2 & \frac{1}{3}\tau_i^3 & , \ (x_i + \lambda_i\tau_i)\tau_i \\ 0 \ , & x_i + \lambda_i\tau_i & (x_i + \lambda_i\tau_i)\tau_i & , \ (x_i + \lambda_i\tau_i)\lambda_i \end{array}\right] \tag{3.7}$$

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

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

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

where

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

$$K(a,b) := \begin{bmatrix} \phi + \varkappa\tau + \frac{\lambda}{2}\tau^2 \\ \varkappa + \lambda\tau \end{bmatrix} \tag{3.9}$$

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

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

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

with partial derivative 2 x 2 matrices

$$A_i \;:=\; D_{(\phi,\varkappa)} J(\phi,\varkappa,\lambda,\tau)|_{P_i}$$

$$B_i \;:=\; D_{(\lambda,\tau)} J(\phi,\varkappa,\lambda,\tau)|_{P_i} \tag{3.11}$$

$$C_i \;:= \begin{bmatrix} 1 \;, & \tau_i \\ 0 \;, & 1 \end{bmatrix} \;, \quad D_i \;:= \begin{bmatrix} \tau_i^2/2 \;, & \varkappa_i + \lambda_i\tau_i \\ \tau_i \;, & \lambda_i \end{bmatrix}$$

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

$$\textit{Minimize } F(\mathrm{P}) \textit{ subject to } G(\mathrm{P}) = 0 \tag{3.12}$$

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 $\overline{P}$ (which we assume to exist):

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

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

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

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

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

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

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

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 $(P^{(k)}, \Lambda^{(k)})$, $k = 0, 1, \ldots$ by solving at each iterate $(P^{(k)}, \Lambda^{(k)})$ the linear equations

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

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

Since computing the Hessian $L_{pp}(P^{(k)}, \Lambda^{(k)})$ may be too costly, we may replace $L_{pp}$ within $\phi'$ 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)

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

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

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

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

$$\left\{ \begin{bmatrix} P^{(k)} \\ \Lambda^{(k)} \end{bmatrix} + \sigma \begin{bmatrix} \delta P^{(k)} \\ \delta\Lambda^{(k)} \end{bmatrix} \;\middle|\; \sigma \geqslant 0 \right\} \cdot$$

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 x 4 block $H_i^{(k)}$ in order to generate another matrix $H_i^{(k+1)}$ for each $i = 0, 1, \ldots, n$, and thereby $H^{(k+1)}$, having the same structure (3.16) as $H^{(k)}$ and satisfying the usual Quasi-Newton equation:

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

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

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

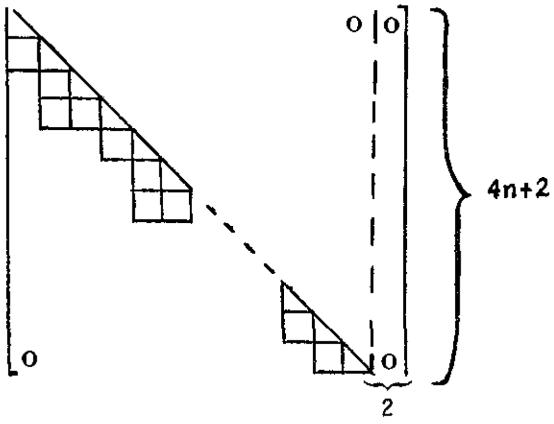
for the right hand side $-\phi(P^{(k)}, \Lambda^{(k)})$ of (3.17). The problem then is to solve an equation of the form

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

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

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

$$G'-_1.\Omega_2 \ldots .\Omega_N = (L, 0) \equiv$$



(3.20)

where all blocks indicated have size 2 x 2 and $L$ is a (4n + 2) x (4n + 2)-lower triangular band matrix. Again, because of the band-structure of (3.10), the number $N = 0(n)$ of Givens reflexions needed is linear in $n$, so that the unitary matrix

$$\Omega := \Omega_1 \cdot \Omega_2 \cdot \ldots \ldots \Omega_N \tag{3.21}$$

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

$$\Omega = (\overline{\Omega}, \overline{\overline{\Omega}})$$

where

$$\overline{\overline{\Omega}} = \Omega \begin{bmatrix} 0 & 0 \\ \cdot & \cdot \\ \cdot & \cdot \\ 1 & 0 \\ 0 & 1 \end{bmatrix} = \Omega_1 . \Omega_2 . \ldots \ldots \Omega_N \begin{bmatrix} 0 & 0 \\ \cdot & \cdot \\ \cdot & \cdot \\ 1 & 0 \\ 0 & 1 \end{bmatrix}$$

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

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

via $\delta P = \Omega \mathrm{t} = \overline{\Omega} t_1 + \overline{\overline{\Omega}} t_2$.

Then because of

$$G' \overline{\Omega} = L \, , G' \overline{\overline{\Omega}} = 0$$

the second set of equations (3.19)

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

can be solved for $t_1$ in $0(n)$ steps using the structure of $L$ (3.20), and the vector

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

is computed using (3.21).

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

$$H \delta P + G'^{\mathrm{T}} \delta \Lambda = c \tag{3.22}$$

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

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

or

$$(\overline{\overline{\Omega}}^T H \overline{\overline{\Omega}}) t_2 = \overline{\overline{\Omega}}^T c - \overline{\overline{\Omega}}^T H P^1 \rightarrow t_2 \tag{3.23}$$

Again, the 2 x 2 matrix $\bar{\bar{\Omega}}^T H \bar{\bar{\Omega}}$ and the vectors $\bar{\bar{\Omega}}^T H P^1$ can be computed with 0(*n*) operations using the block structure of *H* (3.16). $t_2$ is obtained by solving the two linear equations (3.23) and $\delta P$ is calculated by

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

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

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

the right hand side of which can be easily computed with 0(*n*) operations using the structure of H and the product form of $\bar{\Omega}^T$:

$$\bar{\Omega}^T = \begin{bmatrix} 1 & & & 0\,0\,0 \\ & \cdot & & \\ & & \cdot & \\ & & & \cdot \\ 0 & & & 1\,0\,0 \end{bmatrix} \quad \Omega N \Omega_{N-1} \ldots \Omega_1$$

All in all, we can compute the solution of (3.19) with 0(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* $\{\overline{Z_i}\}_{i=0,1,\ldots,n+1}$ *of different points*

$$\overline{Z_i} = \begin{bmatrix} \bar{x}_i \\ \bar{y}_i \end{bmatrix} \varepsilon R^2$$

*and numbers* $S \geqslant 0, \Delta x_i > 0, \Delta y_i > 0, i = 0,1, \ldots, n+1,$ *find parameters*

$$\{\{(\phi_i, x_i, \lambda_i, \tau_i)\}_{i=0,1,\ldots,n}, \{Z_i\}_{i=0,1,\ldots,n+1}, z\}, Z_i = \begin{bmatrix} x_i \\ y_i \end{bmatrix} \varepsilon R^2 \quad , \tag{4.1}$$

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

$$\begin{aligned} &\text{a)} \quad (3.2) \textit{ and } Z(s_{n+1}) = Z_{n+1} \\ &\text{b)} \quad \sum_{i=0}^{n+1} \left( \left( \frac{x_i - \bar{x}_i}{\Delta x_i} \right)^2 + \left( \frac{y_i - \bar{y}_i}{\Delta y_i} \right)^2 \right) + z^2 = S \end{aligned} \tag{4.2}$$

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

Again with the notation [compare (3.4)]

$$\begin{aligned} a_i^T &= (\phi_i, x_i), b_i^T = (\lambda_i, \tau_i) & \\ P_i^T &= (\phi_i, x_i, \lambda_i, \tau_i) & i = 0,1,\ldots,n \\ P_{n+1}^T &= [Z_0^t, Z_1^T, \ldots, Z_{n+1}^T, z] & \\ &= (x_0, y_0, x_1, y_1, \ldots, x_{n+1}, y_{n+1}, z) \varepsilon R^{2n+5} & \\ P^T &= [P_0^T, P_1^T, \ldots, P_n^T, P_{n+1}^T] \varepsilon R^{6n+9} & \end{aligned}$$

the objective function $F(P)$ to be minimized is separable in the $P_i$

$$F(P) := \sum_{i=0}^{n} \int_0^{\tau_i} (x_i + \lambda_i t)^2 dt \tag{4.3}$$

and has a Hessian of the form [compare (3.5)]

$$F''(P) = \begin{bmatrix} F_0 & & & & & & 0 \\ & F_1 & & & & & \\ & & \cdot & & & & \\ & & & \cdot & & & \\ & & & & \cdot & & \\ & & & & & .F_n & \\ 0 & & & & & & F_{n+1} \end{bmatrix} \tag{4.4}$$

with the same 4 x 4 matrices $F_0, \ldots, F_n$ as in (3.7) and a $(2n+5)$ by $(2n+5)$ matrix $F_{n+1} := 0$.

The constraints (4.2) now have the structure [see (3.8)]:

$$G(P) \equiv \begin{bmatrix} J(a_0,b_0) + Z_0 - Z_1 \\ K(a_0,b_0) - a_1 \\ J(a_1,b_1) + Z_1 - Z_2 \\ K(a_1,b_1) - a_2 \\ \cdot \\ \cdot \\ \cdot \\ J(a_{n-1},b_{n-1}) + Z_{n-1} - Z_n \\ K(a_{n-1},b_{n-1}) - a_n \\ J(a_n,b_n) + Z_n - Z_{n+1} \\ \varrho(Z_0,Z_1,\ldots,Z_{n+1},z) \end{bmatrix} = 0 \tag{4.5}$$

where $L$ and $K$ are again given by (3.9) and the scalar function $\varrho$ is defined by [compare (4.2) b)]

$$\varrho(Z_0,\ldots,Z_{n+1},z) := \left(\frac{1}{2}\sum_{i=0}^{n+1}\left(\frac{x_i-\bar{x}_i}{\Delta x_i}\right)^2 + \left(\frac{y_i-\bar{y}_i}{\Delta y_i}\right)^2\right) + z^2 - S \quad .$$

With these new definitions of $F$ and $G$, problem (4.1) has the same structure as (3.12), namely

$$\textit{minimize } F(P) \textit{ subject to } G(P) = 0 \tag{4.6}$$

Consider again the Lagrangean of (4.6)

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

We again assume that (4.6) has an optimal solution $\bar{P}$ and that at $\bar{P}$ the optimality conditions (3.13) are satisfied.

By (3.13), (3.14) the optimal solution $(\bar{P},\bar{\Lambda})$ solves

$$\phi(P,\Lambda) := L'(P,\Lambda) \equiv \begin{bmatrix} \Delta_P L(P,\Lambda) \\ G(P) \end{bmatrix} = 0 \tag{4.7}$$

whose Jacobian is again

$$\phi'(P,\Lambda) = \begin{bmatrix} L_{PP}(P,\Lambda) & , & G'^T \\ G' & , & 0 \end{bmatrix} \tag{4.8}$$

but its structure is slightly more complicated than in section 3 because of our new definitions of $F(P)$ (4.3) and $G(P)$ (4.5). It is easily verified that in the present case $\phi'(P,\Lambda)$ has the following form (illustrated for $n=2$)

$$G'(P) = \begin{array}{c} \left[\begin{array}{lll|cccc|c} A_0,B_0 & & 0 & I, & -I, & 0, & 0 & 0 \\ C_0,D_0,-I & & & 0, & 0, & 0, & 0 & 0 \\ & A_1,B_1 & & 0, & I, & -I, & 0 & 0 \\ & C_1,D_1,-I & & 0, & 0, & 0, & 0 & 0 \\ 0 & & A_2,B_2 & 0, & 0, & I, & -I & 0 \\ \hline 0 & & 0 & \multicolumn{4}{c|}{r} & z \end{array}\right] \begin{array}{l} \}\ 2 \\ \\ \\ \\ \}\ 2 \\ \}\ 1 \end{array} \\ \underbrace{\quad}_{2}\ \underbrace{\quad}_{2} \qquad\qquad\qquad \underbrace{\quad}_{2} \qquad\qquad\qquad \underbrace{\quad}_{1} \qquad \end{array} \tag{4.9}$$

where the 2 by 2 matrices $A_i$, $B_i$, $C_i$, $D_i$ are again given by (3.11) and the vector r is

$$\left( r := \frac{x_0-\bar{x}_0}{(\Delta x_0)^2}, \frac{y_0-\bar{y}_0}{(\Delta y_0)^2}, \ldots, \frac{x_{n+1}-\bar{x}_{n+1}}{(\Delta x_{n+1})^2}, \frac{y_{n+1}-\bar{y}_{n+1}}{(\Delta y_{n+1})^2} \right)$$

Likewise $L_{PP}(P,\Lambda)$ has the structure [compare (4.3), (4.4)]

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

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

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

where $\Lambda_z$ is the last component of $\Lambda$.

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),

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

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

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

After having computed $P^{(k+1)}$, $\Lambda^{(k+1)}$ (see previous section) $H^{(k+1)}$ is obtained from $H^{(k)}$ by updating each $H_i{}^{(k)}$, $i \leqslant n$, 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

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

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 $0(n_3)$ operations to solve (4.14) because it requires the computation and storage of a large dense matrix of the order $0(n)$.

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

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

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 $0(n^3)$ 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

$$\mathrm{Ax} = \mathrm{b}$$

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 $0(n^2)$ operations and $0(n)$ storage to solve (4.14).

It is interesting to note in this context that the system (4.14) can be solved with only $0(n)$ operations, if the block-diagonal matrix $L_{PP}(\overline{P}, \overline{\Lambda})$ (4.10) would be positive definite at the solution $(\overline{P}, \overline{\Lambda})$ 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 $(\overline{P}, \overline{\Lambda})$ and $L_{PP}(\overline{P}, \overline{\Lambda})$, respectively.

If $H$ is positive definite, then a numerically stable method of solving (4.14) requiring only $0(n)$ operations runs as follows:

In a first step compute the Cholesky decomposition of

$$H = R^T R$$

which requires $0(n)$ operations and gives an upper triangular $R$ of the form [compare (4.12)]

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

with 4 x 4 upper triangular $R_i$ for $i \leqslant n$ 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

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

So the next step is to compute

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

which again requires only $0(n)$ 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 $n = 2$):

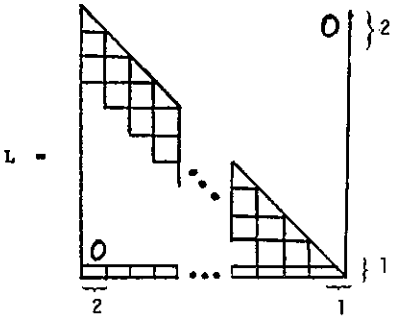
$$A = \left[\begin{array}{cccccccccccc|cccccccc|c}
x & x & x & x & & & & & & & & 0 & x & o & x & o & & & & 0 & 0 \\
x & x & x & x & & & & & & & & & o & x & o & x & & & & & \\
x & x & x & x & x & o & & & & & & & & & & & & & & & \\
x & x & x & x & x & x & & & & & & & & & & & & & & & \\
& & & & x & x & x & x & & & & & & & x & o & x & o & & & \\
& & & & x & x & x & x & & & & & & & o & x & o & x & & & \\
& & & & x & x & x & x & x & o & & & & & & & & & & & \\
& & & & x & x & x & x & x & x & & & & & & & & & & & \\
& & & & & & & & x & x & x & x & & & & & x & o & x & o & o \\
0 & & & & & & & & x & x & x & x & 0 & & & & o & x & o & x & o \\
\hline
\multicolumn{12}{c|}{0} & x & x & x & x & x & x & x & x & x
\end{array}\right] \tag{4.18}$$

We next reduce $A$ to "lower triangular" form by multiplying $A$ from the right by suitable Givens reflexions $\Omega_1, \Omega_2, \ldots, \Omega_N = 0(n)$ matrices $\Omega_i$ and only $0(n)$ operations are needed and the structure of (4.16) is essentially preserved and fill in will occur at most $0(n)$ places. Each will annihilate a particular above diagonal element of $A$; the resulting matrix is of the form

$$A\Omega_1\Omega_2 \ldots \Omega_N = (L, O) \tag{4.19}$$

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

$L =$



Note that the dense $(6n+9)$ by $(6n+9)$ product matrix $\Omega=\Omega_1\Omega_2, \ldots, \Omega_N$ need not be computed. Its storage in product form requires only $0(n)$ places. Concurrently with the elimination process for finding $L$, we can compute the vector

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

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

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

so that

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

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*

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

requires the storage of all $\Omega_i$ (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), $\delta P$ is obtained by solving one more triangular system of linear equations

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

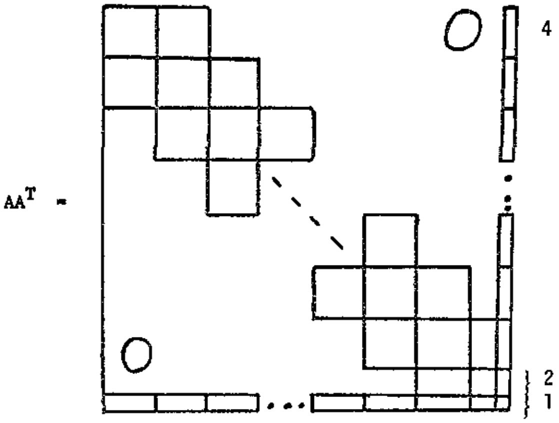
again requiring only $0(n)$ operations.

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

Having computed the Cholesky decomposition of $H = R^TR$, the matrix $A = G'R^{-1}$, the product $AA^T$ and its Cholesky decomposition $AA^T = LL^T$, computing $\delta\Lambda$ and $\delta P$ from (4.20), (4.22) is straightforward:

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

Note in this context that the product $AA^T$ has a simple sparse structure needing only $0(n)$ places for storage:



Both algorithms require only $0(n)$ operations for solving (4.14) in each Newton step, but the former will be numerically more stable, as it avoids the calculation of $AA^T$ and cancels products such as $LL^{-1}$, $RR^{-1}$, which arise inherently during the solution of (4.24), as often as possible.

I wish to thank Christoph Witzgall for numerous discussions. I am also indebted to the National Bureau of Standards for its generous hospitality allowing me to spend a sabbatical leave during the spring and summer of 1980 in an intellectually stimulating environment.

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