# **Project Summary Report**

# Thermophysical Properties of Carbon Dioxide and CO<sub>2</sub>-Rich Mixtures

DOE/NETL Interagency Agreement DE-FE0003931

Performing Agency: Applied Chemicals and Materials Division National Institute of Standards and Technology 325 Broadway Boulder, CO 80305

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# **EXECUTIVE SUMMARY**

This report summarizes the results of work performed under DOE/NETL Interagency Agreement DE- FE0003931, which began in October 2011 and ended (after a 6-month no-cost extension) March 31, 2015. This report is organized by the five primary tasks as described in the Statement of Work (Attachment 1 to the Interagency Agreement). More detailed technical expositions of the work are presented in publications in the scientific literature, which will be supplied to DOE as they are published.

The key objectives for this work were to:

- (1) Measure the dew point of water in compressed carbon dioxide (CO<sub>2</sub>) at temperatures relevant for pipeline transport.
- (2) Use the measured data to optimize a mixture thermodynamic model for the H<sub>2</sub>O/CO<sub>2</sub> system.
- (3) Produce a new, reference-quality correlation for the viscosity of pure CO<sub>2</sub>.
- (4) Measure the thermal conductivity of carbon dioxide over a wide range of conditions.
- (5) Produce a new, reference-quality correlation for the thermal conductivity of pure CO<sub>2</sub>.

We measured the dew point of water in compressed  $CO_2$  at pressures up to 5 MPa on six isotherms, from 10 °C to 80 °C. The experiments combined a newly built saturator with a gravimetric hygrometer originally built for work on humidity standards. The resulting data for water mole fraction in the compressed gas have uncertainties smaller than 1 %, and are more accurate than any existing data for this system. Analysis of the data confirms recent theoretical predictions for the second cross virial coefficient of  $CO_2$  with H<sub>2</sub>O.

These data, together with other data from the literature, have been used to optimize a thermodynamic mixture model for the binary  $H_2O/CO_2$  system. The model is developed in the framework of NIST's widely used REFPROP software [1].

A thorough review of existing literature produced a comprehensive database of experimental data for the viscosity of CO<sub>2</sub>. This included several sources published since the previous reference correlations [2,3] were produced. Recently published results from a high-quality molecular model were used to guide the behavior of the low-density part of the correlation over a wide range of temperatures. Structural optimization was employed to determine the best functional form for the correlation. The final correlation covers temperatures from 100 K to 1000 K, and pressures up to 8000 MPa. The description of data is somewhat improved compared to the previous correlation, and the range of conditions is significantly extended.

For thermal conductivity, two apparatus were used to perform measurements in gas, liquid, and supercritical states. The measurements covered temperatures from 220 K to 750 K at pressures up to 68 MPa, with an uncertainty of 0.5 % for the liquid and compressed gas, increasing to 3 % near the critical point and for the gas below 1 MPa.

The new data and existing data were used to develop a new correlation for the thermal conductivity, replacing the previous correlation from 1990 [2]. The new correlation covers temperatures from 200 K to 1100 K and pressures up to 200 MPa. The uncertainty compared to the previous correlation has been improved significantly – from 5 % to 1 % in most of the liquid phase and from 4 % or 5 % in most of the supercritical region to 2 % or 3 %.

## **INTRODUCTION AND APPROACH**

If carbon capture and sequestration (CCS) becomes widely used, it will be necessary to compress and transport large amounts of CO<sub>2</sub> through pipelines. In contrast with current CO<sub>2</sub> pipelines, this gas is likely to have significant impurities that could cause corrosion, especially if an aqueous liquid phase develops. It is therefore necessary to know the dew point of H<sub>2</sub>O in compressed CO<sub>2</sub> in order to know how much effort is required to dry the CO<sub>2</sub> gas before it is transported. Current thermodynamic modeling of the H<sub>2</sub>O/CO<sub>2</sub> mixture is of dubious accuracy, in large part because of a lack of high-accuracy data to use in fitting mixture models.

In order to address the data gap, we measured the dew-point composition of water-saturated  $CO_2$  at well-defined conditions of temperature and pressure. The composition measurement employed the NIST gravimetric hygrometer [4], a unique metrology-caliber instrument constructed for NIST work in humidity standards. A new saturator was built for this project in order to use the apparatus for conditions up to 7 MPa pressure, and other minor modifications were required in order to use  $CO_2$  rather than air as the gas. The data from this apparatus are more accurate than any existing data in the range of conditions covered. These data were then used to optimize a mixture model in the context of NIST's REFPROP software [1].

The thermophysical properties of the working fluid are essential for design, analysis, and optimization of any power cycle. While thermodynamic properties (vapor pressure, enthalpy, etc.) are usually the most important, the transport properties (thermal conductivity and viscosity) are also important for understanding heat transfer and fluid flow. For the potential working fluid carbon dioxide, the existing reference correlations for transport properties, as used for example in NIST's REFPROP software [1], are based on work that is now over 25 years old [2] and that has significant room for improvement.

For the viscosity, the experimental database (including new data from a group in Germany) was judged to be sufficient, so our work was limited to developing a new correlation that took into account data published since the previous correlation and that obeyed proper theoretical boundary conditions. In the case of the thermal conductivity, developing a reference correlation also involved measuring new experimental data over a wide range of subcritical and supercritical conditions. The measurements use the transient hot-wire method, which has become the method of choice for high-accuracy thermal conductivity measurements.

Note that Task 1 in the Interagency Agreement was "Project Reporting", so this report of technical results begins with Task 2.

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# 1. DEW POINT OF WATER IN COMPRESSED CO<sub>2</sub> (TASK 2)

Complete information on the work performed in this task is given in a paper published in the *AIChE Journal* [5]. We therefore provide only an overview of the experiments and their results here.

# **1.1. Experimental Apparatus and Procedure**

Our dew-point measurements were performed in a facility that has two main components. The first component is a saturation system in which liquid water is equilibrated with the working gas at a precisely controlled temperature and pressure. The saturator temperature is the dew-point temperature corresponding to the pressure in the vessel and the water mole fraction generated. The second component is the NIST gravimetric hygrometer [4], an apparatus that measures the water mole fraction in a gas by separating the water from the gas using desiccants and subsequently determining the amount of water and gas independently.

The saturation system is shown in schematic form in Fig. 1.1. It consists of three elements: a heat exchanger, a pre-saturator, and a final saturator. The gas flowed through each of these elements in the order mentioned. All elements were immersed in a commercial temperature-controlled bath.

The heat exchanger was designed to bring the temperature of the flowing gas to the temperature of the saturator. It was composed of a single electropolished stainless-steel tube of length 10 m, bent into a spiral coil of diameter 23 cm.

The pre-saturator and final saturator had identical designs but different functions. The presaturator performed almost all of the saturation. The final saturator made small final adjustments to the saturation and was the location where the pressure and temperature measurements took place. This separation of functions is done because the large amount of evaporation in the presaturator causes unacceptable temperature non-uniformities. Very little water evaporates in the final saturator, so the temperature inside is very uniform.

The design of the pre-saturator and final saturator was based on the "dish" design used by Hyland and Wexler [6]. Each saturator was made of two machined disks of 316L stainless steel of diameter 19.4 cm that were clamped together by 12 stainless-steel bolts. The bottom disk contained a cylindrical cavity that was filled with approximately 120 ml of distilled water. The gas entered each saturator from the top of the cavity through a tube located at a distance of 6.0 cm from the axial center. The gas exited the saturator through a tube located in the top of the cavity at a distance of 1.5 cm from the axial center. The gas flowed through a set of circularlyconcentric channels of 1.25 cm width as it passed through the cavity. Finite-element analysis was used to determine that the saturator could withstand 11 MPa of pressure inside the cavity.

An expansion (needle) valve separated the final saturator from the manifold leading to the gravimetric hygrometer, allowing pressurization of the saturation system. A platinum resistance thermometer (PRT) was immersed in a well located in the center of the top disk. A tube leading to a commercial strain-gauge pressure transducer was attached to the top disk 1.5 cm from the axial center.

This NIST gravimetric hygrometer has previously been described in detail [4]. Briefly, it separates the water from the gas in water collection tubes, using desiccants to perform the separation. Subsequently, the amounts of water and gas are determined independently, allowing calculation of the water mole fraction.

For each measurement, an amount of moist gas is passed through the gravimetric hygrometer such that approximately 1 g of water will be collected. As the moist gas passes through the hygrometer, the water is trapped in three collection tubes containing the desiccant magnesium perchlorate (Mg(ClO<sub>4</sub>)<sub>2</sub>). The remaining dry gas is directed to a gas collection system. The masses of all three collection tubes are measured both before and after the gas is passed through them. Only the first two tubes are intended to collect water; the third tube serves to verify that all water was collected in the first two tubes.

The gas collection system (see Fig. 1.2) consists of two prover pistons. As gas is collected in the prover tubes, the pistons rise. With gas access controlled by computer-controlled pneumatic valves, the two prover pistons alternate in collecting gas, allowing continuous automated collection. A laser interferometer system is used to accurately determine the vertical position of the pistons. Since the inner diameters of the prover tubes are known from earlier dimensional measurements, the volume of gas under each piston can be calculated by its vertical position. Once a piston reaches a certain height, a valve automatically diverts the gas to the other piston. As the second piston rises, pressure and temperature measurements are made underneath the first piston. Afterwards, a valve opens to allow the gas collected under the first piston to escape, allowing the piston to fall to its original position. A second measurement of pressure and temperature under the piston is made. The first piston is then kept in place until its gas-access valve is reopened. The temperature and pressure measurements and the gas's equation of state [7] are used to calculate the density of the gas underneath the piston. At the end of the experiment, all increments are summed to provide the total amount of gas.

The apparatus was validated by performing saturation experiments with CO<sub>2</sub>-free air. The results agreed within their uncertainties with literature data [8]. Experiments were also performed with varying flow rates in order to verify that full saturation was reached for the flow rate used.

The uncertainty budget for the gravimetric hygrometer is given in [4], and the estimation of uncertainty for the present measurements is described in [5]. Briefly, the composition measurements of the gravimetric hygrometer have a relative expanded uncertainty (k=2, roughly corresponding to a 95 % confidence interval) of 0.12 %, and the overall measurements of dewpoint composition have a relative expanded uncertainty ranging from 0.17 % to 0.75 %, depending on the isotherm.

## **1.2. Results**

We performed measurements of the water content in saturated  $CO_2$  on six isotherms: 10 °C, 21.7 °C, 30 °C, 40 °C, 60 °C, and 80 °C. For most isotherms, the data were taken at ten pressure values from 0.5 MPa to 5.0 MPa in increments of 0.5 MPa. However, for the 10 °C isotherm, data were not taken above 4 MPa because  $CO_2$  hydrates are known to form in this range [9].

Table 1.1 reports the measured water vapor mole fractions  $y_w$  at each experimental temperature and pressure. The table also includes the enhancement factor,  $f = y_w p/p_s$ , where  $p_s$  is the vapor pressure of pure water at the experimental temperature. The enhancement factor is a measure of how much the pressurized gas causes the equilibrium amount of water in the vapor to exceed that for the case of pure saturated water with no gas. It typically increases with pressure and decreases with temperature, primarily because of the effect of these variables on the deviation from ideal-gas behavior. Figure 1.3 shows the measured enhancement factors; we note that the enhancement observed in CO<sub>2</sub> is several times the enhancement observed in air at similar conditions. This is due to the stronger attractive forces between H<sub>2</sub>O and CO<sub>2</sub> compared to H<sub>2</sub>O with the components of air [5].

### **1.3. Data Analysis**

For gaseous mixtures at moderate pressures, it is appropriate to analyze data in terms of the virial expansion, in which the volumetric properties of a fluid are described as deviations from the limiting ideal-gas behavior:

$$\frac{p}{\rho RT} = 1 + B\rho + C\rho^2 + \dots$$
(1.1)

In Eq. (1.1), the second virial coefficient *B* represents interactions between pairs of molecules, the third virial coefficient *C* represents three-molecule interactions, and so forth. Other key thermodynamic properties such as enthalpies, entropies, heat capacities, and fugacity coefficients can be obtained by appropriate manipulation of Eq. (1.1). For the pressures considered in this work, sufficient accuracy can be obtained by truncating Eq. (1.1) after the *B* and *C* terms. For a mixture, the second and third virial coefficients,  $B_{mix}$  and  $C_{mix}$ , are mole-fraction sums of contributions from all pairs (for *B*) and triplets (for *C*) of species in the system:

$$B_{\rm mix} = \sum_{i} \sum_{j} y_i y_j B_{ij} , \qquad (1.2)$$

$$C_{\text{mix}} = \sum_{i} \sum_{j} \sum_{k} y_i y_j y_k C_{ijk} , \qquad (1.3)$$

where  $y_i$  is the mole fraction of species *i* in the mixture. For a binary mixture such as that considered in this work, Eqs. (1.2) and (1.3) become:

$$B_{\rm mix} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} , \qquad (1.4)$$

$$C_{\rm mix} = y_1^3 C_{111} + 3y_1^2 y_2 C_{112} + 3y_1 y_2^2 C_{122} + y_2^3 C_{222} . \qquad (1.5)$$

As shown in [5], a thermodynamic description for the enhancement factor (and therefore the dew point) can be developed in terms of known thermodynamic properties of pure water, the solubility of the gas in liquid water, and (most important) the virial coefficients describing the mixture. *B* and *C* are known from the literature for both pure H<sub>2</sub>O [10,11] and pure CO<sub>2</sub> [7]. This leaves the mixed virial coefficients  $B_{12}$ ,  $C_{112}$ , and  $C_{122}$  (we label CO<sub>2</sub> as component 1 and H<sub>2</sub>O as component 2). In principle, all three of these coefficients could be fit to the experimental data. However, because the mole fraction of H<sub>2</sub>O in the vapor is small,  $C_{122}$  has very little influence on the phase equilibrium. We therefore estimated  $C_{122}$  as described in [5], and fitted  $B_{12}$  and  $C_{112}$  to our experimental data on each isotherm. Our values of these coefficients, along with the uncertainties of our fitted values of  $B_{12}$  and  $C_{112}$ , are given in Tables 1.2 and 1.3.

In Fig. 1.4, we plot the values of  $B_{12}$  resulting from our experiments, along with the theoretical predictions of Wheatley and Harvey [12] and several experimental sources. Our results are in excellent agreement with the work of Wheatley and Harvey, but our uncertainties are much smaller (and also smaller than the uncertainties of previous experimental results).

283.15 $0.5002$ $2.6064$ $1.0614$ $283.15$ $1.0004$ $1.3886$ $1.1310$ $283.15$ $1.5007$ $0.9925$ $1.2127$ $283.15$ $2.0028$ $0.8016$ $1.3073$ $283.15$ $2.028$ $0.6944$ $1.4128$ $283.15$ $3.0182$ $0.6293$ $1.5466$ $283.15$ $3.5099$ $0.5916$ $1.6866$ $283.15$ $3.9937$ $0.5812$ $1.8898$ $294.83$ $0.5000$ $5.4788$ $1.0557$ $294.83$ $1.0003$ $2.8883$ $1.1134$ $294.83$ $2.0008$ $1.6239$ $1.2523$ $294.83$ $2.5010$ $1.3849$ $1.3348$ $294.83$ $2.5010$ $1.3849$ $1.3348$ $294.84$ $4.0112$ $1.0738$ $1.6599$ $294.84$ $4.5027$ $1.0445$ $1.8125$ $294.84$ $4.5027$ $1.0445$ $1.8125$ $294.84$ $4.5027$ $1.0445$ $1.8125$ $294.84$ $4.5027$ $1.0445$ $1.8125$ $294.84$ $4.5027$ $1.0445$ $1.8125$ $294.84$ $4.5027$ $1.0445$ $1.8125$ $294.84$ $4.5027$ $1.0445$ $1.8125$ $294.84$ $4.5027$ $1.0445$ $1.8125$ $294.84$ $4.9854$ $1.0244$ $1.9681$ $303.14$ $1.5008$ $3.2833$ $1.1068$ $303.15$ $3.0013$ $1.9371$ $1.3689$ $303.14$ $4.5020$ $1.5719$ $1.6672$ $303.15$ $5.0055$ <th><i>T</i> [K]</th> <th><i>p</i> [MPa]</th> <th><math>y_{\rm w} \times 10^3</math></th> <th>f</th>	<i>T</i> [K]	<i>p</i> [MPa]	$y_{\rm w} \times 10^3$	f
283.15 $1.0004$ $1.3886$ $1.1310$ $283.15$ $1.5007$ $0.9925$ $1.2127$ $283.15$ $2.0028$ $0.8016$ $1.3073$ $283.15$ $2.4986$ $0.6944$ $1.4128$ $283.15$ $3.0182$ $0.6293$ $1.5466$ $283.15$ $3.5009$ $0.5916$ $1.6866$ $283.15$ $3.9937$ $0.5812$ $1.8898$ $294.83$ $0.5000$ $5.4788$ $1.0557$ $294.83$ $1.0003$ $2.8883$ $1.1134$ $294.83$ $1.5005$ $2.0413$ $1.1805$ $294.83$ $2.0008$ $1.6239$ $1.2523$ $294.83$ $2.0008$ $1.6239$ $1.2523$ $294.83$ $2.0008$ $1.6239$ $1.2523$ $294.84$ $3.5016$ $1.1338$ $1.5299$ $294.84$ $3.5016$ $1.1338$ $1.5299$ $294.84$ $4.5027$ $1.0445$ $1.8125$ $294.84$ $4.5027$ $1.0445$ $1.8125$ $294.84$ $4.5027$ $1.0445$ $1.8125$ $294.84$ $4.5027$ $1.0445$ $1.8125$ $294.84$ $4.5027$ $1.0445$ $1.8125$ $294.84$ $4.5027$ $1.0445$ $1.8125$ $303.14$ $0.5002$ $8.8966$ $1.0482$ $303.15$ $1.0003$ $4.6867$ $1.1038$ $303.14$ $2.5013$ $2.2033$ $1.2982$ $303.15$ $3.0013$ $1.9371$ $1.3689$ $303.14$ $4.5020$ $1.5719$ $1.6672$ $303.15$ $5.0055$ </td <td>283.15</td> <td>0.5002</td> <td>2.6064</td> <td>1.0614</td>	283.15	0.5002	2.6064	1.0614
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	283.15	1.0004	1.3886	1.1310
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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	283.15	2.4986	0.6944	1.4128
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	283.15	3.0182	0.6293	1.5466
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	283.15	3.5009	0.5916	1.6866
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	283.15	3.9937	0.5812	1.8898
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	294.83	0.5000	5.4788	1.0557
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	294.83	1.0003	2.8883	1.1134
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	294.83	1.5005	2.0413	1.1805
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	294.83	2.0008	1.6239	1.2523
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	294.83	2.5010	1.3849	1.3348
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$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	294.84	3.5016	1.1338	1.5299
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	294.84	4.0112	1.0738	1.6599
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	294.84	4.5027	1.0445	1.8125
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	294.84	4.9854	1.0244	1.9681
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	303.14	0.5002	8.8966	1.0482
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	303.15	1.0003	4.6867	1.1038
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	303.14	1.5008	3.2833	1.1608
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	303.15	2.0008	2.6054	1.2273
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	303.14	2.5013	2.2033	1.2982
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	303.15	3.0013	1.9371	1.3689
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	303.14	3.5017	1.7714	1.4611
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	303.15	4.0019	1.6650	1.5689
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	303.14	4.5020	1.5719	1.6672
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	303.15	5.0055	1.5022	1.7705
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	313.17	0.5002	15.340	1.0381
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	313.17	1.0003	8.0707	1.0919
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	313.17	1.5007	5.6219	1.1410
313.172.50123.72111.2589313.173.00133.26491.3252313.173.50162.93701.3914313.174.00192.73201.4787313.164.50222.56641.5635313.175.00242.45691.6623	313.17	2.0010	4.4139	1.1949
313.173.00133.26491.3252313.173.50162.93701.3914313.174.00192.73201.4787313.164.50222.56641.5635313.175.00242.45691.6623	313.17	2.5012	3.7211	1.2589
313.173.50162.93701.3914313.174.00192.73201.4787313.164.50222.56641.5635313.175.00242.45691.6623	313.17	3.0013	3.2649	1.3252
313.174.00192.73201.4787313.164.50222.56641.5635313.175.00242.45691.6623	313.17	3.5016	2.9370	1.3914
313.16       4.5022       2.5664       1.5635         313.17       5.0024       2.4569       1.6623	313.17	4.0019	2.7320	1.4787
313.17 5.0024 2.4569 1.6623	313.16	4.5022	2.5664	1.5635
	313.17	5.0024	2.4569	1.6623
333.19 0.5000 41.504 1.0386	333.19	0.5000	41.504	1.0386
333.18 1.0002 21.461 1.0743	333.18	1.0002	21.461	1.0743
333.18 1.5007 14.798 1.1118	333.18	1.5007	14.798	1.1118

Table 1.1. Measured water vapor mole fractions  $y_w$  and enhancement factors f as a function of pressure for the six isotherms measured in this work. See text and [5] for discussion of uncertainty in  $y_w$  and f.

333.18	2.0009	11.514	1.1534
333.18	2.5010	9.5623	1.1974
333.18	3.0012	8.2871	1.2451
333.18	3.5015	7.3862	1.2948
333.18	4.0018	6.7515	1.3504
333.17	4.5019	6.2355	1.4059
333.18	5.0024	5.8609	1.4681
353.15	0.4999	97.482	1.0280
353.15	1.0001	50.406	1.0633
353.14	1.5005	34.562	1.0941
353.15	2.0007	26.675	1.1257
353.14	2.5010	21.942	1.1576
353.14	3.0012	18.871	1.1948
353.15	3.5017	16.681	1.2320
353.14	4.0016	15.051	1.2705
353.15	4.5020	13.793	1.3095
353.15	5.0023	12.819	1.3523

Table 1.2. Values of the third cross virial coefficients  $C_{122}$  and  $C_{112}$ . The estimated values of  $C_{122}$  are calculated as described in [5]. The values of  $C_{112}$  are optimized as described in [5]. Our estimate for the expanded uncertainty of the determined  $C_{112}$  values is given in the last column.

T	$C_{122}$ (calculated)	$C_{112}$ (optimized)	$U(C_{112})$
[K]	[cm <sup>6</sup> /mol <sup>2</sup> ]	[cm <sup>6</sup> /mol <sup>2</sup> ]	[cm <sup>6</sup> /mol <sup>2</sup> ]
283.15	-380000	-14700	3000
294.83	-290000	-1800	2000
303.15	-240000	-500	5000
313.17	-190000	-3700	6000
333.18	-130000	1800	1500
353.15	-92000	5000	3000

Table 1.3. Optimized values of the second cross virial coefficients  $B_{12}$ . Our estimate for the expanded uncertainty of the determined  $B_{12}$  values is given in the last column.

	Ŭ	
Т	$B_{12}$ (optimized)	$U(B_{12})$
[K]	[cm <sup>3</sup> /mol]	[cm <sup>3</sup> /mol]
283.15	-203	3
294.83	-186	2
303.15	-173	6
313.17	-155	5
333.18	-132	2
353.15	-113	3



Figure 1.1. Diagram of saturation system for H<sub>2</sub>O/CO<sub>2</sub> mixture.



Figure 1.2. Diagram of gas measurement system for NIST gravimetric hygrometer.



Figure 1.3. Enhancement factors for H<sub>2</sub>O in CO<sub>2</sub> measured in this work.



Figure 1.4. Comparison of  $B_{12}(T)$  predicted from theory to available experimental data for the H<sub>2</sub>O/CO<sub>2</sub> binary; shading and error bars represent expanded (*k*=2) uncertainty approximately equivalent to a 95% confidence level.

# 2. THERMODYNAMIC MODEL FOR THE H<sub>2</sub>O/CO<sub>2</sub> MIXTURE (TASK 3)

#### 2.1. Thermodynamic Model

The thermodynamic model employed to characterize the behavior of  $H_2O/CO_2$  mixtures is based on an empirical multiparameter Helmholtz-energy-explicit construction. This approach mixes the reference-quality equations of state available for the pure fluids [7,11], and uses empirical mixing terms to improve the description of mixtures. The approach is fully described elsewhere [13-15] and is used in popular software such as REFPROP [1] and CoolProp [16].

The core of the mixture modeling is the fitting of the interaction parameters that are involved in the reducing functions  $\rho_r$  and  $T_r$  that interpolate the effective mixture density and temperature scales between their pure-component values (which are taken as the critical density and critical temperature of each pure component). In each of the reducing functions, there are two adjustable parameters. These reducing functions are given by

$$T_{\rm r}(\bar{x}) = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \beta_{T,ij} \gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} \left( T_{{\rm c},i} T_{{\rm c},j} \right)^{0.5},$$
(2.1)

$$\frac{1}{\rho_{\rm r}(\bar{x})} = \sum_{i=1}^{N} \sum_{j=1}^{N} x_i x_j \beta_{\nu,ij} \gamma_{\nu,ij} \frac{x_i + x_j}{\beta_{\nu,ij}^2 x_i + x_j} \frac{1}{8} \left( \frac{1}{\rho_{\rm c,i}^{1/3}} + \frac{1}{\rho_{\rm c,j}^{1/3}} \right)^3, \tag{2.2}$$

where the adjustable parameters are  $\beta_{T,ij}$  and  $\gamma_{T,ij}$  for Eq. (2.1), and  $\beta_{V,ij}$  and  $\gamma_{V,ij}$  for Eq. (2.2).  $x_i$  is the mole fraction of component *i*.

The mixture model also contains a "departure function" as described elsewhere [14,15] that accounts for specific binary effects not captured in the simple mixing formalism of Eqs. (2.1) and (2.2). For this work, we used the departure function given by Gernert and Span [15], but adjusted the binary parameter  $F_{ij}$  that appears in that function.

# 2.2. Results

The interaction parameters have been fit to the experimental measurements for the dew points documented in Section 1 of this report and in [5]. The values of the interaction parameters obtained are given in Table 2.1.

Parameter	Value
$\beta_{T,ij}$	1.071 957 12
γT,ij	0.859 767 75
$eta_{V,ij}$	0.947 541 11
γV,ij	0.944 664 04
Fij	0.4

Table 2.1. Values of the binary interaction parameters for the  $H_2O/CO_2$  system as obtained from fitting the dew-point measurements

Figure 2.1 shows the experimentally measured values for the enhancement factor along with curves that represent the enhancement factor calculated by REFPROP [1] with the interaction parameters as given in Table 2.1. Aside from the low-temperature/high-pressure domain where the numerical routines in REFPROP fail to converge (work is ongoing to improve this convergence), the agreement between experimental and model-predicted values is excellent.



Figure 2.1. Calculated (lines) and measured (symbols) values for the enhancement factor for H<sub>2</sub>O in compressed CO<sub>2</sub>.

# 3. REFERENCE CORRELATION FOR THE VISCOSITY OF CO<sub>2</sub> (Task 4)

Complete information on the work performed in this task is given in a paper to be published in the *Journal of Physical and Chemical Reference Data* [17]. We therefore provide only an overview of the new viscosity correlation in the following.

# 3.1. Synopsis

A comprehensive database of experimental and computed data for the viscosity of CO<sub>2</sub> was compiled. This included several sources published since the previous reference correlation was developed in 1990 [2] and modified in 1998 [3]. Recent results from a high-quality molecular model were used to guide the behavior of the low-density gas viscosity over a wide range of temperatures. Symbolic regression was employed to determine the most effective functional terms for the correlation. The final viscosity correlation covers temperatures from 100 K to 2000 K for gaseous CO<sub>2</sub>, and from 220 K to 700 K at pressures along the melting line up to 8000 MPa for compressed and supercritical liquid states. The representation of data is more accurate than the previous correlation, and the pressure and temperature range covered is significantly extended.

# 3.2. Brief Summary of Viscosity Data

Viscosity measurements of CO<sub>2</sub> have been carried out since 1846, but until now have not been assembled in one comprehensive database. In this work, references from six previous correlations of the viscosity of CO<sub>2</sub>, as well as those included in the current versions of the AIChE DIPPR database [18], the NIST ThermoData Engine [19], and the Landolt-Börnstein compilations [20,21] were retrieved. These compilations and databases were mutually incomplete by varying degrees. One result of this project is therefore that all known literature data for the viscosity of CO<sub>2</sub> are now collected in one repository.

The two most recent data analyses and correlations of the viscosity of CO<sub>2</sub> were performed in 1990 [2] and in 1998 [3]. Vesovic et al. [2] found systematic deviations between some data sets in the compressed liquid region, which prompted new viscosity measurements. These were carried out by van der Gulik [22] with a vibrating-wire viscometer at the Van der Waals-Laboratory in Amsterdam. The results formed the basis for the revised viscosity correlation of Fenghour et al. [3]. Since then, a number of data sets have been published for the viscosity of CO<sub>2</sub>, yet only two expanded the temperature and pressure range. The measurements of Estrada-Alexanders and Hurly [23] covered the vapor and gas region at temperatures between 220 K and 370 K up to the vapor pressure or 3.15 MPa, whichever is lower. Abramson [24] measured

extremely compressed liquid states in a diamond-anvil cell at temperatures from 308 K to 670 K with pressures from 480 MPa to 7960 MPa. Several contributions provided results with lower uncertainty in regions where measurements had been carried out before. Mal'tsev et al. [25] published three data points from a coiled capillary viscometer for the dilute gas at 500 K, 800 K, and 1100 K. Sih et al. [26] measured with a falling-body viscometer at three near-critical temperatures at supercritical pressures from 10 MPa to 19 MPa. Pensado et al. [27] reported density and viscosity data measured simultaneously with a vibrating-wire viscometer at six temperatures between 303.15 K and 353.15 K with pressures from 10 MPa to 60 MPa. Heidaryan et al. [28] measured the viscosity of CO<sub>2</sub> with a falling-sphere viscometer from 313.15 K to 523.15 K with pressures between 7.7 MPa and 81.1 MPa. This region had been sparsely explored before. However, the data were neither reported in the publication nor were they provided upon request of the present authors. Davani et al. [29] reported measurements with a rolling-sphere viscometer at nine temperatures from 309.82 K to 388.71 K and at five pressures from 27.6 MPa to 55.2 MPa. In 2014 (published in 2016), Vogel [30] recalculated the results of Vogel and Barkow [31] and those of Hendl et al. [32] by referencing them to a highly accurate first-principles value for the viscosity of helium gas at room temperature. Locke et al. [33] contributed five data points for gaseous CO<sub>2</sub> at 303.2 K and pressures from 0.5 MPa to 4.5 MPa that were measured with a newly developed vibrating-wire viscometer. Most recently, Schäfer et al. [34] reported highly accurate measurements in the dilute-gas region from 253.15 K to 473.15 K with an advanced rotating-body viscometer that were carried out in consultation with this project.

Besides these experimental measurements, an increasing number of computational studies contributed to a more detailed understanding of the viscosity of CO<sub>2</sub>. Major advances were achieved in the *ab initio* (from first principles) calculation of the potential-energy surface (PES) that governs pairwise interactions of CO<sub>2</sub> molecules. The most recent of these studies by Hellmann [35] reviews previous work in this area. It is important to recognize the transition in methodology this represents. For gases at low density where only pairwise interactions occur, *ab initio* computations of increasing accuracy have now superseded experimental capabilities for simple molecules. Due to the more complex molecular structure of CO<sub>2</sub>, *ab initio* calculations of the PES and the properties of dilute CO<sub>2</sub> gas have not yet advanced below the uncertainty of experimental measurements, but they characterize the viscosity in the low-density limit over a wider temperature range than that explored in measurements and thus contributed significantly to the new viscosity correlation. Details will be given in Section 3.5.

The data sets of Estrada-Alexanders and Hurly [23], Abramson [24], and Schäfer et al. [34] were included in the critically analyzed data on which the new viscosity correlation was based. The results of Schäfer et al. confirmed an increased uncertainty of the data of Estrada-Alexanders and Hurly with decreasing density, which had been already noted by these authors themselves [23]. Therefore, data from Ref. [23] below a density of 16 kg·m<sup>-3</sup> were not included in the development of the new viscosity correlation. Fully included were the data of Kestin and Whitelaw [36], Docter et al. [37], Vogel and Barkow [31], and those of Hendl et al. [32] as revised by Vogel [30], as well as the data by van der Gulik [22] and Golubev and Shepeleva [38] in the liquid region. For the data of Golubev and Petrov [39] and those by Michels et al. [40], some points in regions of high compressibility were excluded because the effect of compressibility on the capillary flow was not accounted for in the working theory of these viscometers. For reasons of internal consistency, the data by Haepp [41] were used from 370 K to 450 K with pressures from 3 MPa to 15 MPa. The data by Kurin and Golubev [42] that were included in previous correlations were not considered in this work because they appeared inconsistent with the data by Golubev and Petrov [39] at lower pressures and those by Abramson [24] at higher pressures.

Figure 3.1 shows how the selected experimental viscosity data cover the fluid region of CO<sub>2</sub> relative to the melting curve, the vapor-pressure curve, and the sublimation curve. A wide gap exists at pressures from 0.5 MPa to about 700 MPa for temperatures above 550 K, where only 24 data points were measured by Golubev et al. [43]. New measurements in this region would yield a significant improvement of the knowledge of the viscosity of CO<sub>2</sub>.

# **3.3. Equation of State**

For theoretical and phenomenological reasons, viscosity formulations for the entire fluid region are developed in terms of temperature and density. As a consequence, the experimental viscosity data reported as a function of temperature and pressure must be converted to a common basis of temperature and density by means of an equation of state (EOS). A reference-quality fundamental EOS for CO<sub>2</sub> was published by Span and Wagner in 1996 [7]. This was too late to be incorporated in the revision by Fenghour et al. [3] of the 1990 correlation of Vesovic et al. [2], which was published nevertheless because it was more urgent to remove the uncertainties that existed in the viscosity of the compressed liquid region.

Densities corresponding to CO<sub>2</sub> viscosity data for this work were computed from the EOS of Span and Wagner [7]. Because the pressure conditions of Abramson's measurements [24] exceeded the range of validity of the Span-Wagner EOS, Abramson cited Giordano et al. [44] as

a source of more recent equation-of-state information for fluid CO<sub>2</sub>. A comparison showed that densities from the Span-Wagner EOS are up to 3.24 % higher at the highest temperature (673.8 K) and highest pressure (7960 MPa) where Abramson measured. Therefore, in this work densities from the analytical EOS of Giordano et al. [44] were associated with Abramson's high-pressure viscosity data above 500 K.

### **3.4.** Viscosity Correlation

The viscosity correlation for CO<sub>2</sub> was formulated in the following general structure:

$$\eta(T,\rho) = \eta_0(T) + \eta_1(T)\rho + \Delta\eta_r(T,\rho) + \Delta\eta_c(T,\rho).$$
(3.1)

Here,  $\eta$  is the dynamic viscosity (in units of mPa·s throughout this work), *T* the absolute temperature in K, and  $\rho$  the density in kg·m<sup>-3</sup>. On the right-hand side of Eq. (3.1),  $\eta_0(T)$  is the viscosity in the low-density limit,  $\eta_1(T)$  the linear-in-density viscosity coefficient,  $\Delta \eta_r(T,\rho)$  the temperature- and density-dependent residual viscosity, and  $\Delta \eta_c(T,\rho)$  is the term for the enhancement of the viscosity very near the gas-liquid critical point [45]. The four contributions to the formulation will be detailed in the following sections.

#### **3.5.** Viscosity in the Low-Density Limit

The temperature dependence of the viscosity in the low-density limit  $\eta_0(T)$  was correlated by symbolic regression on the basis of *ab initio* data by Hellmann [35] over the extended range from 100 K to 2000 K. Data below the published lower limit of 150 K were graciously provided by Dr. Hellmann during discussions with the present authors about the appropriate form of  $\eta_0$ correlations, since some correlations have unphysical singularities at low temperatures and do not extrapolate correctly to  $T \rightarrow 0$ . In an effort to avoid such behavior, the symbolic regression was guided to use powers of  $T^{1/6}$  as temperature terms in the denominator because they have been found effective for model potentials such as that of Lennard-Jones. For physically meaningful extrapolation to high temperatures, the correlation was constrained to the square-root term of temperature in the numerator which arises from kinetic theory for the viscosity of a gas of hard spheres [46]. A function that satisfies all objectives was obtained:

$$\eta_0(T) = \frac{1.0055\sqrt{T}}{\left(a_0 + a_1 T^{1/6} + a_2 \exp\left(a_3 T^{1/3}\right) + \frac{a_4 + a_5 T^{1/3}}{\exp\left(T^{1/3}\right)} + a_6 \sqrt{T}\right)}.$$
(3.2)

Equation (3.2), with fitted coefficients  $a_i$  given in Table 3.1, represents the extended data of Hellmann [35] with maximum deviations from -0.05 % to 0.03 %, which are significantly below

their estimated uncertainties (0.2 % between 300 K and 700 K, increasing to 1 % at 150 K and 2000 K). Equation (3.2) has no singularity at any temperature, yields  $\eta_0 = 0$  for  $T \rightarrow 0$ , and extrapolates reliably to 10 000 K. With the absolute temperature *T* in K, the viscosity  $\eta_0(T)$  is obtained in mPa·s. The values of the coefficients  $a_0$  to  $a_6$  are given in Table 3.1. The scaling factor 1.0055 was proposed by Hellmann to match the calculated *ab initio* results with  $\eta_0$  values derived from the most accurate experimental data.

i	ai
0	1749.354893188350
1	-369.069300007128
2	5423856.34887691
3	-2.21283852168356
4	-269503.247933569
5	73145.021531826
6	5.34368649509278

Table 3.1. Values of the parameters  $a_i$  in Eq. (3.2).

The performance of Eq. (3.2) is illustrated in Figs. 3.2 and 3.3. Figure 3.2 shows the representation of the (unscaled)  $\eta_0$  data calculated by Hellmann and the extrapolation behavior of Eq. (3.2) in the temperature range from 0 K to 1000 K. Figure 3.3 shows a comparison of  $\eta_0$  data derived from measurements considered to be most accurate relative to Eq. (3.2) in the temperature range 200 K to 1900 K. The data of Timrot and Traktueva [47], Hunter et al. [48], the revised values of Vogel and Barkow (1986) and of Hendl et al. (1993) [30] as well as those of Schäfer et al. [34] show the smallest deviations from Eq. (3.2) within a range of  $\pm 0.2$  %. They also agree with the temperature dependence of Eq. (3.2). This temperature dependence is also confirmed by the viscosity data that Bock et al. [49] calculated from the potential-energy surface of Bukowski et al. [50], which show a constant offset of -0.22 % above 640 K. The highest deviation of -0.59 % of these values occurs at 185 K. Systematically different temperature dependencies are visible in Fig. 3.3 for some older data sources.

Overall, thanks to the calculations of Hellmann [35] and due to its new functional form, the new correlation for the viscosity of CO<sub>2</sub> in the limit of zero density,  $\eta_0(T)$ , Eq. (3.2), has a lower uncertainty and a significantly wider range of applicability than previous correlations for this quantity.

#### 3.6. Initial Density Dependence of the Viscosity

The linear-in-density viscosity coefficient  $\eta_1(T)$  represents the initial density dependence of the viscosity. It is given by

$$\eta_1(T) = \eta_0(T)B_n^*(T^*)\sigma^3 N_A / M, \qquad (3.3)$$

with  $\eta_0(T)$  according to Eq. (3.2), the temperature-dependent second viscosity virial coefficient  $B_\eta^*(T^*)$  as detailed below, the length scaling parameter  $\sigma$  in meters, the Avogadro constant  $N_A = 6.022 \ 140 \ 857 \times 10^{23} \ \text{mol}^{-1}$  [51], and the molar mass of CO<sub>2</sub>  $M = 44.0095 \times 10^{-3} \ \text{kg} \cdot \text{mol}^{-1}$ . The temperature dependence of the reduced second virial coefficient  $B_\eta^*(T^*)$  was theoretically calculated for the Lennard-Jones potential by Rainwater and Friend [52,53] and later adjusted to experimental results by Vogel and Hendl [54]. An accurate and wide-ranging correlation of their results was published by Vogel et al. [55] and adopted in this work. The correlation is formulated in terms of the reduced temperature  $T^* = kT/\varepsilon$  as:

$$B_{\eta}^{*}(T^{*}) = b_{0} + \sum_{i=1}^{8} \frac{b_{i}}{\left(T^{*}\right)^{t_{i}}}.$$
(3.4)

For convenience of implementation, the values from Vogel et al. [55] of the coefficients  $b_i$  and of the exponents  $t_i$  are reproduced in Table 3.2.

i	$b_i$	ti
0	-19.572 881	
1	219.739 99	0.25
2	-1015.322 6	0.5
3	2471.012 5	0.75
4	-3375.171 7	1
5	2491.659 7	1.25
6	-787.260 86	1.5
7	14.085 455	2.5
8	-0.346 641 58	5.5

Table 3.2. Values of the parameters  $b_i$  and exponents  $t_i$  in Eq. (3.4).

Equation (3.4) was adjusted to data [55] in the range  $0.5 \le T^* \le 100$ , but extrapolates safely to  $T^* = 0.3$  and above  $T^* = 100$ . The energy scaling parameter  $\varepsilon/k$  is required to convert between absolute and reduced temperature  $T^* = kT/\varepsilon$ . This value and that of the length-scaling parameter

 $\sigma$  were determined from the data of Schäfer et al. [34], the temperature of the sign change of  $B_{\eta}^{*}$  at  $T^{*} = 1.2462$  and from its maximum at  $T^{*} = 2.1652$ . The results are  $\sigma = 3.78404 \times 10^{-10}$  m and  $\varepsilon/k = 200.610$  K.

Figure 3.4 shows data and the resulting correlation of the second viscosity virial coefficient  $B_{\eta}$  and of the linear-in-density viscosity coefficient  $\eta_1$  of CO<sub>2</sub> in the temperature range from 200 K to 1000 K. The most noteworthy feature of these properties is their steep decrease below 300 K; this is important behavior to capture in a correlation in a region where there are few experimental data. The measurements of Vogel and colleagues at the University of Rostock did not record this decrease because their viscometer operated from this temperature upward. Figure 3.5 also shows that the revised values for  $B_{\eta}$  and for  $\eta_1$  [30] exhibit considerable scatter and give no clear indication of the temperature dependence of the properties. The importance of measurements below 300 K was communicated during this project to Schäfer et al. at the Ruhr-University Bochum. They responded to this need and carried out the measurements [34] that made it possible to apply Eq. (3.4) to CO<sub>2</sub>. As noted in Section 3.1, the only other data set in the low-density gas region at low temperatures [23] could not be used for the analysis of the initial density dependence of viscosity because of their increased uncertainty at low density.

Figure 3.4 also indicates the improvement of the new viscosity correlation from its predecessors [2,3]. These correlations included temperature-independent constants as linear-in-density viscosity coefficients  $\eta_1$  which are correct only near room temperature but do not represent the steep decrease at lower temperatures, nor the maximum at higher temperatures. The theory-based range of validity of Eq. (3.4) of  $0.3 \le T^* \le 100$  translates with the value of  $\varepsilon/k = 200.610$  K for CO<sub>2</sub> to a fluid-specific range of applicability of Eq. (3.4) of  $60 \le T/K \le 20061$ .

### 3.7. Residual Viscosity Contribution

The temperature- and density-dependence of the residual viscosity term  $\Delta \eta_r(T,\rho)$  was obtained by symbolic regression of the critically evaluated data as

$$\Delta \eta_{\rm r}(T,\rho) = \eta_{\rm tL} \left( c_1 T_{\rm r} \rho_{\rm r}^3 + (\rho_{\rm r}^2 + \rho_{\rm r}^\gamma) / (T_{\rm r} - c_2) \right), \tag{3.5}$$

with the dimensioning factor

$$\eta_{\rm tL} = \frac{\rho_{\rm tL}^{2/3} \sqrt{RT_{\rm t}}}{M^{1/6} N_{\rm A}^{1/3}} \,. \tag{3.6}$$

The reduced temperature  $T_r = T/T_t$  is formed with the triple-point temperature of CO<sub>2</sub>,  $T_t = 216.592$  K, and the reduced density  $\rho_r = \rho/\rho_{tL}$  with the density of the liquid phase at the triple point,  $\rho_{\text{L}} = 1178.53 \text{ kg} \cdot \text{m}^{-3}$  [7]. The value of the molar gas constant is R = 8.3144598J·mol<sup>-1</sup>·K<sup>-1</sup> [51] and the molar mass M of CO<sub>2</sub> and the Avogadro constant  $N_{\text{A}}$  are given in Section 3.6. With these quantities, the value of the dimensioning factor  $\eta_{\text{tL}}$  is approximately 0.094 36 mPa·s (the complete non-rounded result from Eq. (3.6) is used in the correlation). The values of the coefficients  $\gamma$ ,  $c_1$ , and  $c_2$  are given in Table 3.3.

Table 3.3. Values of the parameters in Eq. (3.5).

γ	8.06282737481277
<b>C</b> 1	0.360603235428487
<i>C</i> <sub>2</sub>	0.121550806591497

To balance highly accurate data representation with physically meaningful extrapolation capability, the selection of functional terms for the residual viscosity  $\Delta \eta_{\rm f}(T,\rho)$  was guided by three considerations. First, polynomial density terms were given low priority because the viscosity-density dependence to high densities is intrinsically different from the kinetic approach in gases and can at best be approximated by a virial expansion in density. The previous viscosity correlation of Fenghour et al. [3] included polynomial density terms up to the eighth degree and failed to extrapolate to the high-pressure data of Abramson [24]. Oscillatory patterns in the deviations of the critically selected primary data also indicate the approximate character of polynomial density terms. More meaningful extrapolation capability at equally accurate data representation is offered by free-volume terms. They were avoided here because their inevitable singularity at high density limits their extrapolation capability [56]. A singularity-free representation of viscosities and other properties to high compressions was proposed by Ashurst and Hoover [57,58] based on the congruence of the dynamic evolution of systems with different soft-sphere potentials [59]. This congruence is obtained when the initial conditions of the dynamic evolutions are scaled in terms of time and length and when dimensionless variables are used for temperature, density, viscosity and other properties. It turned out that the reduced residual viscosity, e.g.,  $\Delta \eta_{\rm r}(T,\rho)/\eta_{\rm L}$  from Eq. (3.5), is a function of the single variable  $\rho^{\gamma}/T$  and not of density and temperature separately. This folding of two independent variables into one has become known as thermodynamic scaling. The exponent  $\gamma$  is related to the strength of the repulsive soft-sphere potential. Given the repulsive nature of the interaction between CO<sub>2</sub> molecules, it appeared suitable to include scaling terms into the development of the residual viscosity term  $\Delta \eta_{\rm r}(T,\rho)$ .

The symbolic regression that resulted in the compact function in Eq. (3.5) was a complex and time-consuming process described more fully in [17]. The final function includes only three

adjustable parameters and represents a dataset that covers a wider temperature and pressure range than for most other fluids. Figures 3.5 and 3.6 illustrate the quality of representation of the data that were included in the regression as a function of density and temperature, respectively. Up to a density of 1000 kg·m<sup>-3</sup>, the deviations are within  $\pm 3$  %, increasing to  $\pm 4$  % in the range up to 1400 kg·m<sup>-3</sup>. Deviations from -10.3 % to 12 % occur for the high-pressure data of Abramson in the density range up to 2127 kg·m<sup>-3</sup>. While Abramson [24] estimated an uncertainty of his data of 5 %, deviations of the correlation that was also reported with the data range from -11 % to 7.4 % and significantly exceed the estimated uncertainty. Our discussions with Dr. Abramson give us confidence that the representation of the data by the new correlation is consistent with the true uncertainty of the data.

While they appear close in density in Fig. 3.5, Fig. 3.6 shows that the data sets of van der Gulik [22] and Abramson [24] are far apart in temperature. Further improvements of the correlation require measurements in the gap seen in Fig. 3.1 between the data of Golubev and Petrov [39] and Golubev et al. [43] and those of Abramson [24]. Absent such measurements, and shown in the pressure-temperature diagram of Fig. 3.7, an uncertainty of (5–10) % is assigned to the correlation in this region. In the other areas, the correlation represents the viscosity data within their estimated experimental uncertainties.

# 3.8. Critical Enhancement of the Viscosity

CO<sub>2</sub> is one of the few fluids whose viscosity enhancement near the gas-liquid critical point has been measured in several investigations. Luettmer-Strathmann et al. [45] applied an approximate theory for critical fluctuations to these experimental data and provided representative equations for CO<sub>2</sub> and ethane. Their calculation scheme can be used for CO<sub>2</sub> with the new viscosity correlation developed in this project for the background contribution to calculate the critical enhancement of the viscosity of CO<sub>2</sub> and its singularity at the critical point. Outside of the small region  $304.13 \le T/K \le 306$  with pressures  $7.375 \le p/MPa \le 7.677$ , this contribution is negligible. It will be described more fully in [17].



Figure 3.1. Pressure and temperature coverage of critically analyzed viscosity data for the development of the new correlation for the viscosity of CO<sub>2</sub>. The high-pressure limit of the previous correlation by Fenghour et al. [3] is indicated.





Figure 3.2. Representation of the viscosity of CO<sub>2</sub> in the limit of zero density by Eq. (3.2) compared to the data of Hellmann [35] calculated to 100 K and extrapolation behavior of Eq. (3.2) in the limit  $T \rightarrow 0$ . Note that for this comparison the factor 1.0055 in the numerator of Eq. (3.2) was set to unity.



Figure 3.3. Comparison of  $\eta_0$  data derived from measurements considered to be most accurate relative to Eq. (3.2) in the temperature range 200 K to 1900 K.



Figure 3.4. Data and correlations of the second viscosity virial coefficient  $B_{\eta}$  and of the linear-indensity viscosity coefficient  $\eta_1$  of CO<sub>2</sub>. Square symbols relate to  $B_{\eta}$  while circles relate to  $\eta_1$ .



Figure 3.5. Percent deviations of viscosities calculated with the new correlation from experimental data selected for the regression as a function of density.



Figure 3.6. Percent deviations of viscosities calculated with the new correlation from experimental data selected for the regression as a function of temperature.



Figure 3.7. Estimated uncertainty of viscosities calculated with the new correlation.

## 4. THERMAL CONDUCTIVITY MEASUREMENTS (TASK 5)

## 4.1. Background

Over the years, the thermal conductivity of CO<sub>2</sub> has been measured with a variety of transient and steady-state techniques. The thermal conductivity,  $\lambda$ , can also be estimated from measurements of thermal diffusivity, a, at temperatures and pressures where the density,  $\rho$ , and isobaric specific heat,  $C_p$ , are well known, through the relationship  $\lambda = a\rho C_p$ . A thorough analysis of the thermal conductivity data of CO<sub>2</sub> was given by Vesovic et al. [2], who assessed the reliability of each data source and designated the most reliable data sets as primary; these sets were used during the development of their thermal conductivity correlation. The less reliable data sets were designated as secondary; these data sets provided useful comparisons with the correlation at conditions where more reliable primary data sets were not available. The thermal conductivity was correlated as a function of temperature, T, and density,  $\rho$ , which is typically calculated with an accurate EOS at the temperature and pressure, p, of the measured thermal conductivity. The 1990 work [2] used the 1987 EOS of Ely et al. [60] for calculating densities.

Vesovic et al. [2] designated 10 data sets as primary for the thermal conductivity of the dilute gas. Only six of these primary data sets had an uncertainty of 1 % or less, covering a temperature range from 285 K to 470 K. The low-temperature region from 186 K to 285 K was covered by four primary data sets with an uncertainty of 5 %. Theoretical predictions with lower uncertainty supplemented the available primary data that had uncertainties of 5 %. At higher densities, Vesovic et al. [2] designated five data sets as primary with uncertainties of 1.5 % or less that covered the temperature region from 298 K to 470 K with pressures up to 30 MPa and also included an additional data set with 5 % uncertainty that covered the high-temperature region up to 724 K with pressures up to 100 MPa. Thus, the uncertainty of the data sets used in the 1990 correlation is 5 % at temperatures below 285 K and above 470 K. At pressures above 30 MPa, the uncertainty again increases to 5 %, even at temperatures from 285 K to 470 K. Since this 1990 assessment, there have been a few additional measurements of the thermal conductivity and thermal diffusivity of CO<sub>2</sub>. However, the limitations due to the larger uncertainty of the data at low temperatures and at high temperatures remained.

The measurements reported in the present work cover the liquid, vapor, and supercritical phase regions of CO<sub>2</sub> at temperatures from 219 K (-65 °F), near the triple point, to 751 K (892 °F) and at pressures up to 70 MPa (10 150 psia) with reduced uncertainty compared to available data at temperatures below 285 K and above 470 K.

A paper is in preparation describing these measurements in more detail [61].

#### 4.2. Measurement Technique

The measurements of the thermal conductivity of CO<sub>2</sub> were obtained with two transient hot-wire instruments that have previously been described in detail. The low-temperature apparatus [62] covers the temperature range from 60 K to 340 K, while the high-temperature apparatus [63] covers the temperature range from 300 K to 750 K. Both apparatus can measure in the liquid, vapor, and compressed gas phases at pressures up to 70 MPa. Each measurement cell typically contains a pair of hot wires of differing length operating in a differential arrangement to eliminate errors due to axial heat conduction. A schematic diagram (applicable to both the lowtemperature and high-temperature apparatus) is shown in Fig. 4.1. The outer cavities around the two hot wires have a diameter of 9 mm, and these concentric cavities are enclosed by a pressure vessel that is capable of operation at pressures up to 70 MPa. The low-temperature vessel is copper with 25 ml sample volume and is enclosed in an isothermal shield in a cryostat cooled with liquid nitrogen [62]. The high-temperature pressure vessels are 316-alloy stainless steel with sample volumes of 50 ml for the double-wire cell and 5 ml for the single-wire cell, enclosed in an isothermal shield in a furnace [63]. Initial cell temperatures,  $T_i$ , are determined with a reference platinum resistance thermometer with an uncertainty of 0.005 K, and pressures,  $p_{e}$ , are determined with a pressure transducer with an uncertainty of 7 kPa. The measurements for this work were made with bare platinum hot wires with a diameter of 12.7 µm. All reported uncertainties are for a coverage factor of k = 2, approximately corresponding to a 95 % confidence interval. During an experiment, a current is passed through the wires starting at time zero; the wires function as both electrical heat sources and resistance thermometers to measure the temperature rise of the wire as a function of time.

The basic theory that describes the operation of the transient hot-wire instrument is given by Healy et al. [64]. The hot-wire cell was designed to approximate a transient line source as closely as possible, and deviations from this model are treated as corrections to the experimental temperature rise. The ideal temperature rise of the wire  $\Delta T_{id}$  is given by

$$\Delta T_{\rm id} = \frac{q}{4\pi\lambda} \left[ \ln\left(t\right) + \ln\left(\frac{4a}{r_0^2 C}\right) \right] = \Delta T_{\rm w} + \sum_{i=1}^{10} \delta T_i \quad , \tag{4.1}$$

where *q* is the power applied to the wire per unit length,  $\lambda$  is the thermal conductivity of the fluid, *t* is the elapsed time,  $a = \lambda/(\rho C_p)$  is the thermal diffusivity of the fluid,  $\rho$  is the density of the fluid,  $C_p$  is the isobaric specific heat capacity of the fluid,  $r_0$  is the radius of the hot wire, C = 1.781... is the exponential of Euler's constant,  $\Delta T_w$  is the measured temperature rise of the wire, and  $\delta T_i$  are corrections to account for deviations from ideal line-source conduction. During analysis, a line is fit to a linear section of the  $\Delta T_{id}$  versus  $\ln(t)$  data, and the thermal conductivity is obtained from the slope of this line. Both thermal conductivity and thermal diffusivity can be determined with the transient hot-wire technique as shown in Eq. (4.1), but only the thermal conductivity results are considered here. The experiment temperature,  $T_e$ , associated with the thermal conductivity is the average temperature at the wire's surface over the period that was fitted to obtain the thermal conductivity.

For gas-phase measurements, two corrections must be carefully considered [64-68]. First, since the thermal diffusivity of the gas is much different from that of the wire, the correction for the wire's finite radius becomes very significant. Second, the thermal diffusivity of the dilute gas varies inversely with the pressure, so it is possible for the transient thermal wave to penetrate to the outer boundary of the gas region during an experiment at low pressure. The present transient hot-wire wires require careful correction for the wire's finite radius during such dilute-gas measurements. Measurement times must be selected to minimize the correction for penetration to the outer boundary due to the relatively small diameter of the concentric fluid region around each hot wire. The full heat-capacity correction [64] was applied to the present measurements. For a few of the measurements at the lowest pressures, the outer boundary was encountered by the thermal pulse during the usual one-second duration of the experiment, so the experiment time was reduced to minimize the magnitude of this correction. Transient experiments are generally limited to 1 s in duration, with 250 measurements of temperature rise taken as a function of elapsed time relative to the onset of wire heating. Fluid convection is normally not a problem, except in the critical region.

Thermal radiation corrections increase in proportion to  $T^3$  and become increasingly significant at temperatures above 300 K [63,64,69]. Most gases are nearly transparent to infrared thermal radiation and the radiation correction remains small due to the low emissivity and small surface area of the 12.7 µm diameter platinum hot wires [63,64]. For many liquids and "greenhouse" gases such as methane and carbon dioxide that absorb infrared radiation, absorption/emission from the liquid or gas can dominate the radiation heat transfer. In such cases, the expanding transient thermal gradient effectively increases the radiation heat transfer linearly with elapsed time. This linear-in-time dependence can be used to estimate the mean absorption coefficient of the fluid and then correct for the thermal radiation during a transient hot-wire measurement [63,69]. Liquids that absorb thermal radiation very strongly become effectively opaque and the radiation correction is insignificant.

At very low pressures, the hot-wire system described above can be operated in a steady-state mode, which requires smaller corrections [70]. The working equation for the steady-state mode is based on a different solution of Fourier's law, but the geometry is still that of concentric cylinders. This equation can be solved for the thermal conductivity of the fluid,

$$\lambda = \frac{q \ln(r_2/r_1)}{2\pi(T_1 - T_2)} , \qquad (4.2)$$

where q is the applied power per unit length,  $r_2$  is the internal radius of the outer cylinder,  $r_1$  is the external radius of the inner cylinder (hot wire), and  $(T_1 - T_2)$  is the measured temperature difference between the hot wire and the outer shell of its surrounding cavity.

For the concentric-cylinder geometry described above, the total radial heat flow per unit length, q, remains constant and is not a function of the radial position. Assuming that the thermal conductivity of the fluid is a linear function of temperature, it can be shown that the temperature assigned to the measured thermal conductivity corresponds to the mean temperature of the inner and outer cylinders,  $T_m = (T_1 + T_2)/2$ . This assumption of linear temperature dependence for the thermal conductivity is valid for experiments with small temperature differences. The density assigned to the measured thermal conductivity is calculated from an equation of state at  $T_m$  and the measured pressure. An assessment of corrections during steady-state hot-wire measurements is available [70]. The transparent fluid correction is applied for all steady-state measurements since this technique was only used for low-density measurements.

## 4.3. Results

We performed measurements on a pure (99.994 %) sample of carbon dioxide with the lowtemperature hot-wire apparatus at temperatures from 218 K to 342 K and the high-temperature hot-wire apparatus at temperatures from 315 K to 750 K. These measurements were made along subcritical vapor isotherms at temperatures of (219, 237, 252, 267, 282, 296) K, liquid isotherms at temperatures of (225, 228, 238, 253, 268, 283, 297) K, and along supercritical isotherms at temperatures of (315, 327, 342, 370, 403, 453, 502, 555, 607, 657, 706, 756) K. The transienthot-wire apparatus was operated in the steady-state mode at pressures below 3 MPa with subcritical vapor and supercritical gas. The transient mode was used at pressures from 0.2 MPa up to the saturation line for subcritical-vapor isotherms and up to 68 MPa for supercritical gas. The transient mode was also used for the liquid phase at pressures from the saturation line up to 68 MPa. A significant critical enhancement, centered near the critical density, was observed along the supercritical isotherms. Measurements were made at up to 10 different applied power levels (10 different temperature rises) to verify that natural convection was not a problem during the measurements. Isotherms at 315 K, 327 K, and 342 K were measured with both the lowtemperature and the high-temperature apparatus; the results were mutually consistent within the apparatus uncertainties (which are of similar size).

Transient measurements of the thermal conductivity of  $CO_2$  were obtained for the vapor (531 points) and liquid (702 points) from the low-temperature cell with two platinum hot wires (12.7

μm diameter). Steady-state measurements of thermal conductivity of CO<sub>2</sub> were obtained for the low-pressure vapor (134 points) from this same low-temperature cell. Measurements of thermal conductivity of CO<sub>2</sub> were obtained for the supercritical gas from the high-temperature cell with two platinum hot wires (12.7 μm diameter). There are 2005 transient and 432 steady-state measurements in total from this double-wire cell. Finally, a small volume (5 ml) cell with a single 12.7 μm diameter platinum wire was used for 779 transient and 245 steady-state measurements on supercritical CO<sub>2</sub> at temperatures above 500 K. A total of 4828 measurements of the thermal conductivity of CO<sub>2</sub> in the liquid, vapor and supercritical phases were performed; the detailed results are reported in [61]. The temperatures and pressures of the thermal conductivity data for CO<sub>2</sub> are shown in Fig. 4.2 along with the vapor-liquid and solid-liquid saturation curves.

Thermal conductivity data for CO<sub>2</sub> from transient measurements in the subcritical vapor phase are shown in Fig. 4.3. The density in this and other figures was computed from the measured temperature and pressure by the reference EOS of Span and Wagner [7]. These data were measured with the low-temperature cell with two hot wires that compensate for end effects. The vapor isotherms near the critical temperature begin to cross each other at the highest densities (near saturation) due to the critical enhancement. The measurements at different applied powers and temperature rises are clearly separated and visible at the highest densities along the isotherm at 296 K. Relative deviations between the thermal conductivity data measured in transient mode (Fig. 4.3), along with the corresponding steady-state measurements at low density, and the correlation of Huber et al. [71] are shown in Fig. 4.4. The steady-state measurements are around 3 % higher than the transient results. This offset may be due to increased uncertainty due to lead resistance (only 3 leads in pressure vessel) for this low-temperature cell.

Thermal conductivity data for CO<sub>2</sub> in the subcritical liquid and supercritical phases are shown in Fig. 4.5. These data were measured with the low-temperature cell with two hot wires that was also used for the subcritical vapor measurements. The density dependence of the thermal conductivity clearly dominates the thermal conductivity in the liquid phase. Isotherms at increasing temperature are slightly higher than lower-temperature isotherms. As for the vapor phase, the isotherms near the critical point begin to cross near the vapor-liquid phase boundary due to critical enhancement. Relative deviations between the thermal conductivity data measured in transient mode (Fig. 4.5) and the correlation of Huber et al. [71] are shown in Fig. 4.6. The relative deviations range from 0.25 % to 1.75 % and have a very characteristic pattern. The measurements have lower uncertainty than these deviations in the liquid phase. This pattern

is typical for wide-range correlations for thermal conductivity and is due to difficulty in describing the non-linear nature of the thermal conductivity in the critical region.

Thermal conductivity data measured with the high-temperature double-wire cell for CO<sub>2</sub> in the supercritical region are shown in Fig. 4.7. The supercritical isotherm at 315 K is seen to cross over isotherms up to 604 K near the critical density of  $CO_2$  due to the critical enhancement. These supercritical isotherms are incrementally higher than the corresponding subcritical vapor and liquid isotherms shown in Figs. 4.3 and 4.5. Relative deviations between the thermal conductivity data measured in transient mode (Fig. 4.7) and the correlation of Huber et al. [71] are shown in Fig. 4.8. Increasing scatter and deviations are observed for the three supercritical isotherms at densities near the critical density. The increased scatter is due to increasing contributions and uncertainty from natural convection near the critical point where the fluid becomes highly compressible. Small temperature rises and short experiment durations are required in the critical region to minimize convection during the thermal conductivity measurements. Increasing deviations are also observed at lower pressures and densities, where the data have additional uncertainty due to penetration of the temperature gradient in the fluid to the outer boundary during the transient experiment. The thermal diffusivity of the gas is inversely proportional to the pressure and increases dramatically at these low pressures. The high-temperature double-wire cell developed a persistent electrical conduction (short) problem between one of the lead wires (fiberglass insulated) and ground at temperatures above 600 K. It was decided to continue measurements with a more robust single-wire measurement cell with ceramic electrical insulation

Thermal conductivity data, measured with the high-temperature single-wire cell for CO<sub>2</sub> in the supercritical region from 502 K to 756 K, are shown in Fig. 4.9. The lowest temperature isotherm at 502 K is 1.65 times the critical temperature where the critical enhancement is insignificant, so the isotherms are parallel, without the crossing of isotherms that is present at lower temperatures. Relative deviations between the thermal conductivity data measured in transient mode (Fig. 4.9) and the correlation of Huber et al. [71] are shown in Fig. 4.10. The deviations of the isotherms at temperatures from 502 K to 706 K are all very similar, with the 756 K isotherm falling around 1 % higher. Significant correction for absorbing-emitting (gray body) thermal radiation heat transfer [63,69] was required for these transient isotherms at higher densities.

Relative deviations for all the steady-state dilute-gas data at temperatures from 220 K to 756 K are shown in Fig. 4.11. The deviations are generally in agreement with the 3 % uncertainty associated with the steady-state measurements. The transparent medium correction for thermal

radiation was applied to all the steady-state measurements and was relatively small compared to the gray-body correction required for the transient measurements at temperatures above 300 K.



Figure 4.1. Schematic diagram of transient-hot-wire apparatus.



Figure 4.2. Temperatures and pressures of present thermal conductivity measurements. Data sets are designated:  $\Box$ , 2-wire transient vapor;  $\bigcirc$ , 2-wire transient liquid, \*, 2-wire steady-state vapor;  $\diamondsuit$ , 2-wire transient supercritical, \*, 2-wire steady-state supercritical;  $\triangle$ , 1-wire transient supercritical; +, 1-wire steady-state. Equilibrium curves are: solid-liquid, dotted line; vapor-liquid, solid line.



Figure 4.3. Thermal conductivity of subcritical CO<sub>2</sub> vapor as a function of density. Isotherms are designated:  $\bigcirc$ , 219 K;  $\square$ , 237 K;  $\diamondsuit$ , 252 K;  $\triangle$ , 267 K;  $\times$ , 282 K; +, 296 K. Values along these isotherms calculated with the correlation of Huber et al. [71] are shown as solid lines.



Figure 4.4. Relative deviations between the measured thermal conductivity and values from the correlation of Huber et al. [71] for subcritical CO<sub>2</sub> vapor as a function of density. Transient-mode isotherms are designated:  $\bigcirc$ , 219 K;  $\square$ , 237 K;  $\diamondsuit$ , 252 K;  $\triangle$ , 267 K;  $\times$ , 282 K; +, 296 K. The steady-state deviations are designated by \* for temperatures from 219 K to 343 K.



Figure 4.5. Thermal conductivity of subcritical CO<sub>2</sub> liquid as a function of density. Isotherms are designated: +, 225 and 228 K;  $\bigcirc$ , 236 K; ×, 253 K;  $\triangle$ , 268 K;  $\square$ , 283 K;  $\diamondsuit$ , 297 K. Values calculated with the correlation of Huber et al. [71] are shown as solid lines.



Figure 4.6. Relative deviations between the measured thermal conductivity and values from the correlation of Huber et al. [71] for subcritical CO<sub>2</sub> vapor as a function of density. Isotherms are designated:  $\star$ , 225 K; +, 228 K;  $\bigcirc$ , 236 K;  $\star$ , 253 K;  $\triangle$ , 268 K;  $\square$ , 283 K;  $\diamondsuit$ , 297 K.



Figure 4.7. Thermal conductivity measured with double-wire cell for supercritical CO<sub>2</sub> as a function of density. Isotherms are designated: +, 315 K; ×, 327 K; \*, 342 K;  $\bigcirc$ , 370 K;  $\square$ , 403 K;  $\diamondsuit$ , 453 K;  $\triangle$ , 502 K;  $\bigcirc$ , 555 K;  $\blacktriangle$ , 607 K. Values calculated with the correlation of Huber et al. [71] are shown as solid lines.



Figure 4.8. Relative deviations between the thermal conductivity measured with the double-wire cell and values from the correlation of Huber et al. [71] for supercritical CO<sub>2</sub> vapor as a function of density. Isotherms are designated: +, 315 K; ×, 327 K; \*, 342 K;  $\bigcirc$ , 370 K;  $\square$ , 403 K;  $\diamondsuit$ , 453 K;  $\triangle$ , 502 K; ●, 555 K;  $\blacktriangle$ , 607 K.



Figure 4.9. Thermal conductivity measured with single-wire cell on supercritical CO<sub>2</sub> as a function of density. Isotherms are designated:  $\triangle$ , 502 K;  $\bigcirc$ , 555 K;  $\triangle$ , 607 K; +, 657 K; ×, 706 K;  $\diamondsuit$ , 756 K. Values calculated with the correlation of Huber et al. [71] are shown as lines.



Figure 4.10. Relative deviations between the thermal conductivity measured with the single-wire cell and values from the correlation of Huber et al. [71] for supercritical CO<sub>2</sub> vapor as a function of density. Isotherms are designated:  $\triangle$ , 502 K;  $\blacklozenge$ , 555 K;  $\blacktriangle$ , 607 K; +, 657 K; ×, 706 K;  $\blacklozenge$ , 756 K.



Figure 4.11. Relative deviations between the thermal conductivity measured by the steady-state technique and values from the correlation of Huber et al. [71] for CO<sub>2</sub> vapor as a function of temperature. Measurement series are designated:  $\bigcirc$ , low-temperature double-wire cell;  $\diamondsuit$ , high-temperature single-wire cell.

# 5. REFERENCE CORRELATION FOR THE THERMAL CONDUCTIVITY OF CO<sub>2</sub> (Task 6)

Complete information on the work performed in this task is given in a paper published in the *Journal of Physical and Chemical Reference Data* [71]. We therefore provide only an overview of the new thermal conductivity correlation here.

## **5.1. Structure of Correlation**

Similarly to the viscosity, the thermal conductivity  $\lambda$  can be expressed as the sum of three independent contributions, as

$$\lambda(\rho, T) = \lambda_0(T) + \Delta\lambda(\rho, T) + \Delta\lambda_c(\rho, T) , \qquad (5.1)$$

where  $\rho$  is the density, *T* is the temperature, and the first term,  $\lambda_0(T) = \lambda(0,T)$ , is the thermal conductivity in the dilute-gas limit, where only two-body molecular interactions occur. The residual term,  $\Delta\lambda(\rho,T)$ , represents the contribution of other effects to the thermal conductivity of the fluid at elevated densities including many-body collisions, molecular-velocity correlations, and collisional transfer. The critical enhancement term,  $\Delta\lambda_c(\rho,T)$ , arises from the long-range density fluctuations that occur in a fluid near its critical point, which contribute to divergence of the thermal conductivity at the critical point.

The identification of these three separate contributions to the thermal conductivity, and to transport properties in general, is useful because it is possible, to some extent, to treat both  $\lambda_0(T)$  and  $\Delta\lambda_c(\rho,T)$  theoretically. In addition, it is possible to derive information about  $\lambda_0(T)$  from experiment. In contrast, there is almost no theoretical guidance concerning the residual contribution,  $\Delta\lambda(\rho,T)$ , so its evaluation is based entirely on experimental data.

### 5.2. Dilute-gas Contribution

To develop the zero-density correlation, we followed the procedure used in the development of a standard reference formulation for the thermal conductivity of water [72], which uses the concept of Key Comparison Reference Values [73] to consider the uncertainties from different data sources. We identified from the literature a primary set of experimental data, and restricted the density to less than 50 kg·m<sup>-3</sup>. We then included the new experimental data obtained in this study (see Section 4) from both the low- and high-temperature apparatus operated in both steady-state mode and transient mode at densities less than the cutoff of 50 kg·m<sup>-3</sup>. We did not include data measured in transient mode for temperatures above 505 K; as discussed in Section 4.2, the steady-state measurements are more reliable for the dilute gas at these conditions.

All low-density, primary data points were then arranged into bins encompassing a temperature range of 8 K or less, with at least 4 data points in each bin. Points that were already extrapolated to zero density by the original authors were not put into bins and were treated as separate isotherms. The new data from this study were also treated as separate isotherms. It was not possible to classify all points into bins, since it was not always possible to establish bins with at least 4 points within an 8 K temperature range.

The nominal temperature of an isotherm "bin" was computed as the average temperature of all points in a bin. The thermal conductivity of each point was then corrected to the nominal temperature,  $T_{nom}$ , by

$$\lambda_{\rm corr}(T_{\rm nom},\rho) = \lambda_{\rm exp}(T_{\rm exp},\rho) + \left[\lambda(T_{\rm nom},\rho) - \lambda(T_{\rm exp},\rho)\right]_{\rm calc},$$
(5.2)

where the calculated values were obtained from the Vesovic et al. thermal conductivity formulation [2]. The resulting set of bins was obtained considering 1328 points from 22 sources, obtained with a variety of experimental techniques and with a range of uncertainties. The data covered nominal temperatures from 219 K to 751 K with an average bin size of less than 3 K.

Weighted linear regression was then used to extrapolate the nominal isotherms to obtain values at zero density,  $\lambda_0$ . Points were weighted with a factor equal to the inverse of the square of the estimated relative uncertainty. 95% confidence intervals were constructed from the regression statistics. Isotherms with large inconsistencies in the underlying data were rejected from further consideration. This procedure resulted in 47 zero-density points from 219 K to 751 K.

In order to supplement the experimental data set at very low and at high temperatures where data are unavailable or sparse, we incorporated selected theoretical points from the recent work of Hellmann [35], who used a new four-dimensional rigid-rotor potential-energy surface and the classical trajectory method. We first adjusted the theoretical values by multiplying them by a factor of 1.011, as recommended by Hellmann [35] based on his comparison with reliable experimental values, and ascribed to the theoretical values an uncertainty, namely 1 % for points between 300 K and 700 K, increasing to 2 % at 150 K and 2000 K. We included 8 points from 150 K to 215 K and 14 points from 760 K to 2000 K, so that the final set of zero-density values ranges from 150 K to 2000 K.

The zero-density values were fit using orthogonal distance regression [74] to the equation form used in the IAPWS water formulation [72] for the thermal conductivity in the limit of zero density,

$$\lambda_{0}(T_{\rm r}) = \frac{\sqrt{T_{\rm r}}}{\sum_{k=0}^{J} \frac{L_{k}}{T_{\rm r}^{k}}},$$
(5.3)

where  $T_r = T/T_c$  is a reduced temperature and the  $L_k$  are fitted parameters. We used the critical temperature from the Span and Wagner [7] equation of state,  $T_c = 304.1282$  K. The final set of  $\lambda_0$  values contained 69 data points from 150 K to 2000 K. Four terms were needed, and the weights were equal to the inverse of the square of the estimated uncertainty. The coefficients are given in Table 5.1.

Table 5.1. Coefficients in Eq. (5.3) for  $\lambda_0$ 

k	$L_k$
0	$1.518\ 743\ 07\times 10^{-2}$
1	$2.806\ 740\ 40\times 10^{-2}$
2	$2.285~641~90 \times 10^{-2}$
3	$-7.416\ 242\ 10  imes 10^{-3}$

Figure 5.1 shows the relative deviation between the  $\lambda_0$  data and Eq. (5.3). Also shown are deviations with respect to the correlation of Vesovic et al. [2], the correlation of Scalabrin et al. [75], and with the theoretical calculations of Hellmann [35]. The values of Hellmann have been scaled upward by a factor of 1.011 as mentioned earlier. The correlation of Vesovic was designed to be used only over the range 200 K to 1000 K, and it is obvious that at low temperatures it does not extrapolate well. At high temperatures, the Vesovic correlation extrapolates in a reasonable manner because theoretical considerations were included in its hightemperature behavior. The correlation of Scalabrin et al. [75] did not take into account theoretical considerations and does not extrapolate well to either high or low temperatures. The present work uses the calculations of Hellmann [35] to guide both the low- (150 < T/K < 215)and high-temperature (760 < T/K < 2000) behavior of the correlation outside the range of the best experimental data. Equation (5.3) may be extrapolated safely to 2000 K, the limit of the theoretical data included in the fit, although it does not take into account partial dissociation of CO<sub>2</sub> at very high temperatures. The present work agrees with the experimental points to within about 2 %, and to within 1 % with the theoretical calculations of Hellmann. The correlation of Vesovic et al. [2] relied heavily on data from Millat et al. [76] and Johns et al. [77], particularly in the region 330 K to 470 K; the present work considered additional data (primarily from [61]) that tended to be lower than the data of Millat et al. [76] and Johns et al. [77] and that are in closer agreement with the theoretical calculations of Hellmann [35]. To assess the uncertainty of the dilute-gas correlation, we consider the comparisons with the scaled theoretical values of

Hellmann, which have an estimated uncertainty of 1 % between 300 K and 700 K, increasing to 2 % at both 150 K and 2000 K, and we will adopt those same values for our uncertainty estimate for Eq. (5.3).



Figure 5.1. Comparison of  $\lambda_0$  correlations with the theoretical and experimental data.

### 5.3. Critical Enhancement Term

The thermal conductivities of pure fluids exhibit an enhancement over a large range of densities and temperatures around the critical point and become infinite at the critical point. This behavior can be described by models that produce a smooth crossover from the singular behavior of the thermal conductivity asymptotically close to the critical point to the residual values far away from the critical point. We use a simplified crossover model proposed by Olchowy and Sengers [78] to represent the critical enhancement. The critical enhancement of the thermal conductivity from this simplified model is given by

$$\Delta\lambda_{\rm c} = \frac{\rho C_p R_{\rm D} k_{\rm B} T}{6\pi \bar{\eta}\xi} \left(\bar{\Omega} - \bar{\Omega}_0\right),\tag{5.4}$$

with

$$\overline{\Omega} = \frac{2}{\pi} \left[ \left( \frac{C_p - C_v}{C_p} \right) \arctan\left( \overline{q}_{\rm D} \xi \right) + \frac{C_v}{C_p} \overline{q}_{\rm D} \xi \right]$$
(5.5)

$$\overline{\Omega}_{0} = \frac{2}{\pi} \left[ 1 - \exp\left(-\frac{1}{\left(\overline{q}_{\mathrm{D}}\xi\right)^{-1} + \left(\overline{q}_{\mathrm{D}}\xi\rho_{\mathrm{c}}/\rho\right)^{2}/3}\right) \right],\tag{5.6}$$

and

$$\xi = \xi_0 \left( \frac{p_c \rho}{\Gamma \rho_c^2} \right)^{\nu/\gamma} \left[ \frac{\partial \rho(T, \rho)}{\partial p} \bigg|_T - \left( \frac{T_{\text{ref}}}{T} \right) \frac{\partial \rho(T_{\text{ref}}, \rho)}{\partial p} \bigg|_T \right]^{\nu/\gamma}.$$
(5.7)

In Eqs. (5.4)–(5.7),  $k_{\rm B}$  is Boltzmann's constant,  $\pi$  is the viscosity, and  $C_p$  and  $C_v$  are the isobaric and isochoric specific heat. This model requires thermodynamic properties, the viscosity, and several universal and system-dependent constants. For thermodynamic properties, we use the EOS of Span and Wagner [7], and for the viscosity we use the correlation developed as part of this work [17]. In addition, this crossover model requires the universal constants [79]  $R_{\rm D} = 1.02$ , v = 0.63, and  $\gamma = 1.239$ , and system-dependent amplitudes  $\Gamma$  and  $\xi_0$ . For this work, as done previously by Vesovic et al. [2], we adopted the values  $\Gamma = 0.052$  and  $\xi_0 = 1.50 \times 10^{-10}$  m, determined specifically for carbon dioxide [80], instead of using the general method of Perkins et al. [79]. The reference temperature  $T_{\rm ref}$ , far above the critical temperature where the critical enhancement is negligible, was set to  $T_{\rm ref} = (3/2)T_{\rm c}$  [79], which for carbon dioxide is 456.19 K. The final critical-region parameter is the effective cutoff wavelength  $\overline{q}_{\rm D}^{-1}$ . We found the value in Vesovic et al. [2],  $\overline{q}_{\rm D}^{-1} = 4.0 \times 10^{-10}$  m, worked well. Further details on the critical enhancement model and its validation are given in [71].

### 5.4. Residual Term

The residual thermal conductivity  $\Delta \lambda$  ( $\rho$ , *T*) was represented with a polynomial in temperature and density:

$$\Delta \lambda(\rho, T) = \sum_{i=1}^{6} \left( B_{1,i} + B_{2,i}(T / T_{c}) \right) \left( \rho / \rho_{c} \right)^{i} .$$
(5.8)

The available experimental data, including the new data obtained as part of this work, were critically assessed and a primary data set for regression was identified. Details are given in [71]. The primary data contained over 5000 points covering the dilute gas, dense liquid, and

supercritical regions at pressures up to 200 MPa. The regression package ODRPACK [74] was used with the primary data set to obtain the coefficients for Eq. (5.8) given in Table 5.2.

i	$B_{1,i} $ (W m <sup>-1</sup> K <sup>-1</sup> )	$B_{2,i} $ (W m <sup>-1</sup> K <sup>-1</sup> )
1	$1.001\ 28  imes 10^{-2}$	$4.308\ 29  imes 10^{-3}$
2	$5.604~88  imes 10^{-2}$	$-3.585~63  imes 10^{-2}$
3	$-8.116\ 20  imes 10^{-2}$	$6.714\ 80  imes 10^{-2}$
4	$6.243\ 37  imes 10^{-2}$	$-5.228 55 \times 10^{-2}$
5	$-2.063 \ 36 \times 10^{-2}$	$1.745~71  imes 10^{-2}$
6	$2.532\;48 imes10^{-3}$	$-1.964 \ 14 \times 10^{-3}$

Table 5.2. Coefficients of Eq. (5.8) for the residual thermal conductivity of carbon dioxide.

#### 5.5. Results

A new wide-ranging correlation for the thermal conductivity of carbon dioxide was developed based on critically evaluated experimental data, including new data obtained as part of this work (see Section 4 and [61]). The correlation is valid from the triple point to 1100 K, and at pressures up to 200 MPa. Detailed analysis of the correlation and its representation of experimental data is given in [71]. The most significant improvements over the two wideranging correlations in the literature [2,75] are the dilute-gas extrapolation behavior discussed in Section 5.2 and improvements in the liquid phase, especially at the lowest temperatures, due to the new data provided in this project [61]. This is illustrated in Figs. 5.2–5.4. Figure 5.2 shows the deviations from experimental data in the liquid phase with the correlation developed in this work, while Figs. 5.3 and 5.4 show the deviations computed with two existing correlations, those of Vesovic et al. [2] and Scalabrin et al. [75]. Finally, Fig. 5.5 shows the estimated uncertainties of the new thermal conductivity correlation, excluding the near-critical region (roughly within 1 K of the critical temperature and within 10 % of the critical density) where the uncertainties are higher. Representation of data very near the critical point is adversely affected by some anomalous behavior of the equation of state discussed in [71]; future improvements in the EOS would permit improvements in the critical region. In addition, there is room for improvement in the high-pressure region (100 MPa to 200 MPa) due to limited data in this region.



Figure 5.2. Percentage deviations of primary experimental data of  $CO_2$  from the values calculated by the present model as a function of temperature, for the liquid phase.



Figure 5.3. Percentage deviations of primary experimental data of CO<sub>2</sub> from the values calculated by the Vesovic [2] model as a function of temperature, for the liquid phase.



Figure 5.4. Percentage deviations of primary experimental data of CO<sub>2</sub> from the values calculated by the Scalabrin [75] model as a function of temperature, for the liquid phase.



Figure 5.5. Estimated uncertainty for the CO<sub>2</sub> thermal conductivity correlation excluding the critical region.

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