

# Densities of supercooled H<sub>2</sub>O and D<sub>2</sub>O in 25 $\mu$ glass capillaries

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We have measured the densities of supercooled H<sub>2</sub>O to  $-34.2^\circ\text{C}$ , and D<sub>2</sub>O to  $-19.2^\circ\text{C}$  in 25  $\mu$  i.d. glass capillaries. Because of the small size of our capillaries, some surface energy effects appear to be present in our data. Despite this we found that reasonably accurate values of the thermal expansivity could be obtained from our data. Our expansivity results support the recent contention of Leyendekkers and Hunter that previous estimates of the anomalous expansivity of supercooled water have been overestimated. The results of a power-law analysis of our expansivity were ambiguous due to the poorly known background expansivity.

## I. INTRODUCTION

The possibility of a thermodynamic singularity in supercooled liquid water has stimulated a considerable amount of effort to quantify and explain this behavior.<sup>1-3</sup> Because water is most easily supercooled in small volumes, most of the data supporting a singular temperature have been obtained from small volumes using either capillary tubes or emulsions. Recently Leyendekkers and Hunter<sup>4</sup> have questioned the accuracy of these data for bulk water by presenting arguments that surface energy effects have enhanced the apparent anomalies in the specific heat, compressibility, and expansivity, especially below  $-20^\circ\text{C}$ . They did this by both calculating an estimated surface energy effect on the free energy and by making a variety of reasonable extrapolations of bulk data into the supercooled regime. They concluded that anomalous behavior is still present, but the possible singular temperature is more likely situated at 200–210 K rather than near 228 K as previously<sup>5</sup> estimated.

Because of these arguments, it is worthwhile to perform measurements on supercooled water in volumes where surface effects are negligible. In this paper we present density data for both H<sub>2</sub>O and D<sub>2</sub>O in the supercooled regime using capillaries where surface effects are small but not entirely negligible. There is some compromise necessary here because while smaller samples are more prone to surface energy effects they also supercool further. In earlier work<sup>6</sup> one of us measured the density of water to  $-25^\circ\text{C}$  in 60–90  $\mu$  diameter capillaries which, according to Leyendekkers and Hunter, appear to be free from surface effects. These authors showed that 4 and 10  $\mu$  diameter capillaries used by Schuffe and Venugopalan<sup>7</sup> had considerable surface effect problems. They also argued that the data of Zheleznyi,<sup>8</sup> who used 2  $\mu$  i.d. capillaries, are probably unreliable. The compromise we made here is to use capillaries with inside diameters of  $\sim 25 \mu$ . By using the Leyendekkers and Hunter argument one might expect, to our detriment, surface effects resulting in several parts in  $10^4$  for the density for our samples at  $-30^\circ\text{C}$ . This error is significantly smaller, however, than in earlier measurements using capillaries and emulsions which they estimated led to errors of tens of parts in  $10^4$  from the estimated bulk values. On the other hand, to our credit, we have achieved significantly lower temperatures than our previous work, one capillary to  $T = -34.2^\circ\text{C}$ . We will show that while there is error incurred by surface effects in our

measurements, it is small enough to test their ideas with regard to the density. Furthermore, we will show that the surface energy effect on the thermal expansivity, which we calculate from our density data, is small enough so as to not interfere with our analysis of this quantity.

## II. EXPERIMENTAL METHOD

The H<sub>2</sub>O used in our experiments was distilled and then passed through a mixed bed ion-exchange resin. The D<sub>2</sub>O was Aldrich Gold Label with 99.8% deuterium purity and used without further purification.

The water was contained in sealed glass capillaries drawn from Pyrex tubing with an original o.d. of 6.5 mm and i.d. of 0.8 mm. Before drawing this tubing was cleaned in cold, concentrated nitric acid for several hours, thoroughly rinsed, and oven dried. After drawing, the capillaries had an i.d. of  $25 \pm 5 \mu$  and were 22 cm in length. They were filled by capillary action to a water length of  $\sim 16$  cm. Both ends were then flame sealed, gas space end first.

The density was measured in a manner similar to our earlier measurements.<sup>6</sup> The capillaries were glued to a saw blade shaped strip of metal which was attached to a clear piece of plexiglas and then mounted in a temperature controlled methanol bath. The tips of the saw blade strip acted as fiducial marks to which to compare the meniscus level in the capillary.

Temperature was controlled to  $\pm 0.01^\circ\text{C}$  with the aid of a Neslab EX-300DD bath modified to accept mechanical refrigeration probes. Temperatures were measured with a digital thermometer which was subsequently calibrated with NBS traceable mercury in glass thermometers. Our temperature accuracy was  $\pm 0.03^\circ\text{C}$ .

The meniscus height relative to the fiducial mark was measured with a long working distance, 2.6 power microscope equipped with a filar micrometer. Densities were obtained by calibrating the meniscus-to-fiducial mark distances to the known densities from Kell<sup>9</sup> at 4.61 and 39.66  $^\circ\text{C}$  for H<sub>2</sub>O and 9.53 and 39.66  $^\circ\text{C}$  for D<sub>2</sub>O. Correction for the finite expansion of the Pyrex ( $9 \times 10^{-6} \text{ K}^{-1}$ ) was made. The optical arrangement, bath clarity, and longer samples have improved our overall reproducibility over the earlier work to three parts in  $10^5$ .

Six different capillary samples were used for H<sub>2</sub>O, four for D<sub>2</sub>O. The individual densities of each sample are given in

TABLE I. H<sub>2</sub>O densities (g/ml).

T(°C)	Capillary number						Average density	$\sigma \times 10^5$
	17	18	19	20	22	24		
39.66	0.992 38	0.992 38	0.992 38	0.992 38	0.992 38	0.992 38	0.992 38	...
29.75	0.995 77	0.995 76	0.995 75	0.995 76	0.995 77	0.995 73	0.995 76	2
19.59	0.998 29	0.998 24	0.998 24	0.998 27	0.998 27	0.998 29	0.998 27	2
9.53	0.999 72	0.999 72	0.999 71	0.999 72	0.999 75	0.999 78	0.999 73	3
4.61	1.000 00	1.000 00	1.000 00	1.000 00	1.000 00	1.000 00	1.000 00	...
-0.28	0.999 90	0.999 85	0.999 86	0.999 92	0.999 91	0.999 89	0.999 89	3
-5.35	0.999 35	0.999 32	0.999 37	0.999 37	0.999 37	0.999 35	0.999 36	2
-10.34		0.998 24	0.998 26	0.998 31				
	0.998 18	0.998 20	0.998 25	0.998 27	0.998 24	0.998 27	0.998 25	4
-15.28	0.996 50	0.996 48	0.996 44	0.996 53	0.996 53	0.996 61	0.996 52	6
-20.19	0.993 76	0.993 83	0.993 81	0.993 98	0.993 94	0.994 06	0.993 90	12
-25.19	0.990 03	0.990 10	0.990 10	0.990 22	0.990 05	0.990 10	0.990 10	7
-30.04	0.984 69	0.984 74					0.984 72	4
-34.20	0.978 40						0.978 40	...

Tables I and II. Also tabulated are the averages of the samples and the standard deviations of these averages. These data agree very well with our earlier data<sup>6</sup> for H<sub>2</sub>O which extended down to -25 °C. Comparison to Zheleznyi's<sup>8</sup> data is not good; his density data are systematically smaller than ours. Deviations greater than one part in 10<sup>4</sup> appear for H<sub>2</sub>O for  $T < -20$  °C, and for D<sub>2</sub>O for  $T < -5$  °C. These deviations become as large as 30 parts in 10<sup>4</sup> at the lowest temperatures. As mentioned above, Leyendekkers and Hunter have questioned the validity of Zheleznyi's data. Our data appear to agree well with those of Schufle and Venugopalan<sup>7</sup> when account is made for surface energy effects since, as will be seen below, both sets of data when so corrected agree to within a few parts in 10<sup>4</sup> with extrapolations of empirical fits to nonsupercooled data.

For both H<sub>2</sub>O and D<sub>2</sub>O we combined our density values with those compiled by Kell<sup>9</sup> and fit the whole range to tenth and twelfth order polynomials. The data were weighted by their relative error. These fits were done to allow for differentiation to find the expansivities. We found similar expansi-

vities from our fit functions regardless of whether we used tenth or twelfth order polynomials or whether we used combined data sets or just our data; expansivities never varied by more than several percent.

### III. DISCUSSION

Figures 1 and 2 display our data graphically for H<sub>2</sub>O and D<sub>2</sub>O, respectively. Both show a dramatic decrease of the density in the supercooled regime. The upper part of Fig. 1 compares our average values of density vs temperature for H<sub>2</sub>O to the empirical formulas of Gildseth, Habenschuss, and Spedding<sup>10</sup> (GHS) and Kell.<sup>9</sup> These formulas are empirical fits to highly accurate density data in the  $T > 0$  °C regime which we have extrapolated into the supercooled regime for comparison to our data. The lower half of Fig. 1 plots the deviation between our data and these formulas,  $\rho_{\text{expt}} - \rho_{\text{calc}}$ . Deviations from both our raw data and our data corrected for the surface energy effects in our 25  $\mu$  diameter capillaries using the calculation presented by Leyen-

TABLE II. D<sub>2</sub>O densities (g/ml).

T(°C)	Capillary number				Average density	$\sigma \times 10^5$
	25	26	28	29		
39.66	1.100 12	1.100 12	1.100 12	1.100 12	1.100 12	...
29.75	1.103 25	1.103 23	1.103 30	1.103 28	1.103 27	3
19.59	1.105 35	1.105 33	1.105 40	1.105 37	1.105 36	3
9.53	1.106 00	1.106 00	1.106 00	1.106 00	1.106 00	...
-0.28	1.104 72	1.104 79	1.104 70	1.104 74	1.104 74	3
-5.35	1.103 18	1.103 27	1.103 15	1.103 17	1.103 19	5
-10.34	1.100 69	1.100 86	1.100 64	1.100 76	1.100 74	8
-15.28	1.097 28	1.097 41	1.097 13	1.097 24	1.097 27	10
-17.27	1.095 50	1.095 62	1.095 31	1.095 51	1.095 49	11
-18.25	1.094 55	1.094 64	1.094 37	1.094 57	1.094 53	10
-19.22			1.093 35		1.093 35	...

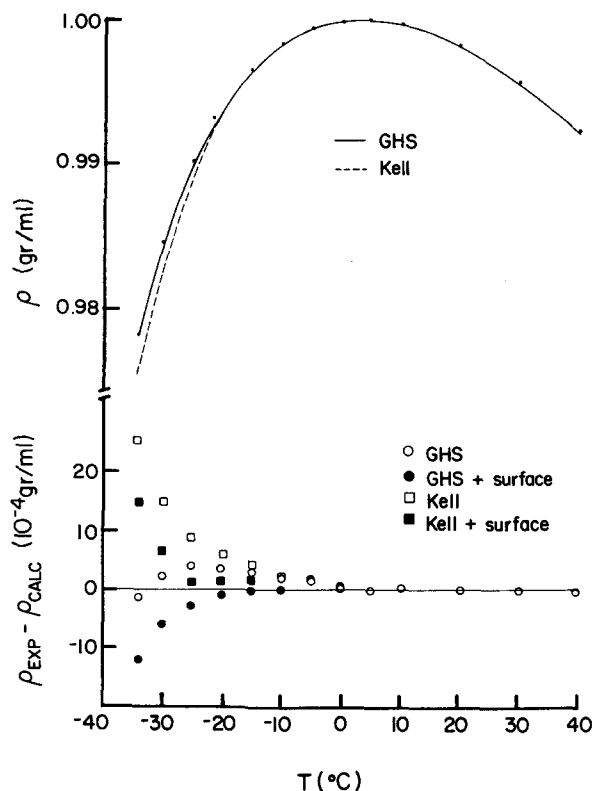


FIG. 1. Upper portion compares our experimental values of the density of H<sub>2</sub>O to the empirical formulas of Gildseth, Habenschuss, and Spedding (Ref. 9), and Kell (Ref. 8) which have been extrapolated into the supercooled regime. Lower portion shows the deviation of our data from these empirical formulas. Raw data are open symbols; data corrected for surface energy effects are closed symbols.

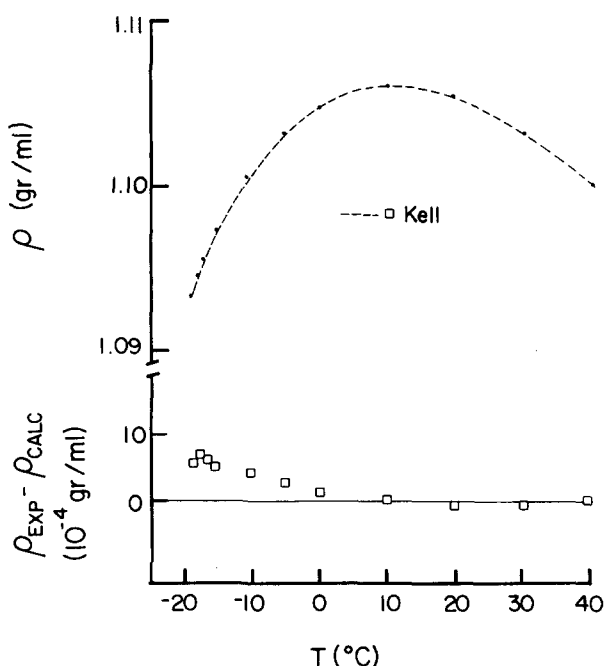


FIG. 2. Upper portion compares our experimental values of the density of D<sub>2</sub>O to the empirical formula of Kell (Ref. 8) for D<sub>2</sub>O which has been extrapolated into the supercooled regime. Lower portion shows the deviation of our data from Kell's formula.

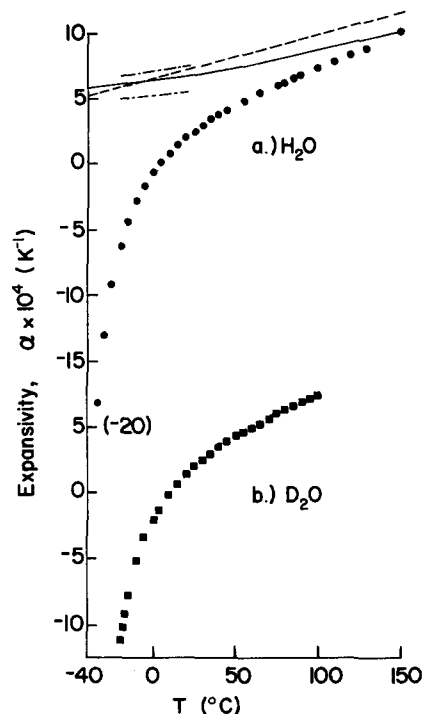


FIG. 3. Plot of the expansivity  $\alpha$  vs temperature for H<sub>2</sub>O and D<sub>2</sub>O. Background expansivities  $\alpha_B$  are also shown for H<sub>2</sub>O. Solid line is  $\alpha_B$  from Leblond and Hareng, dashed line is  $\alpha_B$  from Leyendekkers, and dot-dashed lines are  $\alpha_B$  from Oguni and Angell.

dekkers and Hunter are shown. Agreement for  $T > -25^\circ\text{C}$  is fairly good, but this quickly deteriorates below  $-25^\circ\text{C}$ , especially for the Kell equation.

Figure 2 is a similar graph for D<sub>2</sub>O with a comparison to an empirical formula for D<sub>2</sub>O given by Kell.<sup>9</sup> A surface energy correction for D<sub>2</sub>O is not available. One might estimate, however, it to be of similar magnitude as that in H<sub>2</sub>O, and if so, would give good agreement between Kell's extrapolated formula and experiment.

The expansivities,  $\alpha$ , were calculated from the polynomial fits to our data using  $\alpha = -\rho^{-1} d\rho/dT$ . Estimated errors in  $\alpha$  are  $\pm 0.3 \times 10^{-4} \text{ K}^{-1}$ . Figure 3 displays the expansivities for both H<sub>2</sub>O and D<sub>2</sub>O.

Corrections to  $\alpha$  to account for surface energy effects are small. While these effects cause several parts in  $10^4$  changes in the density at the lowest temperature, the temperature dependence is small hence  $\alpha$  is affected only slightly. We calculate for H<sub>2</sub>O at  $-34.2^\circ\text{C}$  that  $\alpha$  would be  $0.7 \times 10^{-4} \text{ K}^{-1}$  smaller (hence  $|\alpha|$  bigger) if the Leyendekkers and Hunter surface energy correction were used. This is 5% of  $\alpha$ . Smaller corrections occur at larger temperatures. These corrections are roughly the size of our experimental error; thus we analyzed  $\alpha$  without these corrections.

Leyendekkers and Hunter spent considerable effort evaluating  $\alpha$  for bulk H<sub>2</sub>O in the supercooled regime using various empirical relations of  $\alpha$  to other quantities. They concluded that  $|\alpha|$  should be considerably smaller deep in the supercooled regime,  $T < -20^\circ\text{C}$ , than originally used by Speedy and Angell<sup>5</sup> to argue for a singularity at  $-45^\circ\text{C}$ . Speedy and Angell used Zheleznyi's data. Our values of  $|\alpha|$

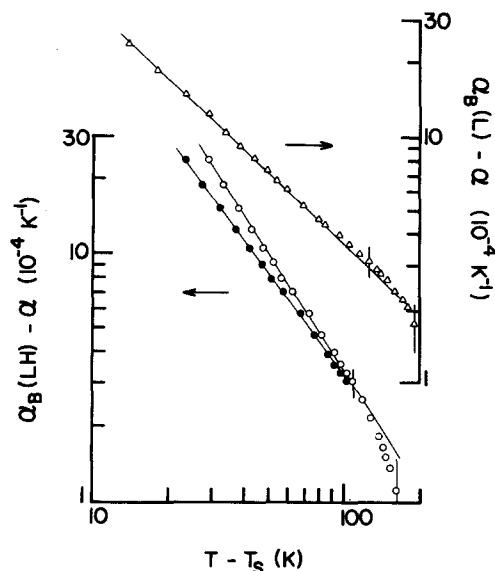


FIG. 4. Singular part of the expansivity,  $\alpha_B - \alpha$  vs  $T - T_s$ , where  $T_s$  is the singular temperature. The data are shown with two different backgrounds:  $\alpha_B$  (LH) is the Leblond and Hareng background (circles), and  $\alpha_B$  (L) is the Leyendekkers background (triangles). Lines are best fits described in the text.

support this contention being  $\sim 22\%$  smaller than those used by Speedy and Angell at  $-30^\circ\text{C}$ . On the other hand, our value of  $|\alpha|$  is  $\sim 22\%$  larger than the average of the Leyendekkers and Hunter "best" values, which they had used to conclude that the anomaly had been overestimated. Our values of  $\alpha$  appear to agree best with those obtained from the uncorrected GHS equation. Extrapolation of our fits to  $-40^\circ\text{C}$  however, changes these conclusions. Now our  $|\alpha|$  value is still  $\sim 20\%$  larger than the Leyendekkers and Hunter best estimates, but  $\sim 70\%$  smaller than the values used by Speedy and Angell. We can conclude that our data support the Leyendekkers and Hunter contention that  $|\alpha|$  has probably been overestimated in the past.

A major contention in the study of the anomalous properties of supercooled water is that one may describe the anomalies in terms of power laws with respect to temperature relative to a singular temperature  $T_s$ . Speedy and Angell showed that this was a reasonable conclusion and, quite significantly,  $T_s$  for a variety of thermodynamic and transport properties was essentially the same,  $T_s = -45^\circ\text{C}$  for H<sub>2</sub>O. Establishment that such a behavior holds is important, not only because it is a useful description of the data, but also because it suggests analogies to the well-known behavior near a critical point.

Analysis of  $\alpha$  in terms of a power law is difficult because exact determination of the background component, i.e., that normal component of  $\alpha$  that would exist even if no anomaly were present, is very difficult. To determine the background component,  $\alpha_B$ , Leblond and Hareng<sup>11</sup> have analyzed  $\alpha$  for superheated H<sub>2</sub>O in the range  $160^\circ\text{C} < T < 220^\circ\text{C}$ . Spectroscopic evidence indicates hydrogen bonding is small in this range. They fit the data to a power law diverging at the gas-liquid spinodal and then extrapolated this fit to  $-40^\circ\text{C}$ .

Their  $\alpha_B$  is shown in Fig. 3. Oguni and Angell<sup>12</sup> have added formamide to water which wipes out the anomaly to leave normal liquid behavior. From this they determined two possible background components which are also shown in Fig. 3. While the temperature range is restricted, one can see these backgrounds bracket the Leblond and Hareng background. Leyendekkers<sup>13</sup> has also suggested a form for  $\alpha_B$  based on the well characterized background compressibility. This  $\alpha_B$  is also shown in Fig. 3 and is seen to have a different slope than the other backgrounds.

To test the power law behavior of  $\alpha$  and to determine the singular temperature  $T_s$ , we fit our H<sub>2</sub>O expansivity data to

$$\alpha_B - \alpha = \alpha_0 (T - T_s)^{-x}. \quad (1)$$

We used  $\alpha_B$  from both Leblond and Hareng, and Leyendekkers. The fit using the Leblond and Hareng background yielded  $T_s = -63 \pm 5^\circ\text{C}$ ,  $x = 1.58 \pm 0.18$ , and  $\alpha_0 = 0.482 \text{ K}^{-1}$  for data in the range  $-34.2^\circ\text{C} < T < 130^\circ\text{C}$ . The fit is displayed in Fig. 4. Some deviation occurs for  $T - T_s > 120 \text{ K}$ . This is not surprising since  $\alpha_B - \alpha$  becomes small here. We refit the data with a limited range,  $-34.2^\circ\text{C} < T < 55^\circ\text{C}$ . This range was chosen to exclude errors due to an apparent underestimate of  $\alpha_B$  at high temperature. This range gave a fit with  $T_s = -57 \pm 4^\circ\text{C}$ ,  $x = 1.35 \pm 0.20$ , and  $\alpha_0 = 0.1654 \text{ K}^{-1}$ . The fit using the Leyendekkers background yielded  $T_s = -48 \pm 2^\circ\text{C}$ ,  $x = 0.95 \pm 0.07$ , and  $\alpha_0 = 2.84 \times 10^{-2} \text{ K}^{-1}$ . These fits are also shown in Fig. 4.<sup>14</sup>

These fits yield significantly different results, and if nothing more, demonstrate the sensitivity of the analysis to the background. The Leblond and Hareng background suggests a singularity at  $\sim -60^\circ\text{C}$  with a critical exponent  $x \sim 1.5$ . This analysis supports the Leyendekkers and Hunter contention that the singularity is nearer  $200\text{--}210 \text{ K}$  ( $-73$  to  $-63^\circ\text{C}$ ) than  $228 \text{ K}$  ( $-45^\circ\text{C}$ ). On the other hand, the Leyendekkers background suggests, ironically,  $T_s = -48^\circ\text{C}$  and  $x \approx 1.0$ . This singular temperature is very comparable to most earlier results.

Qualitative evaluation of the expansivity backgrounds can be made. The Leblond and Hareng value was obtained directly from expansivity data and seems a good compromise between the Oguni and Angell solution values. Extrapolation from  $160$  to  $-34^\circ\text{C}$ , however, is very risky. The Leyendekkers  $\alpha_B$  is based not on expansivity data but on compressibility data, which while better characterized, does not represent an expansivity obtained directly from data. It is impossible at this time to decide between the two backgrounds.

A fit to a power law can be very problematical. Short spans of data, like the decade-and-a-half data above, are easily forced into power law form. We can conclude our data may be fit to a power law, but we have not shown the behavior is in fact a power law.

#### IV. CONCLUSIONS

We have measured the density of H<sub>2</sub>O to  $-34.2^\circ\text{C}$  and D<sub>2</sub>O to  $-19.2^\circ\text{C}$  in glass capillaries with  $25 \mu$  inside diameter. Comparison of our H<sub>2</sub>O data to surface energy effects as

described by Leyendekkers and Hunter<sup>4</sup> and to earlier data in larger capillaries indicated that our densities may be as much as several parts in 10<sup>4</sup> too large at  $-34.2^{\circ}\text{C}$  due to these effects. Nevertheless, this surface effect is considerably smaller than seen in earlier measurements in smaller capillaries at similar degrees of supercooling. Our density data suggest that the earlier data of Zheleznyi are too small. Expansivities calculated from our data led us to the conclusions of Leyendekkers and Hunter that the expansivity anomaly in water was not as large as might seem from the earlier data. Analysis of the expansivity in terms of a power law was critically dependent on the form of the background used. The background of Leblond and Hareng gave a singular temperature of  $T_s \approx -60^{\circ}\text{C}$ . This value supports the contention of Leyendekkers and Hunter that  $T_s$  is lower than previously thought. On the other hand a background proposed by Leyendekkers gave  $T_s = -48^{\circ}\text{C}$  which does not support the Leyendekkers and Hunter contention.

## ACKNOWLEDGMENT

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