

A Review of Deuterium Triple-Point Temperatures

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A Review of Deuterium Triple-Point Temperatures

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A review is presented of the existing measurements of the triple-point temperatures T_{tp} of deuterium. All data are adjusted to a common temperature scale, and error limits are proposed where none was provided in the source publications. The effects of sample contamination are also considered. Impurity corrections, based on estimates from vapor-pressure measurements, are applied to the results. The analytical representation $T_{tp}(x) = 18.680 + 0.155x$, where x is the fraction of p -D₂ ($J = 1$), is found to represent T_{tp} to ± 0.010 K. The value, 18.723 ± 0.010 K, measured most recently on normal deuterium is consistent with the most accurate and precise of the earlier data.

Key words: deuterium; fixed points; hydrogen isotopes; *ortho-para* conversion; triple point.

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1. Introduction

Schwalbe and Grilly¹ described measurements of the melting curve $P_m(T_m)$ of deuterium in the temperature range between the triple point and 20.4 K. Samples in this experiment contained the "normal" spin mixture, which consists of 33.3% *para* ($J = 1$) and 66.6% *ortho* ($J = 0$) species. The melting data were fit by a nonlinear least-squares procedure to the following quadratic function:

$$P_m(T_m) = P_{tp} + A_1(T_m - T_{tp}) + A_2(T_m - T_{tp})^2, \quad (1)$$

where the independent variable T_m denotes the melting temperature. The parameters A_1 , A_2 , and T_{tp} were allowed to vary while P_{tp} was held constant at 0.17 bar (0.017 MPa). The fixed parameter was chosen so that (P_{tp}, T_{tp}) represents the coordinate of the triple-point in the P - T phase diagram.

The value $T_{tp} = 18.7067 \pm 0.002$ K, which was derived from the least-squares fit, was not taken as the triple-point temperature of pure normal deuterium (n -D₂) because of the error introduced by the known sample contamination 0.75% HD. The results of Bereznyak *et al.*² suggest that a small quantity of HD in otherwise pure n -D₂ will shift the triple-point temperature by an amount

$$\Delta T_{tp} = c(\text{HD})[T_{tp}(\text{HD}) - T_{tp}(n\text{-D}_2)], \quad (2)$$

where $c(\text{HD})$ denotes the concentration of HD, $T_{tp}(\text{HD}) = 16.60$ K, and $T_{tp}(n\text{-D}_2) = 18.73$ K. For $c(\text{HD}) = 0.0075$ in Eq. (2), we calculate a $\Delta T_{tp} = -0.016$ K. In view of this substantial effect and several other possible sources of system-

atic error, the value 18.723 ± 0.010 K was given as the most reasonable estimate of T_{tp} for pure n -D₂.

It is interesting to compare this result to those obtained from previous studies,³⁻¹² but there are several problems. One is that most of these data refer to different temperature scales. The international scale prior to 1968 was not defined below 90 K. For intercomparisons, it is necessary to adjust all T_{tp} results to a common scale, and for this we chose the International Practical Temperature Scale of 1968 (IPTS-68).¹³

We also found that few of the existing triple-point data were presented with any estimates of experimental uncertainties. For purposes of quantitative comparison, we have derived tentative error limits where none was provided in the original publications. Finally, the results of any triple-point measurement can be critically affected by sample impurities. We have attempted to provide some estimates for these effects as well.

The conclusions of the following discussion are summarized in Table 1. In the first column of the table, we have listed the source publications for convenient reference. Listed next are triple-point temperatures that were either quoted by the original authors or derived by reanalysis of their data. These results are known to depend upon the composition ratio of the *ortho* and *para* spin modifications. Following each of these entries we have, therefore, included the quoted or inferred *para* composition of the samples. In the fourth column, the triple-point temperatures are adjusted to the IPTS-68. In the last two columns, we have listed the quoted or inferred HD-impurity levels and finally the IPTS-68 triple-point temperatures corrected for HD according to Eq. (2). The "corrected" results of the last column are plotted together in Fig. 1 for comparison.

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TABLE 1. Triple-point temperatures of deuterium

Reference	T_{tp} (original) (K)	Composition (% <i>para</i>)	T_{tp} (IPTS-68) (K)	c(HD) (%)	T_{tp} (corrected) (K)
Grenier and White (Ref. 9)	18.787 ± 0.005	85.0	18.807	(0.05)	18.808 ± 0.005
	18.781 ± 0.005	75.1	18.801	(0.05)	18.802 ± 0.005
	18.698 ± 0.005	36.5	18.718	0.65	18.732 ± 0.005
Lewis and Hanson (Refs. 3 and 4)	$18.66 (\pm 0.020)$	(33.3)	18.66_8		
Scott <i>et al.</i> (Ref. 5)	$18.58 (\pm 0.030)$	(33.3)	18.64_8	(0.5)	$18.65_9 (\pm 0.030)$
Brickwedde <i>et al.</i> (Refs. 6 and 7)	$18.71 (\pm 0.030)$	(33.3)	18.72_5	(0.5)	$18.73_6 (\pm 0.030)$
Schwalbe and Grilly (Ref. 1)	18.707 ± 0.002	(33.3)	18.707	0.75	18.723 ± 0.010
Clusius and Bartholome (Ref. 8)	$18.65 (\pm 0.005)$	(33.3)	18.64_7	(2.6)	$18.70_3 (\pm 0.020)$
Grilly (Refs. 11 and 23)	$18.73 (\pm 0.020)$	(33.3)	18.73_2	(0.72)	$18.74_6 (\pm 0.025)$
Brickwedde <i>et al.</i> (Refs. 6 and 7)	$18.67 (\pm 0.030)$	(2.2)	18.69_5	(0.5)	$18.70_5 (\pm 0.03)$
Kerr <i>et al.</i> (Ref. 10)	18.63 ± 0.01	2.2	18.63_7	1.1 ± 0.3	$18.66_0 (\pm 0.02)$
Bereznyak and Sheinina (Ref. 12)	$18.674 (\pm 0.003)$	2.2	18.674	(0.5)	$18.685 (\pm 0.005)$

2. Data Review and Discussion

2.1. Temperature Scale Corrections

In many of the earlier deuterium experiments,³⁻⁹ simultaneous measurements of hydrogen vapor pressures were taken as the direct temperature probe. Both normal (*n*-H₂) and 20.4 K-equilibrium (*e*-H₂) hydrogen have been used for this purpose. In some cases,³⁻⁷ these data were included ex-

PLICITLY with the deuterium results; in others,^{8,9} they can be easily recovered from the quoted absolute temperatures and the vapor-pressure equations used to establish the scale. In either case, the corresponding IPTS-68 values are derived from the appropriate hydrogen vapor-pressure equation published by Souers *et al.*¹⁴

For the remaining studies,^{10,11,15} calibrated resistance thermometers were used as primary temperature standards. Grilly¹¹ and Hoge and Arnold¹⁵ used platinum thermometers that had been calibrated at the National Bureau of Standards against the NBS-39 scale of Hoge and Brickwedde.¹⁶ For these experiments, the scale correction was made by matching the tabulated *e*-H₂ vapor pressures of Hoge and Arnold to the corresponding analytical function of Souers *et al.*¹⁴

Kerr *et al.*¹⁰ measured their temperatures with a 300- Ω gold wire-resistance thermometer. The resistance was calibrated in the range 13.8–20.9 K against the vapor pressure of liquid *e*-H₂. Centigrade-scale temperatures were derived from the vapor-pressure equation of Keesom *et al.*,¹⁷ and absolute temperatures were then calculated from an empirical linear relationship that had been used in an earlier work by Johnston *et al.*¹⁸ For the Kerr data, corrections to the IPTS-68 were applied in the standard way.

2.2. Measurement Errors

Many of the existing triple-point data^{3-7,11} were derived from measurements of the saturated vapor pressures. By this technique, separate empirical functions are fit to the vapor data in both solid and liquid temperature regimes. The equations are then solved simultaneously. Their intersection defines the triple-point temperature and pressure.

With this approach, the triple-point parameters are not explicitly measured on the sample as it exists in that state. In this sense, the method is an indirect one as are analogous determinations from melting data¹; however, the vapor-pressure technique has one significant disadvantage. The problem results from the relatively small difference in slope

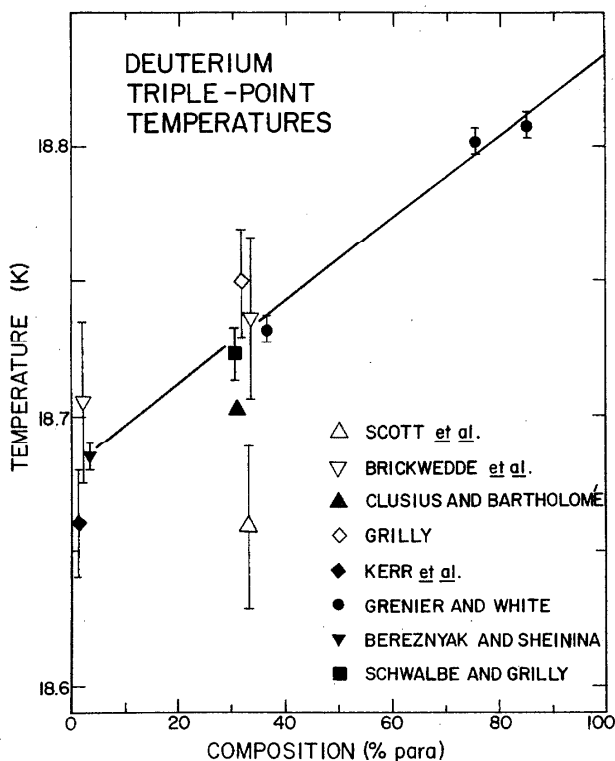


FIG. 1. Plot of the triple-point temperatures of deuterium as a function of the fractional *para* concentration. The results derived from vapor-pressure measurements are shown as open symbols. The shaded symbols represent direct measurements and those obtained by extrapolating melting data.

between the saturated solid and liquid curves. Their point of intersection, and particularly the temperature coordinate of that point, depends critically on the extrapolated behavior of the fitted functions beyond the domains of the measurements.

Ultimately, the severity of this problem depends on the accuracy, precision, and number density of the primary data. It is, therefore, not only misleading but incorrect to simply assign equal error limits to all results derived by the vapor-pressure technique. Instead we have reanalyzed all of the raw experimental data and have explicitly derived quantitative uncertainties for each of the T_{tp} results.

The earliest data that we consider were published by Lewis and Hanson.^{3,4} Saturated vapor pressures for solid and liquid $n\text{-D}_2$ were measured between 15.3 and 20.3 K. Temperatures were derived from simultaneous measurements on a sample of hydrogen that was held in thermal contact with the deuterium. The reference hydrogen was reportedly converted *in situ* to the *para* ($J=0$) form with a small amount of activated charcoal. Lewis and Hanson reported a triple-point temperature of 18.66 K, which they obtained from the simultaneous solution of the fugacity equations for the solid and liquid.

Following this work, Scott *et al.*⁵ published vapor pressures for $n\text{-H}_2$ and $n\text{-D}_2$ at temperatures between 13.9 and 20.4 K. The results of this experiment were expressed in two forms. The first is independent of the temperature scale; the logarithms of the hydrogen and deuterium vapor pressures are related directly as linear functions. The second form has the solid and liquid pressures expressed as functions of temperature explicitly.

For their temperatures, Scott *et al.* measured the vapor pressure of liquid $n\text{-H}_2$. These data were corrected for the *ortho-para* conversion that occurred during the course of the measurements and were then used with an explicit vapor-pressure equation to define the scale. Scott *et al.* observed that their results did not agree with those of Lewis and Hanson: the earlier $n\text{-D}_2$ pressures are consistently higher. To account for the discrepancy, they suggested that Lewis and Hanson probably had greater concentrations of sample impurities and possibly also an incomplete conversion of the reference hydrogen to the stable *para* form.

Curiously, the temperature, 18.58 K, that Scott *et al.*⁵ derived from their measurements is substantially lower than that obtained shortly afterwards at the same laboratory. In the later study, Brickwedde *et al.*^{6,7} applied essentially the same technique to measure both normal and 20.4 K-equilibrium deuterium ($e\text{-D}_2$), which consists of 2.2% *para* ($J=1$) and 97.8% *ortho* ($J=0$) species. The Brickwedde measurements were made in the range between 15 and 20.4 K. Temperatures were again obtained from simultaneous measurements on liquid $n\text{-H}_2$. These data were corrected for *ortho-para* conversion as Scott *et al.* had done, and the identical hydrogen vapor-pressure equation was used for the temperature scale. The triple-point temperatures for $e\text{-D}_2$ and $n\text{-D}_2$ were reported to be 18.67 and 18.71 K, respectively. The latter value is 0.13 K higher than that obtained by Scott *et al.*⁵

Brickwedde *et al.* offered no detailed explanation for

the large difference between the two results, but they preferred their own because they felt they had used higher purity samples. Their analytical relationships for $n\text{-D}_2$ and $e\text{-D}_2$ as functions of $\log P_{\text{vp}}(n\text{-H}_2)$ were later included as preferred data in the Woolley *et al.*¹⁹ review. However, in this publication the explicit functional dependences on temperature had been modified. A more reliable low-temperature scale¹⁶ had been established in the meantime, and more accurate hydrogen vapor-pressure functions had been derived from additional data.

About 15 years after this initial work was done, Grilly¹¹ published measurements on normal hydrogen, deuterium, and tritium. The data on $n\text{-D}_2$, over the range 14–27.8 K, were fit to smooth functions of temperature for both solid and liquid phases. Simultaneous solution of these yielded triple-point parameters that agree with the data of Brickwedde *et al.*^{6,7}

We recalculated the triple-point parameters from the raw data that were reported for each of the above experiments. The analytical method we used is essentially that described originally by Scott *et al.*⁵ These investigators observed that log-log plots of deuterium versus hydrogen pressures are approximately linear for both solid and liquid temperature regimes. The intersection of the two functions defines the triple point.

As we mentioned above, this intersection is difficult to fix precisely because of the small difference in slope between the two linear functions. However, the data can be analyzed most conveniently if the differences between each of the $\log P_{\text{vp}}(\text{D}_2)$ data and the line defined by the two endpoints of the data set are plotted as a function of $\log P_{\text{vp}}(\text{H}_2)$. With this slight modification to the original approach, we verified the quoted triple-point temperatures of Scott *et al.*⁵ and Brickwedde *et al.*^{6,7} and established error limits of ± 0.03 K for these results.

The same procedure was applied to the data of Lewis and Hanson.^{3,4} The result of this calculation is a triple-point temperature 18.685 ± 0.020 K, which is slightly different from the (IPTS-68) value 18.668 K quoted originally. The error limits established for the Lewis and Hanson data are smaller than those obtained from the measurements of Scott *et al.*⁵ and Brickwedde *et al.*^{6,7} One reason for this is that Lewis and Hanson generated more data in the immediate vicinity of the triple point. This allows more precise definition of the functions in this critical region.

A reanalysis of Grilly's data¹¹ was made in a similar way, but because his temperatures were measured with an independently calibrated platinum thermometer, we used $1/T$ rather than $\log P_{\text{vp}}(\text{H}_2)$ along the abscissa in the log plot. The result of this calculation corroborates Grilly's triple-point value, 18.732 K (IPTS-68), and establishes ± 0.02 K error limits for this solution.

Thus far, we have only discussed vapor-pressure measurements. As we mentioned, this approach is indirect, but before the early 1950s, the study by Clusius and Bartholome⁸ is the only one that may have given a more direct result. Clusius and Bartholome published a fairly comprehensive set of measurements of the calorimetric, density, and melting properties of $n\text{-D}_2$. Triple-point parameters were includ-

ed, but it is not clear from their report just how the measurements were made. The data appear in the same subsection with the descriptions and results for the measurements of the melting line. Presumably the same technique was used at the triple point as well.

The temperatures that Clusius and Bartholome quote were obtained from measured pressures of their liquid $n\text{-H}_2$ cryogen bath. No corrections were made for *ortho-para* conversion. Centigrade-scale temperatures, θ (C), were derived from the vapor-pressure function of Keesom *et al.*,¹⁷ and absolute temperatures, according to Bartholome,²⁰ were then calculated from the expression $T(\text{K}) = \theta(\text{C}) + 273.15$. Clusius and Bartholome reported a triple-point temperature that corresponds to the IPTS-68 value 18.647 K. From the experimental procedure described for the measurements of the melting line, we judge this value to be accurate to about ± 0.005 K.

At about the same time Grilly's vapor pressure work was published, Kerr *et al.*¹⁰ reported a series of calorimetric data on $e\text{-D}_2$. Included among these results was a direct measurement of the triple-point temperature on a "half-melted" sample. The rather large error limit assigned to the value in the final column in Table I derives in part from the uncertain HD-impurity levels discussed in their report. The corrected triple-point temperature determined by Kerr is somewhat lower than that published recently by Bereznyak and Sheinina.¹²

Bereznyak and Sheinina measured the melting curves of $e\text{-H}_2$, $n\text{-H}_2$, and $e\text{-D}_2$. Corresponding solid-liquid-vapor triple-point temperatures are included, but it is not clear whether the T_{tp} were obtained by direct measurement or derived from the melting data. We note that Bereznyak and Sheinina observed small discontinuities in the slopes of each of the melting curves. That for $e\text{-D}_2$ was seen at 19.02 K and 14.19 bar. They ascribed the anomalies to an intersection of the melting line by a solid-solid phase boundary. In principle, for ultimate precision in the solid-liquid-vapor triple point, only that portion of the melting line below the slope discontinuity should be used to extrapolate $P_{\text{m}}(T_{\text{m}})$ to P_{tp} . However, in practice, we find the discontinuity to be so small that negligible error is introduced by including all of the data. Bereznyak and Sheinina used the IPTS-68 so that no adjustment is required for their temperatures. We have assumed a value $c(\text{HD}) = 0.005$ from the reported correspondence of their vapor-pressure measurements to those of Hoge and Arnold.¹⁵

Triple-point temperatures at higher *para* concentrations have been measured by Grenier and White.⁹ As in the most recent work,¹ these values represent "first-freeze" temperatures. They were obtained by observing when solid began forming in their liquid sample as the system was cooled. Grenier and White suggested that there might be some dependence of the freezing temperature on the relative fraction of the solid and liquid in the sample. They observed changes on the order of a few millikelvin as the freezing process continued.

The effect may have been associated with a variation of the *ortho-para* composition of the solid and liquid phases on freezing as they suggest, but it is not clear from their paper

whether the variations were toward higher or lower temperatures. Schwalbe and Grilly¹ reported a few direct measurements of the slope of the melting curve in which a single sealed sample was cycled in temperature. The results were found to be consistent with those deduced from successive measurements of the melting pressure where only minimal amounts of solid were present. The influence of the relative phase composition of the sample on its melting characteristics is not well known at present.

The temperature scale for the Grenier and White measurements is based on the $e\text{-H}_2$ vapor-pressure equation proposed by Durieux and others.^{21,22} For the data at high *para* concentrations, corrections for the HD impurity are negligible. Preferential adsorption of the *para* species in the separation column diminishes HD levels by roughly an order of magnitude. Grenier and White used a calibrated carbon-resistance thermometer for their direct temperature measurements. Although they quote error limits of ± 0.002 K for their temperatures, we have increased these to ± 0.005 K, which we consider more appropriate for the thermometry technique they described. Also, with this assumption the points at 75% and 85% *para* concentrations are more nearly consistent.

2.3. Sample Impurity Effects

There are two major problems involved with any attempt to account systematically for the effects of contamination. The first is that only three^{1,9,11} of the experiments included any direct measurements of sample impurities. (The deuterium used by Grilly¹¹ was the same as that used in the liquid density work²³ and contained 0.72% HD.) The remaining studies treated the problem in a rather subjective manner. The usual assumption was that if the samples were contaminated, the only likely impurities would have been the more volatile materials, H_2 or HD. According to Raoult's law, either of these produce overall higher vapor pressures. Low absolute pressures, therefore, became the qualitative criterion for sample purity and general credibility of the results.

The second problem derives from the complexity of the phase diagrams of these multicomponent systems. It may be valid to assume that hydrogen and HD are likely contaminants, but for mixtures of these with deuterium, there is no single phase-space coordinate for coexisting states of the solid, liquid, and vapor. The unique temperature that characterizes the triple point of the pure substance spreads to a range of values for a two-component mixture.^{2,24,25} Different "triple points" are measured for different relative quantities of solid and liquid.

Measurements of the triple-point temperature can be made on contaminated samples, but without knowing the relative phase composition, the correction of the result to the single-component value involves an additional uncertainty. Fortunately, the error is not large for low impurity levels. A sample of $n\text{-D}_2$ containing 0.5% HD will require a correction of $\Delta T_{\text{tp}} = 0.011$ K, according to Eq. (2); however, the additional uncertainty introduced by this correction is only about ± 0.002 K.

It is impossible to account fully for impurity effects in all of the work that we have discussed; but because the corrections are significant in most cases, we give some estimates even though they are admittedly approximate. We base our calculations on the following four assumptions:

(a) In the absence of mass-spectrometric analyses, we use measurements of the saturated liquid-vapor pressure to establish impurity levels. These data are preferred to solid-vapor pressures because they should be subject to fewer systematic errors. In general, the liquid pressures are larger and are, therefore, relatively more precise. In addition to this, we expect distribution of the miscible liquid components to be more nearly homogeneous.

(b) Next, we assume conditions of ideal mixing so that Raoult's law can be applied for the numerical estimates of the impurity levels. There is some experimental evidence to support this assumption. Bereznyak *et al.*²⁵ measured vapor pressures of liquid e-H₂/e-D₂ solutions from 20.4 K down in temperature to the freezing point of each mixture. From these data they produced plots of the vapor pressure as a function of composition at two separate temperatures, 19 and 20 K. For our purposes, the deviation of these curves from the linear functions predicted by Raoult's law are insignificant. They amount to only a few percent at their maximum value, which occurs at hydrogen concentrations of about 30%. Newman and Jackson²⁶ made similar measurements on solutions of *n*-H₂ and *n*-D₂. Their results are very similar to those of Bereznyak *et al.*²⁵

To our knowledge, there are no corresponding data for mixtures of deuterium with HD. Nevertheless, we apply the same prescription for this system as well. Thus, for an observed vapor pressure, $P(\text{obs})$, of a sample mixture of *n*-D₂ and HD, we calculate the relative concentration of HD from the expression:

$$P_{\text{vp}}(\text{obs}) = [1 - c(\text{HD})]P_{\text{vp}}(n\text{-D}_2) + c(\text{HD})P_{\text{vp}}(\text{HD}). \quad (3)$$

(c) One problem with this approach is that some reference data are required. For these, we use the liquid-vapor pressures published by Hoge and Arnold.¹⁵ Their measurements on e-D₂ extend in temperature from the triple point up to the critical point. Data for *n*-D₂ are also available above 21 K. It is unfortunate that Hoge and Arnold were unable to measure pressures in the solid-phase region and could not provide an independent measurement of the triple point. Nevertheless, their work is useful here because they reported mass spectrometric analyses of their samples. The impurity concentrations of their e-D₂ and *n*-D₂ were given as 0.005 HD and 0.008 HD, respectively.

(d) With numerical estimates of the impurity concentration established from Eq. (3), we apply Eq. (2) to calculate ΔT_{tp} . According to the preceding discussion, this operation should introduce some additional uncertainty to the final result. This error is also included when it is significant.

Figure 2 contains the saturated liquid-vapor pressures for most of the experiments that we have discussed. The data were first corrected to the IPTS-68 and then expressed as logarithmic functions of the pressure. These quantities were finally plotted as differences from the log pressure calculated from the liquid-vapor equation that Souers *et al.*¹⁴ gave for *n*-D₂.

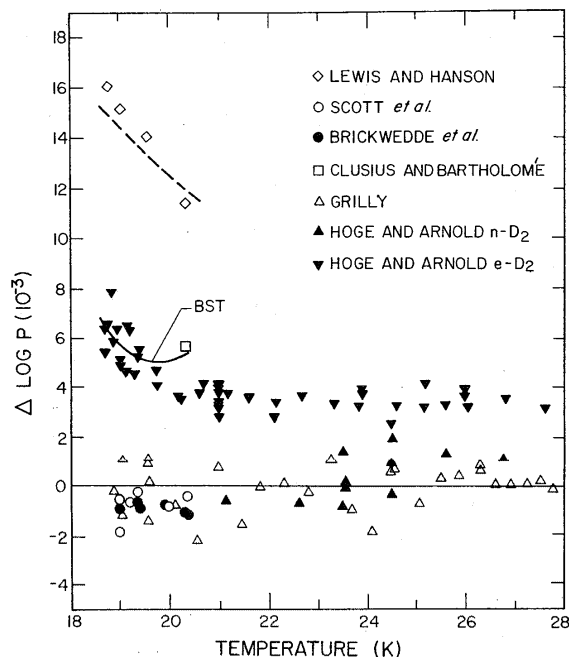


FIG. 2. Plot of liquid-vapor pressure data as a function of temperature. $\Delta \log P$ denotes the logarithmic difference between the measured pressure and that calculated from the function for *n*-D₂ by Souers *et al.* (Ref. 14). The solid curve labeled "BST" represents the analytical function that Brickwedde *et al.* (Refs. 6 and 7) gave for their e-D₂ results. The dashed curve in the vicinity of the Lewis and Hanson (Refs. 3 and 4) data shows the effect of a 1.7% H₂ impurity in otherwise pure *n*-D₂.

We begin our discussion by comparing the measurements of Grilly¹¹ and Hoge and Arnold¹⁵ on *n*-D₂. Figure 2 shows the correspondence of these data in their overlapping temperature range, 21 to 28 K. The agreement is consistent with the nearly equal impurity levels reported. The difference between the $c(\text{HD}) = 0.008$ given by Hoge and Arnold and the value 0.0072 of Grilly²³ is insignificant for our purposes.

Next, we assign $c(\text{HD}) = 0.005$ to the e-D₂ data of Brickwedde *et al.*^{6,7} These data only extended over a short interval, but the correspondence between their analytical representation (labeled "BST" in the figure) and the Hoge and Arnold measurements is evident, particularly at temperatures just above the triple point. For their *n*-D₂ data, we enter the same HD level. Brickwedde showed that their samples of e-D₂ and *n*-D₂ were of comparable purity. They produced *n*-D₂ by conversion of the e-D₂ samples and showed that the vapor pressures agree with those of the original, unconverted material.

For the *n*-D₂ pressures of Scott *et al.*⁵ we assign the same HD level 0.005. As Fig. 2 shows, these data and those of Brickwedde *et al.*^{6,7} are both slightly lower than the Souers curve, which was taken directly from the representation that Grilly¹¹ presented for his liquid *n*-D₂ data. The offset is roughly equal to that expected for the 0.2% to 0.3% difference in $c(\text{HD})$ that we have assumed between the NBS measurements⁵⁻⁷ and Grilly's data.

The only measurements that remain uncorrected are those of Lewis and Hanson^{3,4} and Clusius and Bartholomé.⁸ Figure 2 shows that both sets show very large deviations

from the reference curve. The single measurements by Clusius and Bartholome at 20.329 K gave a pressure for $n\text{-D}_2$ that is about 3 Torr higher than that prescribed by the Souers equation at that temperature. There are several possible sources for the discrepancy. Although Clusius and Bartholome quote an impurity level of 0.3% HD, this estimate may be too small. Calculations show the pressure offset may be accounted for either by a 2.6% quantity of HD or a 1% quantity of H_2 . According to Eq. (2), these impurities would give rise to shifts in the measured triple-point temperature of -0.055 and -0.048 K, respectively. Another possibility is that some *ortho-para* conversion had occurred in their liquid hydrogen refrigerant. If the conversion were complete, the difference in the $n\text{-D}_2$ vapor pressure would be almost entirely accounted for. In this case, the resulting shift in the triple-point temperature would be -0.051 K.

These numerical estimates illustrate an interesting point. Even though vapor-pressure data offer rather nonspecific information about the actual conditions of the sample, they are nonetheless sufficient to correct the triple-point data to nominal pure-component values. For small discrepancies in the vapor-pressure measurements, it is largely irrelevant whether an impurity effect is being observed or whether some *ortho-para* conversion has taken place. The corrections applied to T_{tp} are roughly the same.

With this in mind, we have entered the value $c(\text{HD}) = 0.026$ for the Clusius and Bartholome result in Table I. We then obtain the corrected triple-point temperature, 18.703 ± 0.020 , which is somewhat lower than might be expected from the behavior of the other data plotted in Fig. 1. The 0.03 K discrepancy is larger than the stated error limit, but we feel the lack of agreement is not particularly serious. Recall that Clusius and Bartholome gave no description of their measurement technique. When we extrapolate their melting curve to $P_{\text{tp}} = 0.17$ bar, we find a triple-point temperature that is about 0.015 K higher than the one they quoted.

The same type of analysis was applied to the results of Lewis and Hanson.^{3,4} For this experiment, it is clear that substantial impurity levels must be assumed to account for the large differences shown in Fig. 2. The dashed line represents the effect of a 1.7% admixture of $n\text{-H}_2$ to an otherwise pure $n\text{-D}_2$ sample. An assumed HD impurity of 4.6% describes the vapor-pressure differences nearly as well. However, these numbers in Eq. (2) give ΔT_{tp} values of -0.081 and -0.102 K, respectively. In either case, the Lewis and Hanson result is corrected to very large values.

An impurity effect is not the only possibility, however. Scott *et al.*⁵ had suggested that Lewis and Hanson may have had an incomplete conversion of their reference sample of hydrogen. If this were so, they would have measured lower hydrogen pressures and would have deduced lower temperatures. The actual sample temperatures would have been higher, and the measured $n\text{-D}_2$ pressures would likewise appear to be too large. We calculated the maximum temperature error that Lewis and Hanson could have had under these conditions. For the extreme case of no conversion whatever, the actual temperatures of their samples would have been higher by as much as 0.118 K in the range 18.5–

21.0 K. However, an offset of this magnitude is not necessary. A systematic error of only 0.075 K could account for the observed differences in the $n\text{-D}_2$ pressures.

No attempt has been made to obtain a "final" corrected T_{tp} from the Lewis and Hanson data. We simply observe that with a suitably chosen set of possible sample conditions, any value between 18.3 and 19.0 K can be obtained.

3. Summary and Conclusions

The primary purpose of this work is to compare the most recently reported triple-point temperature¹ with those established from previous studies. In most cases a simple, direct comparison of the data has not been possible. There are several complications. Nearly all of the results have been expressed in terms of different temperature scales. Most were reported without uncertainty limits, and there has apparently been little consideration given to the possible effects of sample impurities.

The problems introduced by mismatching temperature scales are easily overcome. Corrections to the IPTS-68 are made by matching hydrogen vapor pressures to the functions published by Souers *et al.*¹⁴ As the next step, we establish error limits for all of the results derived, in most cases, by complete reanalysis of the original experimental data.

Finally, we attempt to correct for the effects of sample contamination. These calculations involve several assumptions. In the absence of direct measurements of the impurity concentrations, we derive estimates of these from liquid-vapor pressures of the samples. Conditions of ideal mixing are assumed so that Raoult's law can be applied to compute numerical estimates of these impurity levels. As reference data for this calculation, we use the liquid-deuterium vapor-pressure measurements of Hoge and Arnold.¹⁵ Finally, the correction ΔT_{tp} is obtained as the product of the fractional concentration of the impurity and the difference between its triple-point temperature and 18.73 K. We discuss the justification for these assumptions and estimate the additional uncertainties imposed on the final results.

The conclusions of our critical review are summarized in Table I. Generally, we find that the triple-point temperatures derived from vapor-pressure studies are the least precise of the available data. Error limits established for these typically range from ± 0.02 to 0.03 K. The results obtained from other measurement techniques^{1,8-12} are more precise. Of these, we select as preferred data the measurements of Schwalbe and Grilly,¹ Grenier and White,⁹ and Bereznyak and Sheinina.¹² The solid line drawn through these points in Fig. 1 is intended to represent the functional dependence of the triple-point temperature on the *ortho-para* concentration. If we denote the fraction of $p\text{-D}_2$ ($J = 1$) by x , the analytical representation

$$T_{\text{tp}}(x) = 18.680 + 0.155x, \quad (4)$$

should describe the triple-point temperature of deuterium to ± 0.010 K or better.

The slope of Eq. (4) is comparable to that observed for hydrogen. For $n\text{-H}_2$ and $e\text{-H}_2$, the relative fraction of the *ortho* ($J = 1$) species is 0.75 and 0.002, respectively. From the IPTS-68,¹³ we find $T_{\text{tp}}(n\text{-H}_2) = 13.956$ K and

$T_{\text{tp}}(\text{e-H}_2) = 13.81$ K. Together, these data define a slope of 0.195 K per unit change in the *ortho* fraction.

The measurements of Brickwedde *et al.*,^{6,7} Kerr *et al.*,¹⁰ and Grilly¹¹ are consistent with Eq. (4); those of Scott *et al.*⁵ are not. Brickwedde *et al.* first noted the serious disagreement between their result and that of Scott *et al.*, but they did not account for it in any quantitative manner. The earlier measurement was thought to have been influenced by impurity effects. In contrast to this, our analysis suggests that differences in sample purity are probably not significant. From Fig. 2, we see that the liquid-vapor pressures of the two experiments are comparable in magnitude. In our view, the problem more likely results from the solid vapor-pressure data. Both studies produced relatively few direct measurements in the low-temperature region. A small systematic error in these could have produced the large difference observed in the triple-point temperature.

Finally, there are the results of Lewis and Hanson^{3,4} and Clusius and Bartholome.⁸ Both sets of measurements show rather large discrepancies in their liquid-vapor pressures, which indicates that some errors are likely inherent in their triple-point temperatures as well. We have made some estimates for the corrections. Generally, these place the result of Lewis and Hanson higher than Eq. (4) and the result of Clusius and Bartholome lower. However, we have also shown that with a suitably chosen set of possible experimental conditions, either result can be made to agree with Eq. (4). We, therefore, judge these to be the least significant of the available data.

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