

# Recent Progress in Deuterium Triple-Point Measurements

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The triple point of deuterium is a proposed reference for defining the temperature scale between 13.81 and 24.562 K. We review recent measurements of this fixed point; our discussion concentrates on experiments with samples confined in transportable sealed cells. We also present theoretical estimates of the dependence of the triple-point temperature on the spin composition of the sample. Satisfactory agreement is obtained with experimental data on deuterium at low concentrations of the *para* ( $J = 1$ ) species. Present results support the adoption of the triple point of  $e\text{-D}_2$  as a standard temperature reference.

Key words: critically reviewed data; deuterium; effective quadrupole pressure; fixed points; hydrogen isotopes; *ortho-para* conversion; triple point.

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## 1. Introduction

A recent critical review of deuterium triple-point data<sup>1</sup> primarily considered melting and vapor pressure measurements. The result showed that the triple-point temperature  $T_{\text{tp}}$  is well described by the empirical relationship

$$T_{\text{tp}}(x_p) = 18.680 + 0.155x_p, \quad (1)$$

where  $x_p$  is the mole fraction of  $p\text{-D}_2$  ( $J = 1$ ).

To supplement the references of this study,<sup>1</sup> we now discuss several high-precision measurements<sup>2-7</sup> that have appeared in the past half-dozen years. All of this recent work follows ongoing efforts<sup>8-11</sup> to establish an accurately defined international temperature scale that is both convenient and uniformly realizable.

Problems exist in various temperature intervals. In the range between 13.81 and 24.562 K, for example, the fixed points are defined at specified temperatures and pressures of liquid hydrogen. To avoid the inconvenience of simultaneous vapor pressure measurements, the deuterium triple point has been proposed as an alternative reference. Whether

this is practical or not depends on at least two factors. One concerns *para-to-ortho* conversion rates. Normal deuterium  $n\text{-D}_2$  (33%  $J = 1$  and 67%  $J = 0$ ) can only be used if rates of spin conversion are sufficiently small that temperatures remain stable during reasonable measurement periods. The equilibrium form,  $e\text{-D}_2$  (1.5%  $J = 1$  and 98.5%  $J = 0$ ), is practical if some independent method is established to assure complete conversion of samples in their sealed containers. In either case, sample contaminants are a critical consideration. The following studies specifically address these problems.

## 2. Triple-Point Measurements

The first study we review is that of Pavese and Barbero,<sup>2</sup> who measured two small (0.2 mol) samples of  $n\text{-D}_2$  that were permanently sealed in separate metal containers. A calorimetric technique was applied in which the frozen samples were intermittently heated and then allowed to equilibrate. After each equilibration period, temperatures were measured and plotted as a function of  $1/F$ , where  $F$  is the liquid fraction of the sample. Experimental triple-point temperatures were obtained by extrapolating these data to  $1/F = 1$ .

Because each of their runs lasted from 2 to 11 h, Pavese

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and Barbero considered corrections for spin conversion. Consecutive triple-point measurements were made on samples confined at low temperatures for periods up to about 100 h. From the tabulated results of four such experiments, we calculate time rates of change in  $x_o$ , the *ortho* fractions of their samples, to be between 0.9 and  $1.8 \times 10^{-4} \text{ h}^{-1}$ . These data are consistent with the direct measurements of Schwalbe and Grilly<sup>12</sup> and others.<sup>13,14</sup> The maximum correction to the Pavese and Barbero  $T_{\text{tp}}$  is therefore only about 0.3 mK. Smaller still are effects due to the nonadiabaticity of their calorimeter and the heat input from spin conversion, which they also considered.

Sample contamination forced a larger correction. Apparently, Pavese and Barbero did not measure the impurity levels of their samples directly, but rather inferred a concentration of 0.14% HD from the certified purity of their supply (99.86%  $\text{D}_2$ ). They then multiplied this by  $1.5 \mu\text{K}/\text{ppm HD}$ , an approximate slope of the liquidus line that Bereznyak *et al.*<sup>15</sup> published from their phase studies of *o*- $\text{D}_2$ /HD mixtures, to obtain a correction of 2.1 mK to the triple-point value.

The ultimate precision attainable with the type of experiment Pavese and Barbero describe is perhaps a few tenths of a mK, but the stated uncertainty of their final result,  $\pm 0.002 \text{ K}$ , is considerably larger. The major limitation is in the temperature calibrations. Five separate platinum resistance thermometers were used in the experiment. Calibrations against the IPTS-68 scale at three laboratories, the National Bureau of Standards (NBS), USA, the National Physical Laboratory (NPL), UK, and the Physico-Technical and Radio-Technical Measurements Institute (PRMI), USSR, obtained values that differ by as much as 4.2 mK. Pavese and Barbero gave their result in terms of the NPL realization, but on the NBS scale they obtained  $18.727 \pm 0.002 \text{ K}$  (IPTS-68).

In a later publication, McConville, Menke, and Pavese<sup>6</sup> revised this result. The original impurity estimate of 0.14% is now thought to represent only a protium contamination, which corresponds to an HD-impurity level of 0.28%. In addition, McConville *et al.*<sup>6</sup> apply a somewhat larger correction factor,  $2.1 \mu\text{K}/\text{ppm HD}$ , which is the same one used by Schwalbe and Grilly.<sup>1</sup> With the revised impurity correction of 5.9 mK (instead of the 2.1 mK applied originally), the Pavese and Barbero result for the  $T_{\text{tp}}$  of *n*- $\text{D}_2$  becomes  $18.731 \pm 0.002 \text{ K}$  (NBS-IPTS-68). The higher impurity estimate not only yields a triple-point value that is consistent with Eq. (1) and with later measurements (to be discussed below), but it also accounts for the relatively large melting range, 2–3 mK, that was initially attributed to the shape of the sample chamber.

Following the original work on *n*- $\text{D}_2$ , Pavese<sup>3</sup> reported triple-point measurements on the equilibrium hydrogen isotopes, *e*- $\text{H}_2$  and *e*- $\text{D}_2$ . In these experiments, a hydrous ferric oxide catalyst was used to convert the normal spin mixtures to their low-temperature forms. The deuterium sample material was drawn from the same supply used in the earlier work.<sup>2</sup> Thus, all of the error considerations discussed above, except those deriving from spin conversion, are applicable to the results for *e*- $\text{D}_2$ . Pavese<sup>3</sup> reported a triple-point tempera-

ture of 18.676 K on the NBS scale. When we apply the revised impurity correction<sup>6</sup> to this result, we obtain  $18.680 \pm 0.002 \text{ K}$  (NBS-IPTS-68), which is consistent with Eq. (1) and with the result of Bereznyak and Sheinina<sup>16</sup> if a 0.5% HD impurity correction is applied to the latter.<sup>1</sup>

The greatest uncertainty in Pavese's result for *e*- $\text{D}_2$  again derives from the nonuniqueness of the temperature scale. However, the difference in triple-point temperatures between the normal and equilibrium forms,  $51.0 \pm 0.5 \text{ mK}$ , is not subject to this calibration problem. The corresponding value calculated from Eq. (1), 49.6 mK, is only slightly lower than the measured result.

In 1982, another set of triple-point measurements was reported. Kemp<sup>4</sup> followed essentially the same experimental procedures that Pavese<sup>2,3</sup> described. The results Kemp gave for *n*- $\text{D}_2$  and *e*- $\text{D}_2$  are  $18.709 \pm 0.001 \text{ K}$  and  $18.6906 \text{ K}$  (NPL-IPTS-68), respectively. Although no error limit was placed on the latter result, its reproducibility was better than  $\pm 0.1 \text{ mK}$ .

According to Pavese and Barbero<sup>2</sup> and to Pavese,<sup>3</sup> the NBS scale is between 2 and 4 mK lower than the NPL scale that Kemp used. To re-express Kemp's data, we therefore subtract an average difference of 3 mK to obtain the values  $18.706 \pm 0.001 \text{ K}$  for *n*- $\text{D}_2$  and  $18.6876 (\pm 0.001) \text{ K}$  for *e*- $\text{D}_2$  on the NBS-IPTS-68. The result for *e*- $\text{D}_2$  is higher than that of Pavese<sup>3</sup> but it agrees satisfactorily with the measurement of Bereznyak and Sheinina,<sup>16</sup> corrected by Schwalbe and Grilly.<sup>1</sup>

Kemp did not explicitly analyze for sample impurities in either set of runs, although his attempts at purification had little, if any, effect. However, he reported 0.2-mK variations in his melting plateau, which suggest that he had higher sample purities than did Bereznyak and Sheinina<sup>16</sup> and Pavese,<sup>3</sup> who reported variations of 4 and 5 mK, respectively.

The result for *n*- $\text{D}_2$  is not easily explained, as Kemp himself pointed out. The *n*- $\text{D}_2$  triple point is substantially lower than any of the higher-precision results found in the literature<sup>1,2</sup> up to that time. Kemp observed melting plateaus for *n*- $\text{D}_2$  that were not as flat as those observed for *e*- $\text{D}_2$ , which suggests that some differential sample contamination may have occurred. Another possibility for the low *n*- $\text{D}_2$  value is that a partial conversion was inadvertently catalyzed in the assumed normal spin mixture. Compared with the differences between  $T_{\text{tp}}$  of the normal and equilibrium forms that we discussed above, the relatively small value Kemp obtained,  $\Delta T_{\text{tp}} = 18 \pm 2 \text{ mK}$ , is consistent with both of these hypotheses, as is the noted irreproducibility of his *n*- $\text{D}_2$  data.

Kemp's seemingly anomalous result for *n*- $\text{D}_2$  might be easily dismissed if subsequent measurements by Ancsin<sup>5</sup> had not produced a similarly low result. Ancsin reported a triple-point temperature for *e*- $\text{D}_2$  that corresponds to 18.660 K (NBS-IPTS-68), which we deduce from the relative data he presented. Similarly, Ancsin's result for *n*- $\text{D}_2$  is 18.711 K (NBS-IPTS-68). The 51-mK difference is again consistent with Eq. (1) and the corresponding result obtained by Pavese.<sup>3</sup> However, when the Ancsin data are compared with all others, a disparity appears as a uniform shift in the temperature scale by about 20 mK. Although impurity effects are not

treated explicitly in Ancsin's paper, he did provide an estimate of 0.5% HD by private communication. With this correction we obtain *n*-D<sub>2</sub> and *e*-D<sub>2</sub> triple-point temperatures of 18.721 and 18.670 K (NBS-IPTS-68), respectively. Both values are still somewhat low. An impurity concentration of 1% could fully explain the offset.

The most accurate and precise measurements so far reported for deuterium are by McConville, Menke, and Pavese<sup>6</sup> on *n*-D<sub>2</sub> and by Pavese and McConville<sup>7</sup> on *e*-D<sub>2</sub>. Special efforts were made in these experiments to eliminate contaminants from both the material supply and the sample containers. The deuterium was drawn from a 7-m thermal diffusion column, which yields impurity levels below 10 ppm.

In the first experiment,<sup>6</sup> samples from the diffusion column were placed directly into two specially constructed stainless-steel cells. To eliminate contamination, both cells were prepared by vacuum baking, and one was flushed with D<sub>2</sub>O to exchange with protium in residual FeOH on its inner surface. Contamination levels in the confined samples were estimated at less than 100 ppm. The most reliable of the *T*<sub>tp</sub> results were obtained from the cell that had been treated with deuterated water. This triple-point temperature, 18.732 ± 0.001 K (NBS-IPTS-68), agrees with the result of Pavese and Barbero<sup>2</sup> when the revised impurity correction is applied to the latter.

McConville *et al.*<sup>6</sup> observed rapid spin conversion in both of their samples, although particularly in the cell that was chemically etched but not treated with D<sub>2</sub>O. Conversion rates were measured on both samples and fit to an exponential form to give a difference in *T*<sub>tp</sub> between *n*-D<sub>2</sub> and *e*-D<sub>2</sub>. From the values of Δ*R* given in their Table I and the temperature sensitivities quoted in Table 2 of Pavese and Barbero,<sup>2</sup> we calculate a *T*<sub>tp</sub> difference of 34 ± 1 mK. This result is significantly smaller than 50 mK, the best estimate up to that time. McConville *et al.* conclude that conversion rates of *n*-D<sub>2</sub> are too rapid to allow its adoption as a practical fixed point in the definition of the international temperature scale.

Subsequent measurements<sup>7</sup> on *e*-D<sub>2</sub> are more encouraging in this regard. In the work of Pavese and McConville, the same special efforts as described by McConville *et al.*<sup>6</sup> were made to obtain and hold ultrapure samples. However, in addition to this, a special deuterated catalyst was used to efficiently convert the sample without allowing progressive HD contamination. The result of Pavese and McConville for *e*-D<sub>2</sub> is 18.6982 (NBS-IPTS-68) with a stated precision of ± 0.0002 K. This *T*<sub>tp</sub> value is significantly higher than any of the measurements that we have discussed here so far. We note, however, that this value is consistent with that for *n*-D<sub>2</sub> of McConville *et al.*<sup>6</sup> and their estimated Δ*T*<sub>tp</sub> of 34 ± 1 mK discussed in the previous paragraph.

For convenient reference, we summarize all of these data in Table 1. Also included is a result by White and Gaines<sup>17</sup> that we omitted in our previous work.<sup>1</sup> This measurement on *n*-D<sub>2</sub> gave a triple-point temperature of 18.69 K on the *e*-H<sub>2</sub> vapor pressure scale of Durieux<sup>18</sup> and Ter Harnsel *et al.*<sup>19</sup> By matching this scale to the IPTS-68 in the manner described previously,<sup>1</sup> we obtain the corrected value

Table 1. Summary of triple-point temperatures of deuterium referred to the NBS realization of the International Practical Temperature Scale of 1968. Inferred impurity concentrations and *T*<sub>tp</sub> uncertainties are enclosed in parentheses. All *T*<sub>tp</sub> values in the last column are corrected for impurity effects.

Reference	Composition (% <i>para</i> )	<i>c</i> (HD) (%)	<i>T</i> <sub>tp</sub> (NBS-IPTS-68) (K)
Pavese and Barbero <sup>2</sup>	33.3	(0.28) <sup>a</sup>	18.731 ± 0.002
Pavese <sup>3</sup>	1.55	(0.28) <sup>a</sup>	18.680 ± 0.002
Kemp <sup>4</sup>	1.14	(0.5)	18.688 ± 0.001
	33.3	(0.5)	18.706 ± 0.001
Ancsin <sup>5</sup>	1.55	(0.5) <sup>b</sup>	18.670(± 0.005)
	33.3	(0.5) <sup>b</sup>	18.721(± 0.005)
White and Gaines <sup>17</sup>	33.3	0.6	18.723 (± 0.010)
McConville, Menke, and Pavese <sup>6</sup>	33.3	<0.01	18.732 ± 0.001
Pavese and McConville <sup>7</sup>	1.55	<0.01	18.6982 ± 0.0002

<sup>a</sup> Revised impurity estimate taken from reference 6.

<sup>b</sup> J. Ancsin, private communication.

18.71 K (IPTS-68). White and Gaines<sup>17</sup> reported 0.6% HD as the major impurity in their sample. By applying the standard correction of 2.1 μK/ppm HD,<sup>1,6</sup> we have the final result of 18.723 K (IPTS-68). With an estimated error limit of ± 0.010 K, this result agrees with the most accurate and precise measurements<sup>1,2,6</sup> to date.

### 3. Semiempirical Considerations

The latest *T*<sub>tp</sub> measurement<sup>7</sup> on *e*-D<sub>2</sub> is nearly 20 mK higher than the value given by Eq. (1) for the equilibrium *para* concentration *x*<sub>*p*</sub> = 1.55%. If this result is accurate and if the data of Grenier and White<sup>14</sup> at *x*<sub>*p*</sub> = 75.1 and 85.0 are valid, the linear relationship expressed by Eq. (1) no longer provides an adequate description of the *ortho-para* dependence of the deuterium triple point. The experimental data suggest a positive curvature in the plot of *T*<sub>tp</sub> versus *x*<sub>*p*</sub>.

In this section, we show how this behavior is qualitatively consistent with some simple thermodynamic arguments and a theoretical model first developed by Berlinsky and Harris<sup>20,21</sup> and later applied to solid H<sub>2</sub> and D<sub>2</sub> equations of state by Driessen *et al.*<sup>22</sup> For our purposes it is sufficient to consider the phase boundaries in the *P-T* diagram shown schematically in Fig. 1. For deuterium, the solid lines denote coordinates for phase transitions of the pure *ortho* (*J* = 0) modification. The dashed line represents the melting line corresponding to some 0 < *x*<sub>*p*</sub> < 1.

At constant temperature, the melting pressure is decreased by an amount Δ*P*<sub>*m*</sub>, which by straightforward thermodynamic arguments, is given by

$$\Delta P_m = \frac{1}{V_1 - V_s} \int_{V_s}^{V_1} P_Q dV. \quad (2)$$

Here, *V*<sub>*s*</sub> and *V*<sub>*l*</sub> are the molar volumes of the solid and liquid, and *P*<sub>*Q*</sub> is an effective pressure induced by the quadrupole moments of the *para* molecules in the mixture.

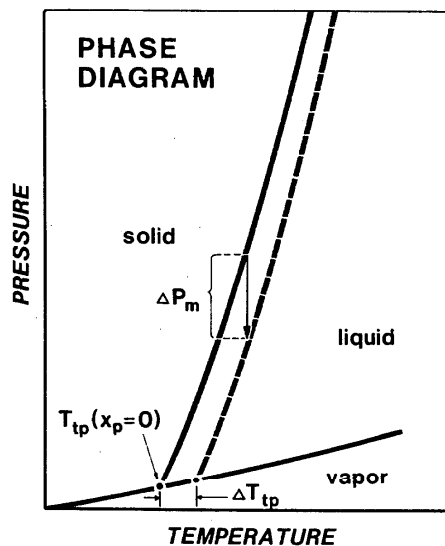


FIG. 1. Schematic phase diagram for deuterium. The solid lines represent the phase boundaries of pure  $o\text{-D}_2$ . The vapor curves are not significantly affected by admixtures of  $p\text{-D}_2$ , but melting pressures are reduced by an amount  $\Delta P_m$  defined by Eq. (2) and corresponding triple-point temperatures are shifted by  $\Delta T_{tp}$ .

Expressions similar to Eq. (2) follow for the sublimation and liquid-vaporization curves, but because of the very low densities of the vapor and the short range of the electric-quadrupole coupling, we neglect any effects on the vapor-phase boundaries. The measurements of Brickwedde *et al.*<sup>23</sup> support this assumption: near 18.7 K, they give pressure differences of 7 Torr (0.009 bar) between the pure  $o\text{-D}_2$  and  $p\text{-D}_2$ . These differences are three orders of magnitude smaller than corresponding shifts in the melting line. Similar conclusions hold for  $\text{H}_2$  near its triple point.

To our knowledge, no direct measurements of the effective quadrupole pressure are available. We therefore adopt the analytical expression for  $P_Q$  that Driessen *et al.*<sup>22</sup> derived for their solid equation-of-state data and apply it to both solid and liquid phases. Numerical integration gives the displacement of the melting line as a function of  $x_p$ . The intersection of this with the vapor-phase boundary defines the triple point. Changes in the triple-point temperature  $\Delta T_{tp}$  are calculated from

$$\Delta T_{tp} = \frac{\Delta P_m}{dP_m/dT_m}, \quad (3)$$

where  $dP_m/dT_m$  is the slope of the melting line.

To evaluate Eq. (3), it is sufficient to consider the slope  $dP_m/dT_m$  as constant because the quadrupole contribution to the latent heat of fusion is negligible. To show this explicitly, we calculate

$$\Delta h_{fQ} = \int_{V_s}^{V_l} \frac{\gamma_Q}{V} C_{VQ} dV, \quad (4)$$

where  $\gamma_Q$  is the logarithmic volume derivative of the quadrupole coupling parameter,<sup>22</sup> and  $C_{VQ}$  is the quadrupolar specific heat.<sup>20,22</sup> At the triple point, Schwalbe and Grilly<sup>12</sup> measured  $V_l = 23.053$  and  $V_s = 20.340$   $\text{cm}^3/\text{mol}$ . These

values in Eq. (4) with  $x_p = 1$  give  $\Delta h_{fQ} = 2.6$  J/mol, which is only 1.3% of the total latent heat of fusion,  $\Delta H_f = 197 \pm 2$  J/mol.<sup>12</sup> Differences in the volume change on melting  $\Delta V_m$  are comparably small. For the slope of the melting curve we therefore assume the constant value  $dP_m/dT_m = 38.8$  bar/K.<sup>12</sup>

The results obtained from Eqs. (2) and (3) are temperature differences. To express  $\Delta T_{tp}$  in absolute terms requires that we reference them to some fixed  $T_{tp}$  value. In our opinion, the best established temperature is at the normal spin concentration,  $T_{tp}(n\text{-D}_2) = 18.732$  K.<sup>1,2,6</sup> With this reference, we plot our semiempirical results in Fig. 2. The positive curvature derives from a dominant  $x_p^2$  dependence in  $P_Q$  and is in qualitative agreement with the data plotted in the figure. We fit values obtained from the rigorous expression to a quadratic form and obtained

$$T_{tp}(x_p) = 18.694 + 0.0256x_p + 0.278x_p^2. \quad (5)$$

Equation (5) represents the data to within a few mK.

From our model the predicted difference in  $T_{tp}$  between  $n\text{-D}_2$  and  $e\text{-D}_2$  is 35 mK, which agrees with the latest measured values  $34 \pm 1$  mK.<sup>6,7</sup> However, for values of  $x_p$  larger than 30%, there is significant disagreement. At  $x_p = 80\%$ , for example, the model predicts  $\Delta T_{tp} = 0.196$  K, which is nearly double the value inferred from the experimental data of Grenier and White.<sup>14</sup> Therefore, to further test our theory, we calculate the difference in triple-point temperatures between  $e\text{-H}_2$  and  $n\text{-H}_2$ , which contains 75%  $o\text{-H}_2$  ( $J = 1$ ) and 25%  $p\text{-H}_2$  ( $J = 0$ ).

The parameters required for this calculation are the molar volumes of solid and liquid hydrogen at the triple point,  $T_{tp} = 13.81$  K for  $e\text{-H}_2$ . For liquid  $p\text{-H}_2$  we use the value  $V_l = 26.176$   $\text{cm}^3/\text{mol}$ , given by Goodwin and Roder.<sup>24</sup> This  $V_l$  combined with Grilly's measured

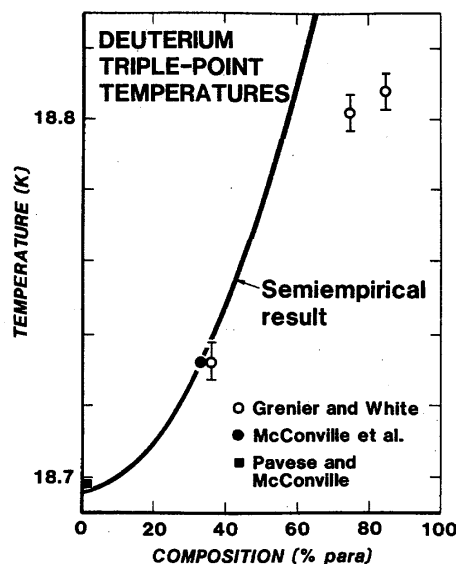


FIG. 2. Plot of the triple-point temperatures of deuterium as a function of the *para* concentration. The shaded symbols represent the latest high-precision results of Refs. 6 and 7. The open circles are from Ref. 14.

$\Delta V_m = 2.79 \text{ cm}^3/\text{mol}$  (quoted in Ref. 25) yields a solid molar volume of  $V_s = 23.386 \text{ cm}^3/\text{mol}$ . The latter value is smaller than  $23.483 \text{ cm}^3/\text{mol}$  that Krause and Swenson<sup>25</sup> obtained by extrapolating values along their melting curve. But it is somewhat larger than the x-ray diffraction results  $23.313 \pm 0.016 \text{ cm}^3/\text{mol}$  measured by Krupskii *et al.*<sup>26</sup> For our purposes, the intermediate value is sufficient. A difference to  $\pm 0.1 \text{ cm}^3/\text{mol}$  introduces an uncertainty of only  $\pm 1 \text{ mK}$  in the final result for  $T_{\text{tp}}$ .

For the slope of the melting curve, we use  $dP_m/dT_m = 31.7 \text{ bar/K}$ , which is an average between 31.6 and 31.8 bar/K—values we found by fitting the melting data of Bereznyak and Sheinina<sup>16</sup> on  $n\text{-H}_2$  and  $e\text{-H}_2$ , respectively. [The small difference in slopes is consistent with the small quadrupole contribution to the latent heat of fusion for hydrogen. We evaluated Eq. (4) at the triple point and found  $\Delta h_{\text{fQ}} = 1.17 \text{ J/mol}$ , which is only 1% of the total latent heat of fusion,  $\Delta H_f = 117.6 \pm 0.5 \text{ J/mol}$ .<sup>28-30</sup>]

Equations (2) and (3) with  $x_p = 0.75$  give  $\Delta T_{\text{tp}} = 0.159 \pm 0.001 \text{ K}$ , which is only about 10% higher than the value  $\Delta T_{\text{tp}} = 0.146 \text{ K}$  inferred from IPTS-68.<sup>27</sup> Bereznyak and Sheinina<sup>16</sup> measured  $\Delta T_{\text{tp}} = 0.134 \text{ K}$ , a somewhat lower value, but the difference between experiment and theory in the case of hydrogen is much smaller than that found above for deuterium. Our theoretical model may therefore overestimate  $\Delta T_{\text{tp}}$  by 10% or 20%, but the large discrepancy with the Grenier and White<sup>14</sup> data suggests to us that either the triple-point temperatures or the estimated *para* concentrations of their samples may have been considerably smaller than those reported.

#### 4. Summary and Conclusions

The triple point of deuterium is receiving considerable attention as a possible reference for defining the temperature scale between the hydrogen and neon fixed points. In support of this effort, four sets of high-precision measurements have been carried out in the past six years. We review these and present some theoretical arguments to complement the experimental results.

It has long been known that measured triple-point temperatures of  $\text{D}_2$  are quite sensitive to HD contamination. Most recent experiments<sup>6,7</sup> have taken great care to obtain and preserve ultrapure samples. We believe the best established  $T_{\text{tp}}$  is that for  $n\text{-D}_2$ ,  $18.732 \pm 0.001 \text{ K}$  (NBS-IPTS-68), measured by McConville *et al.*<sup>6</sup> This value is consistent with the most accurate and precise results previously available.<sup>1,2</sup> The data of Kemp<sup>4</sup> and Ancsin<sup>5</sup> are considerably lower. However, direct impurity analyses were not run on these samples; therefore, in view of the critical influence of HD contamination, we do not consider these results to seriously challenge our conclusion.

In general, the triple point of  $n\text{-D}_2$  is not favored as a temperature reference<sup>6</sup> because spin conversion renders the samples too unstable. Equilibrium  $\text{D}_2$  avoids this problem, but the necessary catalyst introduces additional complications. Measurements of the triple-point temperature of  $e\text{-D}_2$  have produced results that vary by almost 30 mK. Among these results, we believe the latest,  $18.6982 \pm 0.0002 \text{ K}$

(NBS-IPTS-68), by Pavese and McConville<sup>7</sup> to be the most reliable. More than in previous work, great care was given in this experiment to eliminate contamination both in the original sample and in the conversion catalyst. Our own theoretical considerations corroborate this result. The difference between the latest measurements of  $T_{\text{tp}}$  for  $e\text{-D}_2$  and  $n\text{-D}_2$  agrees quantitatively with estimates derived from an existing model for effective pressures induced by quadrupole interactions and some basic thermodynamic arguments. At higher concentrations of  $p\text{-D}_2$  ( $J = 1$ ), experiment and theory disagree, but a less severe disparity in hydrogen suggests that our theory may need only minor modifications.

We see that our model is useful in providing theoretical confirmation of differences in measured  $T_{\text{tp}}$  values. But besides this, its predictions support the adoption of  $e\text{-D}_2$  over  $n\text{-D}_2$  as a reference material because they demonstrate the relative insensitivity of the former triple point to absolute uncertainties in  $x_p$ . For example, we calculate the difference in  $\Delta T_{\text{tp}}$  between  $x_p = 0$  and  $x_p = 0.05$  to be only 1 mK, whereas between  $x_p = 0.30$  and 0.35 we find a difference of 11 mK, which is more than a factor of 10 larger.

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