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On the Melting Curve of Sulfur Hexafluoride

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A previous correlation for the melting curve of sulfur hexafluoride (SF₆) is inconsistent with the thermodynamic slope at the triple point derived from the Clapeyron equation. It is shown that this is probably due to the previous authors combining an accurate measurement of the triple point with melting-curve data that were distorted by impurities. A new equation is proposed that is consistent with the Clapeyron slope. © 2017 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved. <https://doi.org/10.1063/1.5005537>

Key words: freezing; melting; metrology; SF₆; temperature; thermodynamics; triple point.

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1. Introduction

In 2009, Guder and Wagner published a reference-quality equation of state (EOS) for sulfur hexafluoride (SF₆).¹ This EOS successfully provides thermodynamic properties of SF₆ over a wide range of fluid conditions with small uncertainties.

As a boundary for the validity of their EOS, Guder and Wagner gave an equation for the melting pressure, p_m , as a function of temperature T . The melting curve $p_m(T)$ (in particular its initial slope at the triple-point temperature T_t) is important in metrology because of recent work toward developing the triple point of SF₆ (at approximately 223.555 K) as a non-toxic alternative to the triple point of mercury (234.3156 K) for realization of the temperature scale.^{2,3}

In the course of the work reported in Ref. 3, it was realized that the slope dp_m/dT given by the Guder–Wagner correlation at the triple point was significantly larger than that given by a thermodynamic estimate based on the Clapeyron equation. In the following, we derive the Clapeyron slope from thermodynamic data, diagnose the probable reason for the inaccurate initial slope of the correlation of Guder and Wagner, and present a new correlation for $p_m(T)$ that is consistent with the Clapeyron slope.

2. The Clapeyron Equation for the Melting Curve of SF₆

The Clapeyron equation is a rigorous thermodynamic relationship connecting the slope of a phase-transition boundary to the enthalpy and volume change of the transition. For the melting curve, it is

$$\frac{dp_m}{dT} = \frac{\Delta h_m}{T\Delta v_m}, \quad (1)$$

where Δh_m and Δv_m are the changes in molar enthalpy and molar volume for the melting transition (liquid property minus solid property).

There have been two high-precision measurements of the enthalpy of melting Δh_m at the triple point. Ohta *et al.*⁴ reported 5.225(2) kJ mol⁻¹. Rourke² reported 5.28 kJ mol⁻¹ and did not state an uncertainty. It is difficult to say which value is more reliable; while the study of Ohta *et al.* was specifically devoted to calorimetry, their SF₆ appears to have been less pure than that used by Rourke. We choose $\Delta h_m = 5.25$ kJ mol⁻¹, which is roughly the mean of the two values. Because of the discrepancy between the sources and the possibility of impurity effects, we estimate the expanded ($k = 2$) uncertainty of this value to be 0.04 kJ mol⁻¹.

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To evaluate Δv_m , the molar volumes of both the liquid and solid at the triple point are needed. For the liquid, the EOS of Guder and Wagner¹ yields a volume of $79.16 \text{ cm}^3 \text{ mol}^{-1}$ with a relative expanded uncertainty of 0.02%.

Unfortunately, there appear to be no high-accuracy measurements of the solid volume at the triple point. This may be because the triple-point pressure, p_t , is roughly 0.23 MPa,⁵ so that pressurized apparatus would be required for a measurement. Kiefe *et al.*⁶ give a solid density at 221 K, just below the triple-point temperature, but this was only a linear extrapolation from two data points below 200 K.

There have been several crystallographic measurements^{7–13} of the lattice spacing near ambient pressure in the high-temperature form of SF₆, which is stable from roughly 94 K to the triple point. These data can be converted to molar volumes since the structure (body-centered cubic) is known. Konstantinov *et al.*¹⁴ reported solid volumes closest to the triple point (up to 212 K), but the measurement method was not stated. For extrapolation to the triple point, the studies at temperatures near 100 K (Refs. 7, 9, 10, and 12) are not very useful. In Fig. 1, we plot the data for temperatures above 150 K. There is a small inconsistency between the data of Konstantinov *et al.*¹⁴ and the points of Taylor and Waugh⁸ and of Powell,¹¹ and we also note that the function is not quite linear on these coordinates. Visually extrapolating Fig. 1 to the triple point, we estimate a volume of $64.1 \text{ cm}^3 \text{ mol}^{-1}$, with an expanded uncertainty of $0.5 \text{ cm}^3 \text{ mol}^{-1}$. Combining this with the liquid density yields $\Delta v_m = 15.06 \text{ cm}^3 \text{ mol}^{-1}$ with an expanded uncertainty of $0.5 \text{ cm}^3 \text{ mol}^{-1}$.

Inserting the above numbers into Eq. (1) yields a slope of $dp_m/dT = 1.56 \text{ MPa K}^{-1}$, with an expanded ($k = 2$) uncertainty of 0.05 MPa K^{-1} (roughly 3% in relative terms). This uncertainty is dominated by the uncertainty in the solid molar volume at the triple point.

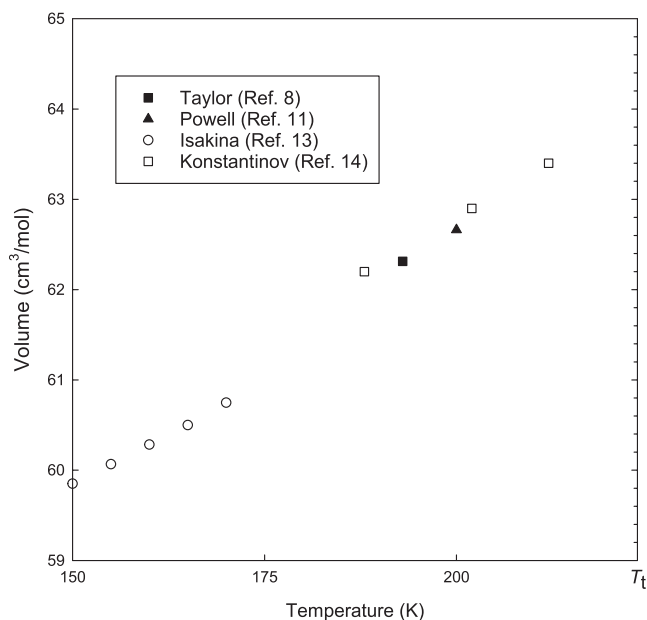


FIG. 1. Solid molar volumes of SF₆ near the triple-point temperature T_t .

3. Analysis of Guder–Wagner Melting Equation

The Clapeyron slope of 1.56 MPa K^{-1} is inconsistent with the value 1.83 MPa K^{-1} obtained at T_t from the correlation of Guder and Wagner.¹ It is instructive to consider the cause of this discrepancy.

Guder and Wagner anchored their $p_m(T)$ correlation at the triple-point temperature (223.555 K) and pressure (0.231 429 MPa) reported by Funke *et al.*⁵ The consistency of their value of T_t with the recent state-of-the-art determination by Rourke² (223.555 23 K) confirms the accuracy of that starting point. Guder and Wagner then fit their correlation through the freezing points reported by Vacek and Zollweg,¹⁵ which were at pressures between 12 MPa and 48 MPa.

However, Vacek and Zollweg reported that their freezing data extrapolate to a triple-point temperature of 222.63 K. If one begins with that temperature instead of the 223.555 K used by Guder and Wagner, the slope dp_m/dT of a fit through the data is in good agreement with the Clapeyron equation. So, the freezing points of Vacek and Zollweg seem to be self-consistent, but they lead to a triple-point temperature that is too low.

The most likely explanation is that all the freezing temperatures reported by Vacek and Zollweg¹⁵ are too low. This probably represents a freezing-point depression due to impurities in SF₆. Only recently has SF₆ of high purity become available; this is evident from older determinations of the triple-point temperature, where all data prior to 1993 were about 1 K too low.³ This matches the approximately 0.9 K difference between the true triple point and that given by Vacek and Zollweg. Since the amount by which impurities depress the freezing point should not vary strongly with pressure, this suggests that all the freezing temperatures of Vacek and Zollweg are too low by roughly 0.9 K.

Therefore, the likely reason that Guder and Wagner obtained an inaccurate slope is that they constrained their equation to an accurate triple point corresponding to highly pure SF₆ but then fitted it to freezing points that were depressed, probably due to impurities.

4. Correlation of Melting Curve

Once we recognize that older data are likely distorted by freezing-point depression, we can correct the data based on the deviation of the reported triple point. For the data of Vacek and Zollweg, this involves shifting the reported temperatures by 0.9 K as mentioned above. Konstantinov *et al.*¹⁴ mention a freezing point of 222.4 K, although it is not clear whether they measured the value or simply quoted it from another source. In the absence of details, we increase their reported melting temperatures by 1.1 K while recognizing that this can only be a rough estimate of the proper adjustment.

Vacek and Zollweg¹⁵ cite additional melting-curve data of Semenova *et al.*,¹⁶ but we were unable to obtain these data. From a plot in the paper of Vacek and Zollweg, it appears that the melting pressures of Semenova *et al.*¹⁶ are systematically higher by at least 10 MPa in the region where the studies

overlap. We therefore used only Refs. 14 and 15 for our correlation.

In the range of temperatures where the studies overlap, the melting pressures reported by Konstantinov *et al.*¹⁴ are systematically higher than those of Vacek and Zollweg.¹⁵ Some difference would be expected because Vacek and Zollweg report that their data correspond to a lower bound for the melting pressure. However, they state that the difference from the true melting pressure is unlikely to be more than 0.4 MPa, which is much smaller than the 2-4 MPa difference between their data and those of Konstantinov *et al.* Another factor to consider is that the data of Vacek and Zollweg appear to be more consistent with the Clapeyron slope derived in Sec. 2. Taking all of this into account, we chose to weight each point from Refs. 14 and 15 equally. This effectively gave priority to the data of Vacek and Zollweg, because they reported eight points while Konstantinov *et al.* reported three points.

The small number of rather uncertain data do not justify a complex fitting equation. The widely used Simon–Glatzel equation¹⁷ is

$$p_m(T) = p_t + a \left[\left(\frac{T}{T_t} \right)^c - 1 \right]. \quad (2)$$

Equation (2) was fitted to the data while constraining the initial slope dp_m/dT at the triple point to be consistent with that derived in Sec. 2. The resulting parameters are $a = 223.7$ MPa and $c = 1.555$. For consistency with the fluid EOS, the triple-point parameters are those used by Guder and Wagner,¹ $T_t = 223.555$ K and $p_t = 0.231\,429$ MPa.

Figure 2 compares Eq. (2) to the data of Refs. 14 and 15, showing both the originally reported experimental values (open symbols) and those obtained by correcting the reported temperatures as described above (filled symbols). It is evident

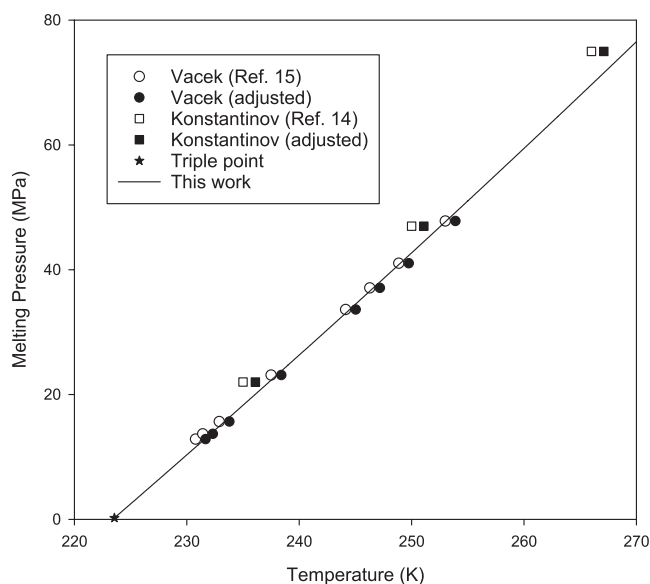


Fig. 2. Experimental melting pressures of SF₆ compared with Eq. (2).

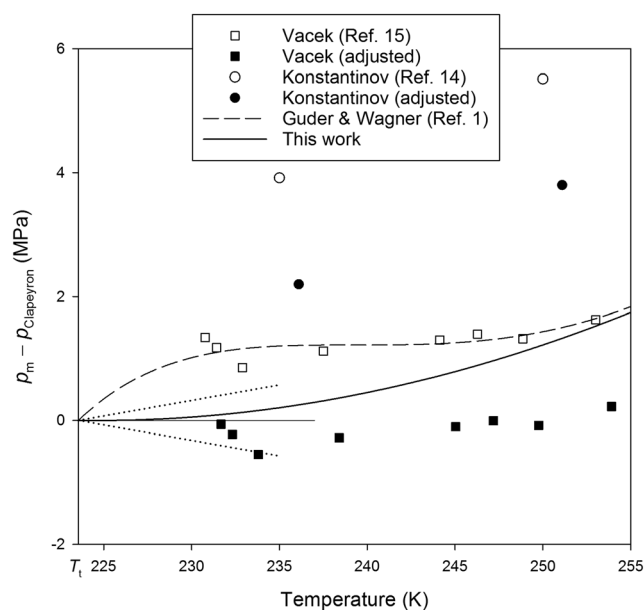


Fig. 3. Experimental melting data and correlations compared with the initial Clapeyron slope for SF₆. Dotted lines correspond to the uncertainty in the initial Clapeyron slope $(dp_m/dT)_t$.

that the data are fitted reasonably, with the fit a compromise that gives heavier weight to the data of Vacek and Zollweg.¹⁵

To see the relationship of the Clapeyron slope to Eq. (2) and to the correlation of Guder and Wagner,¹ Fig. 3 plots the data and correlations in a format where the zero line represents melting pressures obtained by extrapolating in temperature with the initial Clapeyron slope $(dp_m/dT)_t$ [$p_m = p_t + (dp_m/dT)_t(T - T_t)$]. The dotted lines represent the expanded uncertainty of that slope. Figure 3 makes clear that the incorrect initial slope of Guder and Wagner is a result of combining an accurate triple point with the uncorrected melting points of Vacek and Zollweg. Equation (2) reproduces the corrected experimental melting data and (by construction) agrees with the initial dp_m/dT derived from other thermophysical data.

5. Discussion

Because of the probable effect of impurities on the available experimental data and the lack of consistency among published data, there is significant uncertainty in the course of $p_m(T)$ at higher pressures. However, the only concern for temperature metrology is the slope of this function at the triple point. That initial slope can be estimated with good accuracy (expanded uncertainty of approximately 3%) from the Clapeyron equation. Reduction in the uncertainty of this slope would require a more accurate determination of the molar volume of the solid phase at the triple point.

Equation (2) reproduces this initial Clapeyron slope and reasonably represents the melting data that have been corrected for the probable effect of impurities. It is recommended that Eq. (2) replace the equation given by Guder and Wagner¹ for the melting curve of SF₆.

Acknowledgments

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