

Recommended Thermophysical Data for Ferrocene - an Interlaboratory Study

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Ferrocene is a good candidate for calibrating vapor pressure measurements [1], and ICTAC recommends it as a primary standard for sublimation enthalpy [2]. However, the ICTAC recommendation was based mainly on Clausius-Clapeyron calculations from vapor pressure data with empirical corrections. The resulting values span a range of approximately $5 \text{ kJ}\cdot\text{mol}^{-1}$, which is much greater than the experimental uncertainty. This work presents a joint effort of three laboratories (ICT Prague, University of Porto and NIST) to develop improved thermophysical data for ferrocene. Calculated ideal gas heat capacities and critically assessed experimental data for vapor pressure, crystalline heat capacity, and enthalpy of sublimation were treated simultaneously to obtain a consistent thermodynamic description. All of the physicochemical properties needed as input for the simultaneous correlation were newly determined in this work. The measurements were performed with the same sample of ferrocene, which was purified by vacuum sublimation and then distributed among the three laboratories. Vapor pressures were measured using the static method with three apparatuses over the temperature range from 293 to 452 K. Heat capacities of the crystalline phase were determined by Calvet and drop calorimetry. These values of heat capacity, while in mutual agreement, significantly deviate from the previously published values. The direct measurements of enthalpies of sublimation were carried out by Calvet microcalorimeter. The thermodynamic properties in the ideal gaseous state were calculated using the methods of statistical thermodynamics based on experimental as well as calculated fundamental vibrational frequencies and molecular structure data.

[1] A.C.G. van Genderen, H.A.J. Oonk, *Colloid Surf. A-Physicochem. Eng. Asp.* 213, 107-115 (2003).

[2] R. Sabbah, A. Xu-wu, J.S. Chickos, M.L. Planas Leitao, M.V. Roux, L.A. Torres, *Thermochim. Acta* 331, 93-204 (1999).

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