The Wagner Equation and the Extrapolation of Vapor Pressure Data to the Triple Point

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Vapor pressures are important thermodynamic properties of pure organic substances and many equations have been proposed to represent them. One of the most successful is the Wagner Equation. The most commonly used form of the Wagner Equation has four adjustable parameters. The first two parameters are always to the power of 1 and 1.5; the most popular form contains the power 2.5 and 5 for the last two terms. Other forms of the equation, for example the 3 and 6 or 2 and 4 have been used as well in the literature. We have found that five adjustable parameters are needed for correlation of accurate data over a wide temperature range. The regression analysis with only four parameters produces systematic deviations and the equations do not fit the experimental data to within the experimental uncertainty. In this work we have used our vapor pressures measured using comparative ebulliometry, over a pressure range of 10 kPa up to approximately 200 kPa below the critical pressure of the following compounds: pentane, hexane, heptane, octane and cyclohexane. Our final equation has five parameters plus the critical pressure and has the following exponents: 1, 1.5, 2, 3, and 4. Other less successful forms were analyzed and they will be discussed in the presentation. Since the vapor pressures were measured over a wide temperature range, we found that the equation can extrapolate to the triple point pressure without any thermal data such as enthalpies of vaporization and heat capacities. In this case, dp/dT decreases smoothly and is positive at all stages of the extrapolation, demonstrating that the Wagner equation based on accurate vapor pressures, does indeed extrapolate downwards in a reliable way.