Influence of Adsorption and Precondensation on the Calculation of Virial Coefficients of Carbon Dioxide

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Recently Hellmann [*J. Chem. Phys.* **2017,** *146*, 054302] calculated the density virial coefficients of carbon dioxide. Excellent agreement of the *ab initio* values with experimental results was seen for the second virial coefficient. For the third virial, however, there were significant differences between theory and multiple experimental data sets at temperatures between 240 K and 300 K. Significant differences were also observed between the *ab initio* values and those calculated by an equation of state (EOS) fitted to high-accuracy experimental data. These differences were as large as 1000 cm^6-mol^{-2} (approximately 20 % of the value) at T = 270 K. The location of the maximum in the third virial varied by 31 K between theory and the equation of state. This raises the question: Was there an error in the *ab initio* calculations or was there a systematic error in the experiments? Thus, we measured the vapor-phase (p, r, T) properties of CO_2 between 230 K and 310 K at pressures up to approximately 99 % of the dew-point pressure utilizing a highly accurate two-sinker densimeter. We used these data to fit virial coefficients and found that adsorption of CO_2 onto the densimeter sinkers affected the measured densities and, thus, the calculated virial coefficients, at pressures greater than about 85 % of the dew-point pressure. Furthermore, higher-order (fourth and fifth) virial coefficients must be included in the fit to obtain reliable values for the second and third virials. Considering these factors, we obtain good agreement of the experimental third virial coefficient with the *ab initio* values and conclude that adsorption can exert a distorting influence on the calculation of virial coefficients.