First-Principles Calculations for Humidity Standards

A.H. Harvey^{C,S}
Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, CO, U.S.A.
aharvey@boulder.nist.gov

P.H. Huang
Process Measurements Division, NIST, Gaithersburg, MD, U.S.A.

Characterization of humidity standards requires accurate values for the enhancement factor, which represents the correction of the equilibrium partial pressure of water in the gas phase to that given by water's vapor pressure. At most conditions of interest, the primary contributor to the nonideality in the gas phase is the second virial coefficient for interactions between water and air molecules. This quantity is difficult to measure accurately; while some good data exist, they cover a relatively narrow temperature range.

Computational chemistry provides an alternative approach to the calculation of second virial coefficients. For pairs of small molecules (like water with air components), it is now possible to develop quantitatively accurate pair potentials for the molecular interaction. Integration of these potentials then yields second virial coefficients over a wide range of temperatures; in most cases, these have smaller uncertainties than can be obtained with current experimental techniques.

In this work, we make use of second virial coefficients recently developed from high-quality pair potentials for water with argon, nitrogen, and oxygen to derive second virial coefficients for water with "air." The calculations cover the entire temperature range of interest for humidity standards. Estimates of uncertainty are also given. These results are compared with the available experimental data for the water/air second virial coefficient, and we discuss implications for improvements in humidity standards.