

Thermodynamic Properties of Humid Gases from First Principles

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Numerous scientific and industrial situations require thermodynamic properties of gas mixtures containing water. Examples include the development of humidity standards (where the dominant correction is the nonideality of water in the vapor phase) and design calculations for the utilization of synthesis and combustion gases in advanced power-generation cycles. In many of these cases, the conditions of temperature and pressure are such that the appropriate level of description is that of the second virial coefficient, the first-order correction to the ideal-gas law.

Unfortunately, the experimental measurement of cross second virial coefficients for water/gas binaries is very difficult, due to adsorption of water on apparatus and/or difficulty in measuring small concentrations of water in the vapor phase. As a result, the available experimental data have large uncertainties and cover an insufficient temperature range for many applications.

Our approach uses *ab initio* computational quantum chemistry to develop quantitatively accurate intermolecular potential-energy surfaces for the binary systems of interest. Because the computational expense for a sufficiently high-level calculation of the entire surface would be prohibitive, a two-part approach is used. First, the full surface is calculated at a "medium" level of theory (such as MP2). Then, a small number of high-level calculations are used to scale the surface (or, in a recent refinement, each of several independent contributions to the surface) to a final result corresponding to a high level of theory.

Once the potential-energy surface is obtained, the second virial coefficient can be computed rigorously (with quantum corrections) from statistical mechanics; this calculation covers all temperatures of interest in contrast to the limited range of most experimental studies. Because we can make a reasonable estimate of the uncertainty in our pair potentials, we can propagate that into uncertainties in our calculated second virial coefficients.

This approach was first applied to water with the first three noble gases [1,2]. For water-argon, the only system for which significant experimental data are available, our results are consistent with the experimental data but have substantially smaller uncertainties. Similar results have been obtained for water with hydrogen [3], a system of interest for fuel cells, and for water with the air components nitrogen [4] and oxygen [5].

Our results for water with argon, nitrogen, and oxygen can be combined to produce an effective second virial coefficient for water with "air." This is a key quantity for humidity standards, and it has been the subject of painstaking experimental work [6-8]. Preliminary calculations [9] indicate that our results are consistent with the existing high-accuracy data, but cover a much wider temperature range than the experimental data.

Efforts are underway on the water/CO pair; carbon monoxide is a major component of the synthesis gas in the integrated gasification combined cycle (IGCC) process for "clean coal" power generation. In addition to the properties of the synthesis gas itself, there is interest in the equilibrium water-vapor content of the gas after it is "quenched" with liquid water; current engineering models do not seem to give a reliable description of this problem. In the near future, we will study the water/CO₂ system in order to improve the knowledge of the properties of combustion gases in power cycles.

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