A CRITICAL REVIEW OF THE SECOND VIRIAL COEFFICIENTS FOR WATER VAPOR WITH AIR AND WITH ARGON

Peter H. Huang 1, Allan H. Harvey 2

1 National Institute of Standards and Technology, Gaithersburg, Maryland, U.S.A.
2 National Institute of Standards and Technology, Boulder, Colorado, U.S.A.

ABSTRACT

The equations defining the interaction second virial coefficients for water vapor with air and with argon are presented with the experimental and computational methods used in deriving the coefficients. Comparative tabulations of the coefficients ranged from −20 °C to 100 °C are given along with the associated uncertainties. Based on ab initio quantum calculations, it is feasible to construct highly accurate pair potential for Ar-H2O mixture to achieve a smaller uncertainty in the second virial coefficient than that derived from an experiment. For Air-H2O mixture, the uncertainty obtained from vapor-liquid water isothermal equilibrium experiment is comparable to that of Ar-H2O mixture obtained from first principle calculations.

1. INTRODUCTION

Humidity standards, such as two-pressure/two-temperature type of generators, currently used by national metrology institutes and industrial laboratories for calibration of hygrometers, are based on air-water vapor/liquid water or air-water vapor/solid ice phase equilibrium data. These data are of major importance for our knowledge of thermodynamic properties of air-water vapor mixtures including water vapor density, enthalpy, entropy, and Gibbs free energy [1]. Their molar quantities are directly related to the mole fraction of water vapor and the effects of interaction between water molecules and air molecules. The interactions are mainly characterized by the second interaction virial coefficient, which represents the first order corrections to the ideal gas law to describe appropriate thermodynamic properties of gas-water vapor mixtures. Second virial coefficients are useful both in solving equation-of-state problems in gas mixtures, and for evaluating fugacities of gas mixture components, such as in research work involving solution theories and intermolecular interactions, in experimental thermodynamics studying the properties of substances and substance mixtures, and in chemical engineering design calculations.

From the earlier work [2–4] for the temperature range of −20 °C to 70 °C, it appears that the experimental data of second virial coefficient for water vapor in air is now one of the best defined of second interaction virial coefficients. The properties of air-water vapor mixture are important for humidity standards, meteorological modeling, design of combustion turbines used in the power industry, and of heating, ventilation, and air conditioning systems. The properties of argon-water vapor mixture are equally important for humidity standards, semiconductor processing, electric/nuclear power generation, and biological as well as chemical processes. Molecular interactions between water and argon have been studied using microwave and laser spectroscopy [5–7]. Recently, Ar-H2O has received much more attention and is interesting because the potential-energy surface has been studied both by ab initio calculations and by a constrained fit of a suitable functional form to spectroscopic data.

This paper reviews the critically evaluated second cross virial coefficients for Air-H2O and Ar-H2O mixtures based on open worldwide literature. Tables are presented for comparison of the most recent theoretical calculations and the experimental data covering the range from −20 °C to 100 °C for the interest of humidity measurement and standards.
2. THEORETICAL BACKGROUND

An equation of state for non-ideal gases can be expressed by the form of the virial expansion

\[
\frac{pV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \ldots
\]

(1)

wherein \( p, V, R \) and \( T \) are the pressure, molar volume, gas constant and absolute temperature, respectively, \( B(T), C(T), D(T) \), etc. are the second, third, fourth, … virial coefficient. According to statistical mechanics, the values of the virial coefficients \( B, C, \) and \( D \), accounting for the experimental divergences of imperfect gases form the equation of state of a perfect gas, will provide valuable information on the intermolecular forces.

In the case of a gas mixture, the second virial coefficient \( B(T) \) in the equation of state (1) is given as follows

\[
B(T) = \sum_{i=1}^{\nu} \sum_{j=1}^{\nu} x_i x_j B^{(ij)},
\]

(2)

where \( \nu \) is the number of components of the mixture, and \( x_i \) is the mole fraction of the \( i \)-th component in the gas mixture,

\[
\sum_{i=1}^{\nu} x_i = 1.
\]

(3)

Classical statistical mechanics yields \( B(T) \) in the form of

\[
B(T) = -\frac{N}{2\Omega} \iiint \left\{ e^{-\frac{u^{(12)}_{ij}}{kT}} - 1 \right\} d\mathbf{r}_{ij} d\omega_i d\omega_j
\]

(4)

with \( N \) denoting Avogadro’s number, \( k \) Boltzmann’s constant, \( T \) the Kelvin temperature, \( u^{(12)}_{ij} \) the total potential energy of interaction between the molecules "1" and "2" of species "1" and species "2", \( \mathbf{r}_{ij} \) the vector connecting their centers, and \( \omega_i \), \( \omega_j \) variables describing their orientation; \( \Omega = \int d\omega = \int d\omega_j \).

The total potential energy can be expressed in the form

\[
u^{(12)}_{ij} = u^{(0)}_{ij}(\mathbf{r}_{ij}) + V^{(12)}_{ij}(\mathbf{r}_{ij}, \omega_i, \omega_j)
\]

(5)

\( u^{(0)}_{ij}(\mathbf{r}_{ij}) \) being the potential energy due to the central forces (angle-dependent potentials), and \( V^{(12)}_{ij}(\mathbf{r}_{ij}, \omega_i, \omega_j) \) the energy due to the tensorial forces (angle-dependent potentials). \( V^{(12)}_{ij} \) may be considered as a perturbation in the energy \( u^{(0)}_{ij}(\mathbf{r}_{ij}) \) so that the second virial coefficient of Eq. (4) can be expressed by a series of expansion

\[
B^{(ij)} = B^{(ij)}_0 + \sum_{n=1}^{\infty} B^{(ij)}_n,
\]

(6)
wherein the zero term

\[ B_0^{(ij)} = -2\pi N \int_0^\infty \left( e^{-\frac{u^{(0)}(r_{ij})}{kT}} - 1 \right) r_{ij}^2 dr_{ij} \]  \hspace{1cm} (7)

is the second virial coefficient for a central force field \( u^{(0)}(r_{ij}) \), and the subsequent terms given by

\[ B_n^{(ij)} = -\frac{N}{2\Omega^2 n!} \left( -\frac{1}{kT} \right)^n \iint \left[ \int r_{ij}^{(12)}(r_{ij}, \omega_i, \omega_j) \right] e^{-\frac{u^{(0)}(r_{ij})}{kT}} d\omega_i^{(1)} d\omega_j^{(2)} \]  \hspace{1cm} (8)

are contributions thereto resulting from various directional forces acting between two dipole or two quadrupole molecules. Eq. (8) is not used for Air-H\(_2\)O and Ar-H\(_2\)O mixtures because air and argon molecules have zero dipole moments.

For central forces, where the intermolecular energy is assumed to depend only on the distance between the molecules, the most widely used type of \( u^{(0)}(r_{ij}) \) is an inverse sixth-power attraction to represent the dispersion forces superposed on an inverse twelfth-power repulsion representing the repulsive forces due to the overlap of closed shells of electrons. This type of field is the well-known Lennard-Jones (LJ) (12-6) potential, which has been very successful in correlating the thermodynamic properties of inert gases, given by

\[ u^{(0)}(r_{ij}) = 4\varepsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} \]  \hspace{1cm} (9)

wherein the parameters \( \varepsilon_{ij} \) and \( \sigma_{ij} \), having the dimensions of a length and energy, respectively, are constants characteristic of the interacting molecules. For non-polar spherical molecules, the second virial coefficient can be expressed by a reduced quantity, \( B^* \), as a function of the reduced temperature, \( T^* \), where

\[ B_j^*(T^*) = \frac{B_j}{\frac{2\pi N}{3} \sigma_j} = \frac{B_j}{(b_0)_j} ; \quad T^* = \frac{T\kappa}{\varepsilon} \]  \hspace{1cm} (10)

The force constants between unlike molecules relate to those between like molecules by the empirical combining rules

\[ \sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) ; \quad \varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2} \]  \hspace{1cm} (11)

3. EXPERIMENTAL METHODS

There is no direct method of measuring the second virial coefficients of the pair Air-H\(_2\)O and Ar-H\(_2\)O molecules. It must be obtained from Eq. (2) for a binary mixture. Experimental methods based on the vapor-solid ice equilibrium and the vapor-liquid water equilibrium had been used. In these methods,
the water vapor concentration in the vapor phase was measured as function of the total equilibrium pressure, which ranged from 10 atmospheric pressures to 150 atmospheric pressures [2,4]. The virial equation of state, Eq. (1), was then used to determine the second virial coefficients, $B_{12}$, of Air-H$_2$O and Ar-H$_2$O along with the known values of the pure-component second virial coefficients of air or argon, $B_{11}$, and water vapor, $B_{22}$, as well as the saturation water vapor pressure at a given temperature.

There are two known independent determinations of the water vapor concentration in air from which the second interaction virial coefficient was derived. Both Hyland [2] and Wylie and Fisher [4] performed single saturation isotherm experiments at various saturator pressures and temperatures. The mean values of for each temperature and the associated expanded uncertainty ($k = 2$) are given in table 1 showing a very close agreement. It appears that the experimental data of $B_{12}$ for Air-H$_2$O is now one of the best defined of second interaction virial coefficients.

In contrast to vapor-liquid/solid isothermal equilibrium experiments, molecular beam elastic differential scattering experiments had been used to study non-polar molecule-polar molecule and polar molecule-polar molecule interactions [8,9]. These experiments yielded information about the parameters of the intermolecular potential model chosen to characterize the interaction of molecules studied. The method consists of determining the laboratory collision cross sections, obtained from the computed quantum mechanical center-of-mass cross sections, over the experimental parameters such as beam velocity distributions and the total apparatus resolution. The data were analyzed via the best-fit procedure using a (LJ) 12-6 model potential of Eq. (9) to determine the potential parameter, $\epsilon_{12}$, the well depth, and $\sigma_{12}$, the zero of the pair potential.

For Ar-H$_2$O pair potential, the results of data analysis were $\sigma_{12} = (2.93 \pm 0.22)$ Å and $\epsilon_{12}/k = (164 \pm 11)$ K obtained by Bickes et al. [8] and $\sigma_{12} = 3.00$ Å and $\epsilon_{12}/k = 179$ K by Brooks et al.[9], respectively. The agreement is most satisfactory. By averaging their mean values and retaining the standard deviation, one obtains $\sigma_{12} = (2.97 \pm 0.22)$ Å and $\epsilon_{12}/k = (172 \pm 11)$ K. In equations (7), (9), and (11), these potential parameters are used to determine the second virial coefficients given in table 2 for a comparison with these from vapor-liquid water isothermal equilibrium experiment of Rigby and Prausnitz at 25 °C, 50 °C, 75 °C and 100 °C [10].

The second virial coefficient for a binary vapor mixture has also been determined from the Joule-Thomson experiment. Measurements of the excess enthalpy of Ar-H$_2$O vapor had been made using a flow calorimeter [11]. Analysis of the excess enthalpy yields the cross term isothermal Joule-Thomson coefficient $\phi_{12}$ and second virial coefficient $B_{12}$. The $B_{12}$ obtained at 100 °C is in agreement with that from differential cross section measurements [8,9] as shown in table 2.

Table 1: Comparison of the second virial coefficients with expanded uncertainty ($k = 2$) for Air-H$_2$O

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$B_{12}$ (cm$^3$/mol)</td>
<td>$B_{12}$ (cm$^3$/mol)</td>
</tr>
<tr>
<td>−20</td>
<td>−43.3 ± 3.9</td>
<td></td>
</tr>
<tr>
<td>−10</td>
<td>−40.8 ± 2.7</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>−32.4 ± 1.4</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>−29.2 ± 2.4</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>−26.3 ± 2.1</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>−23.6 ± 2.9</td>
<td>−24.3 ± 2.5</td>
</tr>
<tr>
<td>70</td>
<td>−17.7 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>−18.7 ± 3.9</td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Comparison of the second virial coefficients with one standard deviation for Ar-H$_2$O
4. COMPUTATIONAL METHODS

The second virial coefficient $B_{12}$ for a pair of molecules may be calculated exactly if the intermolecular potential is known. This is an attractive option due to the difficulty of experimental determination of $B_{12}$. The equation relating $B_{12}$ to the pair potential $U_{12}$ is:

$$B_{12} = -\frac{1}{2} \int_{0}^{\infty} \left( e^{-U_{12}/k_B T} - 1 \right) \omega_1 \omega_2 \mathrm{d}r + \Delta B_{12} \text{(trans)} + \Delta B_{12} \text{(rot)}$$

where the angle brackets indicate Boltzmann-weighted averaging over all orientations $\omega_1$ and $\omega_2$ of molecules 1 and 2 and $r$ is the volume element of a spherical shell. The first term is the classical result with pair potential represented by Eq. (5); the next two terms are corrections for rotational and translational quantum effects. As temperature decreases, $B$ and all higher virial coefficients are negative and their absolute values increase indefinitely. Thus at very low temperatures the virial equation (1) diverges. Certainly Eq. (5) ceases to be valid because of quantum corrections especially for light molecules. These corrections are appreciable at above 100 K for He, H$_2$ and perhaps Ne. Simple first-order expressions for quantum effects [12] are sufficient for water with air components at temperatures of interest here.

The capabilities of ab initio quantum chemistry have advanced to the point where it is feasible to construct highly accurate pair potentials for H$_2$O with monatomic and diatomic molecules. Hodges et al. [13] used scaled perturbation theory to construct a potential-energy surface for H$_2$O with argon, and used this surface to calculate $B_{12}$. The results are fitted closely from 100 K to 2000 K by:

$$B_{12}(T) = a_1 (T^*)^{-0.31} + a_2 (T^*)^{-0.82} + a_3 (T^*)^{-2.24} + a_4 (T^*)^{-4.6}$$

where $T^* = T/(100 \text{ K})$, with $a_1 = 96.1591$, $a_2 = -211.074$, $a_3 = -96.4425$, and $a_4 = -12.6006$.

The calculated values are compared with the experimental data in table 3.
Table 3: Comparison of calculated and experimental values of $B_{12}$ with one standard deviation for Ar-H$_2$O

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Calculated [13] $B_{12}$ (cm$^3$/mol)</th>
<th>Experimental $B_{12}$ (cm$^3$/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>−20</td>
<td>−38.67 ± 3.85</td>
<td>−54 ± 13</td>
<td>[14]</td>
</tr>
<tr>
<td>−20</td>
<td>−20</td>
<td>−79 ± 14</td>
<td>[15]</td>
</tr>
<tr>
<td>25</td>
<td>−26.07 ± 3.17</td>
<td>−31 ± 11</td>
<td>[8,9]</td>
</tr>
<tr>
<td>25</td>
<td>−37 ± 6</td>
<td>−21 ± 8</td>
<td>[10]</td>
</tr>
<tr>
<td>75</td>
<td>−16.50 ± 2.72</td>
<td>−20 ± 4</td>
<td>[10]</td>
</tr>
</tbody>
</table>

In principle, similar development of intermolecular potential-energy surfaces for the pairs H$_2$O-N$_2$ and H$_2$O-O$_2$ should lead (when combined with the existing H$_2$O-Ar result) to values of $B_{12}$ for water with air that would be more accurate than the present results obtained from experiment. This effort is making progress; the work on H$_2$O-N$_2$ is nearly complete [16]. The development of a potential-energy surface for H$_2$O-O$_2$ is a more difficult undertaking, due to the open-shell electronic structure of the O$_2$ molecule. While the problem is not insurmountable, it is likely to be 2 or 3 more years before improved values of $B_{12}$ from first-principles calculations are available for water with air.

2. UNCERTAINTY

The experimental data of Ar-H$_2$O are not mutually consistent and have relatively large uncertainties, especially at lower temperatures below −20 °C as discussed in [13]. At −20 °C, results derived from two independent solubility measurements are not in agreement as shown in table 3. Above 0 °C, experimental values are in good agreement as shown in table 2, but not in good agreement with ab initio calculations as shown in table 3. For their values of $B_{12}$ for H$_2$O-Ar, Hodges et al. [13] were able to estimate an uncertainty based on the uncertainty in the pair potential. Because of the way in which quantum calculations converge as higher-level methods are used, they were able to make reasonable upper and lower bounds on the potential. Calculation with Eq. (1) from the most attractive and least attractive possible potentials produces a minimum and maximum possible value of $B_{12}$. The resulting uncertainty in $B_{12}$ varied slowly and smoothly with temperature, taking values of 3.85 cm$^3$/mol at 250 K, 3.17 cm$^3$/mol at 300 K, and 2.72 cm$^3$/mol at 350 K. These uncertainties are smaller than those associated with the experimental data as shown in table 3. However, they are comparable with those obtained from vapor isothermal equilibrium experiments for Air-H$_2$O mixture as shown in table 1.

The excellent agreement between values calculated with two independently-derived potential energy surfaces as discussed in [13] indicates that ab initio calculations now provides the most accurate values of $B_{12}$ for the water-argon system. Another advantage of this approach is that, given the pair potential, $B_{12}$ may be calculated at any temperature, including temperatures where experiments are not feasible.

REFERENCES


**Addresses of the Authors:**

Peter H. Huang, National Institute of Standards and Technology, Gaithersburg, Maryland, U. S. A., tel. +1 301 9752621, e-mail: peter.huang@nist.gov