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Second virial coefficients in vapor systems: Insights from air and argon mixtures

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Abstract

The second virial coefficient is a crucial parameter in understanding intermolecular interactions and non-ideal behavior in gas mixtures. This study focuses on evaluating the second virial coefficients of vapor mixtures with air and argon. The coefficients, ranging from $-20\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$, are provided in comparative tabulations together with the corresponding uncertainties. It is possible to build a very accurate pair potential for the Ar-H₂O mixture based on initial quantum calculations in order to achieve a lower uncertainty in the second virial coefficient than that which is derived from an experiment. The air-water mixture's uncertainty from the vapor-liquid water isothermal equilibrium experiment matches the air-water mixture's uncertainty from the alphabet calculations. These mixtures are essential in various industrial applications, including environmental monitoring, cryogenics, and aerospace technologies. Using a combination of empirical data and theoretical models, the research investigates the deviations from ideal gas behavior, providing insight into the interactions between vapor molecules and air or argon. Results indicate significant influence from intermolecular forces and temperature variations, offering improved predictive models for real-world applications.

Keywords: Second virial coefficient, vapor mixtures, air, argon, intermolecular interactions, non-ideal gas behavior, cryogenics, predictive models

Introduction

Air-water vapor/liquid water or air-water vapor/solid ice phase equilibrium data support humidity standards, such as the two-pressure/two-temperature style of generators that are now used by national metrology institutes and industrial laboratories for the calibration of hygrometers. Our understanding of the thermodynamic parameters of air-water vapor mixtures, such as water vapour density, enthalpy, entropy, and Gibbs free energy, is greatly aided by these data [1]. Their molar quantities are directly related to both the effects of the interaction between air and water molecules as well as the mole fraction of vapour. The second interaction virial coefficient, which denotes the first order corrections to the optimal gas law to explain suitable thermodynamic features of gas-water vapor mixtures, is the key characterization of the interactions. Second virial coefficients have applications in experimental thermodynamics studying the properties of gas and substance mixtures, chemical engineering design calculations, and research involving solution theories and intermolecular interactions. They are also helpful in solving equation-of-state problems in gas mixtures and evaluating the fugacities of gas mixture components.

From the sooner work [2-4] for the temperature range of $-20\text{ }^{\circ}\text{C}$ to $70\text{ }^{\circ}\text{C}$, it appears that the experimental data of second virial coefficient for vapor in air is now one amongst the most effective defined of second interaction virial coefficients. The properties of air-water vapor mixture are important for humidity standards, meteorological modeling, design of combustion turbines utilized in the facility industry, and of heating, ventilation, and air-con systems. The properties of argon-water vapor mixture are equally important for humidity standards, semiconductor processing, electric/nuclear power generation, and biological still as chemical processes. Molecular interactions between water and argon are studied using microwave and laser spectroscopy [5-7]. Recently, Ar- H₂O has received way more attention and is interesting because the potential-energy surface has been studied both by at the start calculations and by a constrained fit of an appropriate functional form to spectroscopic data.

The second cross virial coefficients for air-H₂O and ar-H₂O mixes that are supported by open, international literature are reviewed critically in this work. For the purpose of measuring and

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establishing humidity standards, tables are provided that compare the most recent theoretical calculations and, consequently, the experimental data spanning the temperature range of $-20\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$.

Theoretical background

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

$$\frac{pV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \dots \quad (1)$$

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 from 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

$$B(T) = \sum_{i=1}^{\nu} \sum_{j=1}^{\nu} x_i x_j B^{(ij)}, \quad (2)$$

where ν is the number of components of the mixture, and x_i is the mole fraction of the i -th component in the gas mixture,

$$\sum_{i=1}^{\nu} x_i = 1. \quad (3)$$

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

$$B(T) = -\frac{N}{2\Omega^2} \iiint \left\{ e^{-\frac{u_{ij}^{(12)}}{kT}} - 1 \right\} d\mathbf{r}_{ij}^{(12)} d\omega_i^{(1)} d\omega_j^{(2)} \quad (4)$$

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

The total potential energy can be expressed in the form

$$u_{ij}^{(12)} = u^{(0)}(r_{ij}) + V_{ij}^{(12)}(r_{ij}, \omega_i, \omega_j) \quad (5)$$

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

$$B^{(ij)} = B_0^{(ij)} + \sum_{n=1}^{\infty} B_n^{ij}, \quad (6)$$

Where in the zero term

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

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

$$B_n^{ij} = -\frac{N}{2\Omega^2 n!} \left(-\frac{1}{kT}\right)^n \iiint \left\{ V_{ij}^{(12)}(\mathbf{r}_{ij}, \omega_i, \omega_j) \right\}^n e^{-\frac{u^{(0)}(r_{ij})}{kT}} d\mathbf{r}_{ij}^{(12)} d\omega_i^{(1)} d\omega_j^{(2)} \quad (8)$$

are contributions there to resulting from various directional forces acting between two dipole or two quadrupole molecules. Eq. (8) is not used for Air- H₂O and Ar-H₂O 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 model potential, which has been very successful in correlating the thermodynamic properties of inert gases, given by

$$u^{(0)}(r_{ij}) = 4\varepsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6 \right\} \quad (9)$$

Where in the parameters ε_{ij} and σ_{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

$$B_{ij}^*(T^*) = \frac{B_{ij}}{\frac{2\pi}{3} N \sigma_{ij}^3} = \frac{B_{ij}}{(b_0)_{ij}} ; \quad T^* = T\kappa/\varepsilon \quad (10)$$

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

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

Experimental Methods

The second virial coefficients of the Air-H₂O and Ar-H₂O molecule pairs cannot be measured directly. Eq. (2) must be used to obtain it for a binary mixture. The vapor-liquid water equilibrium was employed since experimental techniques validated the vapor-solid ice equilibrium. These techniques monitored the concentration of vapor in the vapor phase as a function of the total equilibrium pressure, which varied between 10 and 150 atmosphere pressures^{2,4}. The second virial coefficients were then determined using the virial equation of state, Eq. (1). B_{12} , of Air- H₂O and Ar- H₂O together with the known values of the pure-component second virial coefficients of air or argon, B_{11} , and vapor, B_{22} , moreover because the saturation vapor pressure at a given temperature.

There are two known independent determinations of the water vapour concentration in air from which the second interaction virial coefficient was derived. Both Hyland² and Wylie and Fisher⁴ performed single saturation isotherm experiments at various saturator pressures and temperatures. The mean values of for every temperature and therefore the associated expanded uncertainty ($k=2$) are given in table 1 showing a really close agreement. It appears that that the experimental data of B_{12} for Air- H₂O is now one in all the most effective defined of second interaction virial coefficients.

In contrast to vapor-liquid/solid isothermal equilibrium experiments, molecular beam elastic differential scattering experiments had been went 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 strategy consists of determining the laboratory collision cross sections, obtained from the computed quantum mechanical center-of-mass cross sections, over the experimental parameters like beam velocity distributions and therefore the total apparatus resolution. the info were analyzed via the best-fit procedure employing a (LJ) 12-6 model potential of Eq. (9) to see the potential parameter, ε_{12} , the well depth, and σ_{12} , the zero of the pair potential.

For Ar- H₂O pair potential, the results of data analysis were $\sigma_{12} = (2.93 \pm 0.22)$ Å and $\varepsilon_{12}/\kappa = (164 \pm 11)$ K obtained by Bickes *et al.*^[8] and $\sigma_{12} = 3.00$ Å and $\varepsilon_{12}/\kappa = 179$ 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 $\varepsilon_{12}/\kappa = (172 \pm 11)$ K. In equations (7), (9), and (11), these potential parameters are went 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 °C¹⁰.

The second virial coefficient for a binary vapor mixture has also been determined from the Joule-Thomson experiment. Measurements of the surplus enthalpy of Ar- H₂O vapor had been made employing a flow calorimeter¹¹. Analysis of the surplus enthalpy yields the cross term isothermal Joule-Thomson coefficient ϕ_{12} and second virial coefficient B_{12} . The B_{12} obtained at 100 °C is in agreement therewith 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- H₂O

Temperature (°C)	Hyland [2]	Wylie and Fisher [4]
	B ₁₂ (cm ³ /mol)	B ₁₂ (cm ³ /mol)
-20	-43.3±3.9	
-10	-40.8±2.7	-32.4±1.4
20		
30	-29.2±2.4	
40	-26.3±2.1	-24.3±2.5
50	-23.6±2.9	
70	-17.7±1.1	
75		-18.7±3.9

Table 2: Comparison of the second virial coefficients with one standard deviation for Ar- H₂O

Temperature (°C)	Bickes <i>et al.</i> [8] and Brooks <i>et al.</i> [9] B ₁₂ (cm ³ /mol)	Rigby and Prausnitz [10] B ₁₂ (cm ³ /mol)	Richards and Wormald [11] B ₁₂ (cm ³ /mol)
25	-31±11	-37±6	-
50	-26±9	-25±5	-
75	-21±8	-20±4	-
100	-18±7	-14±3	-19±7

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:

$$B_{12} = -\frac{1}{2} \int_0^{\infty} \left\langle e^{-U_{12}/k_B T} - 1 \right\rangle_{\omega_1, \omega_2} \mathbf{dr} + \Delta B_{12}(\text{trans}) + \Delta B_{12}(\text{rot}) \quad (12)$$

Where the angle brackets indicate Boltzmann-weighted averaging over all orientations ω_1 and ω_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, H₂ and perhaps Ne. Simple first-order expressions for quantum effects¹² 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 H₂O with monatomic and diatomic molecules. Hodges *et al.*¹³ used scaled perturbation theory to construct a potential-energy surface for H₂O with argon, and used this surface to calculate B_{12} . The results are fitted closely from 100 K to 2000 K by:

$$B_{12}(T) = a_1(T^*)^{-0.31} + a_2(T^*)^{-0.82} + a_3(T^*)^{-2.24} + a_4(T^*)^{-4.6} \quad (13)$$

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-H₂O

Temperature (°C)	Calculated [13]	Experimental	Reference
	B ¹² (cm ³ /mol)	B ¹² (cm ³ /mol)	
-20	-38.67±3.85	-54±13	[14]
-20	-	-79±14	[15]
25	-26.07±3.17	-31±11	[8, 9]
25	-	-37±6	[10]
75	-16.50±2.72	-21±8	[8, 9]
75	-	-20±4	[10]

In principle, similar development of intermolecular potential-energy surfaces for the pairs H₂O-N₂ and H₂O-O₂ should lead (when combined with the present H₂O-Ar result) to values of B_{12} for water with air that may be more accurate than the current results obtained from experiment. This effort is making progress; the work on H₂O-N₂ is almost complete^[16]. The event of a potential-energy surface for H₂O-O₂ may be a tougher undertaking, thanks to the open-shell electronic structure of the O₂ molecule. While the matter isn't insurmountable, it's likely to be 2 or 3 more years before improved values of B_{12} from first-principles calculations are available for water with air.

Conclusion

The experimental data of Ar-H₂O 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 aren't 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 the start calculations as shown in table 3. For his or her values of B₁₂ for H₂O-Ar, Hodges *et al.* [13] were ready to estimate an uncertainty supported the uncertainty within the pair potential. Due to the way during which quantum calculations converge as higher-level methods are used, they were ready to make reasonable upper and lower bounds on the potential. Calculation with Eq. (1) from the foremost attractive and least attractive possible potentials produces a minimum and maximum possible value of B₁₂. The resulting uncertainty in BB₁₂ varied slowly and smoothly with temperature, taking values of three.85 cm³/mol at 250 K, 3.17 cm³/mol at 300 K, and 2.72 cm³/mol at 350 K. These uncertainties are smaller than those related to the experimental data as shown in table 3. However, they're comparable those obtained from vapor isothermal equilibrium experiments for Air- H₂O mixture as shown in table 1.

The excellent agreement between values calculated with two independently-derived P.E. surfaces as discussed in [13] indicates that initially calculations now provides the foremost accurate values of BB₁₂ for the water-argon system. Another advantage of this approach is that, given the pair potential, B₁₂ could also be calculated at any temperature, including temperatures where experiments don't seem to be feasible.

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