# Virial coefficients of mixtures of water vapor and simple gases from first-principles calculations

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#### 1 Introduction

2 Interaction potential energy surfaces

**3** Cross second and third virial coefficients

# Introduction

- Thermophysical properties of mixtures of water vapor with simple gases such as nitrogen, oxygen, argon, carbon dioxide, and hydrogen important for atmospheric modeling and humidity standards
- Measurements of thermophysical properties of gases, particularly if water vapor is involved, difficult and often severely limited in terms of temperature range and accuracy
- Alternative to experiments: first-principles-based approaches



# Introduction

- Mixtures involving H<sub>2</sub>O for which virial coefficients were investigated by us using first-principles approaches:
  - H<sub>2</sub>O-CO<sub>2</sub><sup>1</sup>
  - **H**<sub>2</sub>**O**– $N_2$ <sup>2</sup>
  - $H_2O-O_2$ ,  $H_2O-air^3$
  - H<sub>2</sub>O-CO <sup>4</sup>
  - H<sub>2</sub>O−H<sub>2</sub>S, H<sub>2</sub>O−SO<sub>2</sub> <sup>5</sup>
  - H<sub>2</sub>O−H<sub>2</sub><sup>6</sup>
  - H<sub>2</sub>O–Ar <sup>7</sup>

<sup>1</sup>R. Hellmann, *Fluid Phase Equilib.* **485**, 251–263 (2019) and **518**, 112624 (2020) <sup>2</sup>R. Hellmann, *J. Chem. Eng. Data* **64**, 5959–5973 (2019) and **65**, 2251–2252 (2020) <sup>3</sup>R. Hellmann, *J. Chem. Eng. Data* **65**, 4130–4141 (2020)

- <sup>4</sup>R. Hellmann, Int. J. Thermophys. **43**, 25 (2022)
- <sup>5</sup>R. Hellmann, *J. Chem. Eng. Data* **68**, 108–117 (2023)
- <sup>6</sup>R. Hellmann, J. Chem. Eng. Data **68**, 2212–2222 (2023)
- <sup>7</sup>R. Hellmann, J. Chem. Eng. Data, accepted for publication

#### 1 Introduction

#### 2 Interaction potential energy surfaces

**3** Cross second and third virial coefficients

# Modeling of $H_2O-N_2$ , $H_2O-H_2$ , $H_2O-Ar$ , and $H_2O-Ar-Ar$ interactions

- H<sub>2</sub>O–N<sub>2</sub>, H<sub>2</sub>O–H<sub>2</sub>, and H<sub>2</sub>O–Ar two-body potential energy surfaces and an H<sub>2</sub>O–Ar–Ar nonadditive three-body potential energy surface developed based on quantum-chemical *ab initio* calculations:
  - Supermolecular approach: Schrödinger equation solved for the molecule pair (the supermolecule) in various geometric arrangements and the two individual molecules to obtain the respective total electronic energies
  - Interaction energy obtained as difference between energy of the supermolecule and energies of the individual molecules for a given geometric arrangement
  - Applied level of theory: frozen-core CCSD(T) or CCSDT(Q) with counterpoise correction and extrapolation to the complete basis set limit; in some cases also relativistic corrections
  - Site-site Ansatz with nine sites for  $H_2O$ , five sites for  $N_2$  and  $H_2$ , and one site for Ar used to represent the two-body potential energy surfaces analytically
  - Extended Axilrod–Teller–Muto Ansatz with a single H<sub>2</sub>O site and an analytical induction term used to represent H<sub>2</sub>O–Ar–Ar nonadditive three-body potential energy surface

#### H<sub>2</sub>O–Ar two-body potential energy for selected angular arrangements



Solid lines: fitted analytical function

#### 1 Introduction

2 Interaction potential energy surfaces

**3** Cross second and third virial coefficients

# Virial equation of state

• Virial equation of state is a theoretically derived extension of the ideal gas law:

$$\frac{p}{\rho_{\mathrm{m}}RT} = 1 + B(T)\,\rho_{\mathrm{m}} + C(T)\,\rho_{\mathrm{m}}^2 + \dots$$

with pressure p, molar density  $\rho_m$ , molar gas constant R, temperature T, second virial coefficient B(T), third virial coefficient C(T), ...

- Statistical physics provides exact link between virial coefficients and potential energy surfaces for intermolecular interactions between the gas molecules:
  - Second virial coefficient B(T): interactions between two molecules
  - Third virial coefficient C(T): interactions between up to three molecules

Alternative notation for the virial coefficients:  $B_2(T) \equiv B(T)$ ,  $B_3(T) \equiv C(T)$ , ...

# Calculation of second and third cross virial coefficients

Second virial coefficient of a binary gas mixture:

$$B = x_1^2 B_{11} + 2x_1 x_2 \frac{B_{12}}{B_{12}} + x_2^2 B_{22}$$

• Third virial coefficient of a binary gas mixture:

$$C = x_1^3 C_{111} + 3x_1^2 x_2 C_{112} + 3x_1 x_2^2 C_{122} + x_2^3 C_{222}$$

Classical cross second virial coefficient for rigid molecules:

$$B_{12}^{\rm cl} = -\frac{N_{\rm A}}{2} \int_0^\infty \left\langle \exp\left[-\frac{V(\mathbf{R}, \Omega_1, \Omega_2)}{k_{\rm B}T}\right] - 1 \right\rangle_{\Omega_1, \Omega_2} \mathrm{d}\mathbf{R}$$

- Integrals for *B*<sub>12</sub> (H<sub>2</sub>O–N<sub>2</sub>, H<sub>2</sub>O–H<sub>2</sub>, and H<sub>2</sub>O–Ar) and *C*<sub>122</sub> (only H<sub>2</sub>O–Ar) evaluated by means of the Mayer-sampling Monte Carlo method<sup>1</sup> for temperatures up to 2000 K
- Quantum effects included semiclassically by using the quadratic Feynman–Hibbs (QFH) modification of the two-body potential energy surface

<sup>1</sup>J. K. Singh, D. A. Kofke, Phys. Rev. Lett. 92, 220601 (2004)

# Correlations of the calculated $B_{12}$ and $C_{122}$ values

$$\begin{array}{l} H_2 O-N_2: \\ \hline \frac{B_{12}}{\mathrm{cm}^3/\mathrm{mol}} = 14.376 + \frac{103.47}{(T^*)^{1/2}} - \frac{296.90}{T^*} - \frac{131.68}{(T^*)^3} - \frac{64.256}{(T^*)^4} \\ \end{array} \\ \begin{array}{l} H_2 O-H_2: \\ \hline \frac{B_{12}}{\mathrm{cm}^3/\mathrm{mol}} = 7.3316 + \frac{67.952}{(T^*)^{1/2}} - \frac{150.37}{T^*} - \frac{20.132}{(T^*)^5} \\ \end{array} \\ \begin{array}{l} H_2 O-\mathrm{Ar:} \\ \hline \frac{B_{12}}{\mathrm{cm}^3/\mathrm{mol}} = 14.482 + \frac{81.432}{(T^*)^{1/2}} - \frac{254.54}{T^*} - \frac{66.384}{(T^*)^3} - \frac{2.8391}{(T^*)^{11/2}} \\ \hline \frac{C_{122}}{\mathrm{cm}^6/\mathrm{mol}^2} = -124.92 + \frac{4347.4}{(T^*)^{1/2}} - \frac{7769.6}{T^*} + \frac{11175}{(T^*)^2} - \frac{8135.9}{(T^*)^5} - \frac{4320.7}{(T^*)^8} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array}$$

• Derived property accessible from the  $B_{12}$  correlations: dilute-gas cross isothermal Joule–Thomson coefficient  $\phi_{12} = B_{12} - T \frac{dB_{12}}{dT}$ 

## $B_{12}$ for H<sub>2</sub>O–N<sub>2</sub>: comparison with exp. data and other calculated values



 $\phi_{12}$  for H<sub>2</sub>O–N<sub>2</sub>: comparison with exp. data and other calculated values



T/K

### $B_{12}$ for H<sub>2</sub>O–H<sub>2</sub>: comparison with exp. data and other calculated values



#### $\phi_{12}$ for H<sub>2</sub>O–H<sub>2</sub>: comparison with exp. data and other calculated values



 $B_{12}$  for H<sub>2</sub>O–Ar: comparison with exp. data and other calculated values



 $\phi_{12}$  for H<sub>2</sub>O–Ar: comparison with exp. data and other calculated values



### $C_{122}$ for H<sub>2</sub>O–Ar: results for different levels of theory



#### 1 Introduction

Interaction potential energy surfaces

**3** Cross second and third virial coefficients

- Accurate values of the cross second virial coefficients  $B_{12}$  of  $H_2O-N_2$ ,  $H_2O-H_2$ , and  $H_2O-Ar$  mixtures and the cross third virial coefficient  $C_{122}$  of  $H_2O-Ar$  mixtures obtained at temperatures up to 2000 K from first-principles calculations
- Calculated values significantly more accurate than the few available experimental data
- $C_{122}$  for H<sub>2</sub>O–Ar mixtures previously completely unknown
- Practical correlations fitted to the calculated  $B_{12}$  and  $C_{122}$  values
- Correlations suitable for calculation of fugacities and enhancement factors using standard expressions from thermodynamics of multi-component systems



Thank you very much for your attention!