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PREDICTION OF CROSS SECOND VIRIAL COEFFICIENTS FOR DIMER H_2-O_2 FROM *AB INITIO* CALCULATIONS OF INTERMOLECULAR POTENTIALS

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SUMMARY

The intermolecular interaction potentials of the dimer H_2-O_2 were calculated from quantum mechanics, using coupled-cluster theory CCSD(T) and correlation-consistent basis sets aug-cc-pVmZ (m = 2, 3); the results were extrapolated to the basis set limit aug-cc-pV23Z. The quantum mechanical results were used to construct 5-site pair potential functions. The cross second virial coefficients of the dimer hydrogen-oxygen were obtained by integration; in these cases corrections for quantum effects were included. The results agree well with experimental data and empirical correlations.

I - INTRODUCTION

Computer simulation techniques, Monte Carlo as well as Molecular Dynamics, cannot work without some input, however: It is necessary to know the interaction potentials of the systems under study. The usual procedure is to assume a simple model potential. A system is the fluid mixture (H_2-O_2). Its thermodynamic properties are important for the design of efficient rocket engines [1], but there are remarkably few publications of experimental results only -for evident reasons.

Recently an alternative approach has become feasible, for which the name "global simulation" has been coined [2]. One of the first attempts in such global simulations was that of Deiters, Hloucha and Leonhard [3] for neon to predict the vapour-liquid phase equilibria without recourse to experimental data. Further global simulation attempts for noble gases were published by the group of Huber [4]. Using a functional form for the dispersion potentials of argon and krypton proposed by Korona et al. [5]. Leonhard and Deiters constructed a 5-site Morse potential to represent the pair potential of nitrogen [8] and were able to predict vapour pressures and orthobaric densities. Nasrabad and Deiters even predicted phase high-pressure vapour-liquid phase equilibria of noblegas mixtures [7]. Bock et al. also used a 5-site pair potential for carbon dioxide [9]. Naicker et al. used SAPT (symmetry-adapted perturbation theory) to develop a 3-site pair potential for hydrogen chloride [11]; they then successfully predicted the vapour-liquid equilibria of hydrogen chloride with Gibbs ensemble Monte Carlo simulations.

In this work we use quantum mechanical calculations at a sufficiently high level of approximation to obtain pair potential data of the dimer H_2-O_2. These data are then represented by analytical pair potential functions. These in turn are used to calculate cross 2nd virial coefficients. The virial coefficients can then be compared to experimental data - as far as such data are available.

II - COMPUTATIONAL DETAILS

1. Molecular Orientation

Hydrogen and oxygen molecules are represented as 5-site models, with two sites placed on the atoms (H or O), one site in the center of gravity (M), and two sites halfways between the atoms and the center (N). The molecules are treated as rigid; the interatomic distances are set to 0.74130 Å for hydrogen and 1.20741 □ for oxygen [12]. As hydrogen and oxygen are linear molecules, the intermolecular pair potential is a function of distance *r* (distance between the centers of gravity) and three angular coordinates, α, β and ϕ. Interaction energies were calculated for all values of *r* from 2.6 to 15 Å with increment 0.2 Å; the angles α, β and ϕ; were varied from 0 to 180° with increment 45°.

2. Quantum chemical calculations

The method CCSD(T) and the correlation-consistent basis sets of Dunning et al. [13]: aug-cc-pVDZ (for oxygen: 10s5p2d/4s3p2d, for hydrogen: 5s2p/3s2p), aug-cc-pVTZ (for oxygen: 12s6p3d2f/5s4p3d2f, for hydrogen: 6s3p2d/4s3p2d) were used in this work. The *ab initio* energy results were corrected for the basis set superposition error (BSSE) [14]:

$$\Delta E_{\text{int}} = E_{AB} - (E_{Ab} + E_{aB}) \qquad (1)$$

where E_{AB} denotes the total electronic energy of a dimer *AB*, E_{Ab} the energy of a dimer consisting of an *A* atom and a *B* ghost atom (an atom without nucleus and electrons, but having its orbital), and E_{aB} vice versa. The electronic energies are then extrapolated to the complete basis set limit [15]:

$$\Delta E(m) = \Delta E(\infty) + cm^{-3} \qquad (2)$$

with $m = 2$ (for the aug-cc-pVDZ basis set) or 3 (for the aug-cc-pVTZ basis set). If results for two basis sets are available, it is possible to calculate the energy value for an infinite basis set from Eq.2; this result is referred to as aug-cc-pV23Z below.

3. Potential function

Two our new 5-site pair potential functions were developed for dimer H_2-O_2:

$$u = \sum_{i=1}^{5}\sum_{j=1}^{5}\left[D_e^{ij}\, e^{-\alpha_{ij} r_{ij}} + f_{1a}(r_{ij}) \sum_{n=6,8,10} \frac{C_n^{ij}}{r_{ij}^n} + f_2(r_{ij}) \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right] \qquad (3)$$

with $f_{1a}(r_{ij}) = (1+e^{-2(\delta_{ij} r_{ij}-2)})^{-15}$ and $f_2(r_{ij}) = 1-e^{-\beta_{ij} r_{ij}}$

$$u = \sum_{i=1}^{5}\sum_{j=1}^{5}\left[D_e^{ij}\, e^{-\alpha_{ij} r_{ij}} + f_{1b}(r_{ij}) \sum_{n=6,8,10,12} \frac{C_n^{ij}}{r_{ij}^n} + f_2(r_{ij}) \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right] \qquad (4)$$

with $f_{1b}(r_{ij}) = 1-e^{-\delta_{ij} r_{ij}} \sum_{k=0}^{10} \frac{(\delta_{ij} r_{ij})^k}{k!}$ and $f_2(r_{ij}) = 1-e^{-\beta_{ij} r_{ij}}$

Here the r_{ij} site-site distances, the q_i, q_j electric charges of sites, and the C_{ij}^n dispersion coefficients; the leading dispersion term is always proportional to *r*. The two models differ mostly in the choice of the damping functions $f_{1a}(r_{ij})$ and $f_{1b}(r_{ij})$.

4. Fitting potential function

The adjustable parameters of the *ab initio* pair potential functions can be estimated by nonlinear least-square fitting to the *ab initio* interaction energy values.

The fit process has to be carried out by two steps. The global minima are coarsely located by means of the Genetic algorithm (GA), and the parameters resulting from the Genetic algorithm are used as initial values for the Marquardt-Levenberg algorithm. The values of root mean-square deviations (rms), multiple correlation coefficients (R^2), and residuals of the fitted analytical potential functions are given in table 1. The statistical estimates here are important for assessing the fitting quality. The fitting results in Table 1 show that the residual discrepancies between the pair potentials Eq. 3 and Eq. 4 resulting from the least-square fit are insignificant.

Table 1: The statistical results for fitting the intermolecular potentials Eq. 3 and Eq. 4. The values are in μE_H

Potential	R^2	rms	Residual	
			min	max
Eq. 3	0.9981	6.3268	-7.903	7.347
Eq. 4	0.9978	6.5214	-8.742	5.106

III - SECOND VIRIAL COEFFICIENTS

1. Classical virial coefficients

The classical viral coefficients B_{cl}^{0} of hydrogen resulting from the formula Eq. 7 using the *ab initio* 5-site pair potentials Eq. 3 and Eq. 4 are shown in table 2.

Table 2: Cross second viral coefficient, $B_2(T)$ (given in cm^3/mol) of the mixture hydrogen-oxygen; correl.: empirical correlation [24]; exp.: experimental data.

T/K	Method	B_{cl}^{0}	B_{r}^{1}	$B_{\mathrm{a}I}^{1}$	$B_{\mathrm{a}m}^{1}$	$B_2(T)$	Ref.
49.8	Eq.3	-138.338	0.267	0.199	0.015	-137.857	
	Eq.4	-136.921	0.057	0.037	0.028	-136.798	
	correl.					-142.097	
	exp.					-110.0	[20]
80.0	Eq.3	-61.875	0.283	0.228	0.057	-61.307	
	Eq.4	-60.906	0.085	0.037	0.032	-60.751	
	correl.					-63.887	
	exp.					-72.9	[19]
85.0	Eq.3	-55.745	0.405	0.388	0.078	-54.874	
	Eq.4	-54.678	0.325	0.073	0.057	-54.223	
	correl.					-56.806	
	exp.					-54.0	[19]
86.5	Eq.3	-54.073	0.314	0.177	0.047	-53.535	
	Eq.4	-52.976	0.128	0.073	0.014	-52.761	
	correl.					-54.881	
	exp.					-58.1	Eq.11
90.0	Eq.3	-50.428	0.352	0.344	0.070	-49.662	
	Eq.4	-49.261	0.191	0.054	0.046	-48.971	
	correl.					-50.664	
	exp.					-32.5	[19]

2. Quantum corrections

In the case of hydrogen the matter is more complicated because of quantum effects. The first order corrections to the second virial coefficient of linear molecules have been worked out by Pack [10] and Wang [17]. Following the latter, the virial coefficient up to first order can be written as:

$$B_2 = \frac{N_A}{2u\iint d\Omega_1 d\Omega_2} \iiiint \left\{ 1 - \exp(-u/k_B T) \left[1 + \frac{1}{12(k_B T)^2} H_0 u \right] \right\} dr_1\, dr_2\, d\Omega_1\, d\Omega_2 \tag{5}$$

Here N_A is Avogradro's constant, k_B Boltzmann's constant, T the temperature, and $u(r, \alpha, \beta, \phi)$ the pair potential; its parameters, the center-center distance and the relative orientation angles must be calculated from the center vectors r_i and the absolute orientations i. H_0 is the translation-rotation Hamiltonian for a pair of molecules.

This expression can be broken down into a classical term and first-order quantum corrections (radial part, angular part proportional to I^{-1} (moment of inertia), angular part proportional to μ^{-1} (reduced mass)):

$$B(T) = B^0_\mathrm{cl}(T) + B^1_r(T) + B^1_{\mathrm{a}I}(T) + B^1_{\mathrm{a}m}(T) \tag{6}$$

The classical part is given by

$$B^0_\mathrm{cl} = -\frac{N_A}{4} \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\beta\, d\beta \int_0^{\pi} \sin\alpha\, d\alpha \int_0^{\infty} \left(\exp\left(-\frac{u}{k_B T} \right) - 1 \right) r^2\, dr \tag{7}$$

All these integrals were evaluated numerically with a 4D Gauss quadrature method [18].

Experimental values for the cross 2nd virial coefficients of the hydrogen-oxygen interaction are difficult to find in the literature. There are some experiments, however, from which these virial coefficients can be calculated:

- Van Itterbeek and van Doninck measured the speed of sound in (hydrogen + oxygen) mixtures at low temperatures and pressures [19]. The pressure dependence of this property is related to the virial coefficients. The values of the cross virial coefficient obtained by these authors lie reasonably close to our predictions (see Fig. 1); it should be noted, however, that their evaluation method involved several simplifications (linearizations, neglect of temperature derivatives of the virial coefficient), and that their results exhibit an uncertainty of about 20%.

- McKinley at al. measured solid-fluid equilibria of the (hydrogen + oxygen) system [20]. With the usual assumptions and simplifications (no hydrogen dissolved in the solid oxygen, neglect of higher virial coefficients) it is possible to estimate cross second virial coefficients from these data. The result agrees reasonably well with the ab initio prediction. The sublimation pressure of g-oxygen, which is required for the equilibrium calculation, was taken from the work of Roder [21].

In an earlier publication on high-pressure phase equilibria of the (hydrogen + oxygen) system it had been suggested that the parameters of the hydrogen-oxygen interaction could be interpolated from those of the the systems (hydrogen + nitrogen), (neon + nitrogen), and (neon + oxygen) [22]. This idea can be extended to second virial coefficients as follows: Eq. 7 can be simplified although with some loss of accuracy - by performing the integrations of the orientation variables:

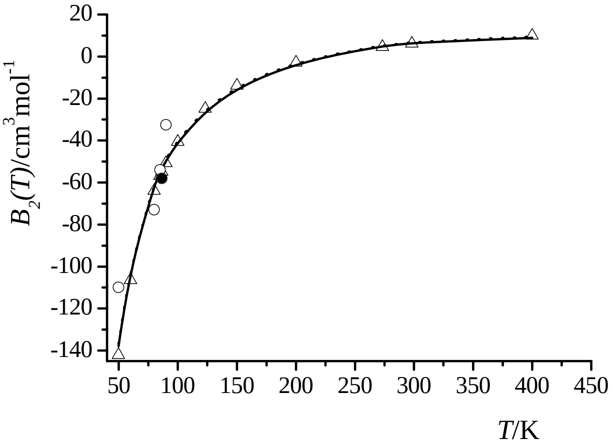

Figure 1: Cross second virial coefficient of the hydrogen-oxygen system. —: *ab initio* prediction (this work) based on Eq. 3; ...: *ab initio* prediction based on Eq. 4 (this work); V: empirical correlation [24]; □ : interpolation from Eq. 11; other symbols: experimental data.

$$B^0(T) = -2\pi N_A \int_0^\infty \left[\exp\left(-\frac{\bar{u}(r,T)}{k_B T} \right) - 1 \right] r^2 dr \tag{8}$$

Here $\bar{u}(r,T)$ denotes an angle-averaged pair potential. For small molecules like the ones studied here the assumption of conformal pair potentials is usually acceptable, i.e., pair potentials can be written as

$$\bar{u}(r,T) = \varepsilon \tilde{u}(\tilde{r},\tilde{T}) \text{ with } \tilde{r} = \frac{r}{\sigma} \text{ and } \tilde{T} = \frac{k_B T}{\varepsilon} \tag{9}$$

where $\tilde{u}(\tilde{r},\tilde{T})$ is a universal (reduced) pair potential function. Then Eq. 8 becomes

$$B^0(T) = -2\pi N_A \sigma^3 \int_0^\infty \left[\exp\left(-\frac{\tilde{u}(\tilde{r},\tilde{T})}{\tilde{T}} \right) - 1 \right] \tilde{r}^2 d\tilde{r} \tag{10}$$

We use this equation for the cross virial coefficient of the hydrogen-oxygen system, assuming $\varepsilon_{H_2;O_2} = \varepsilon_{H_2;N_2} + \Delta\varepsilon_{O_2;N_2}$, where the last term is supposed to be small. Taylor expansion of the Boltzmann factor of this term, truncation after the linear term, and rearrangement yield

$$\frac{B^0_{H_2,O_2}(T)}{N_A \sigma_{H_2,O_2}} \approx \frac{B^0_{H_2,N_2}(T)}{N_A \sigma_{H_2,O_2}} - 2\pi \frac{\Delta\varepsilon_{O_2,N_2}}{\tilde{T}_{H_2,N_2}} \int_0^\infty \tilde{u}(\tilde{r},\tilde{T}_{H_2,N_2}) \left[\exp\left(-\frac{\tilde{u}(\tilde{r},\tilde{T}_{H_2,N_2})}{\tilde{T}_{H_2,N_2}} \right) - 1 \right] \tilde{r}^2 d\tilde{r} \tag{11}$$

Where the integral is a function of the reduced temperature T only. A similar equation holds for the cross virial coefficients of the (neon + oxygen) and (neon + nitrogen) systems, for which experimental data are available [23]. Therefore $\Delta\varepsilon_{O_2;N_2}$ can be determined from the neon data and then substituted into Eq. 11 to give the second virial coefficient of (hydrogen + oxygen) at the same reduced temperature as the (neon + oxygen) system (tacitly assuming that this value also holds for the hydrogen systems). For the parameters ε and σ usual Lennard-Jones parameters [16] and Berthelot-Lorentz combining rules were used. It turns out that the hydrogen-oxygen cross virial coefficient obtained from this interpolation (-58 cm^3/mol) agrees reasonably well with the *ab initio* predictions as well as with the experimental values (see Fig. 1).

Recently Estela-Uribe and Jaramillo [24] published empirical correlation equations for second virial coefficients which are based on the corresponding-states approach of Lee and Kesler [25]. In their work, binary interactions are characterized by so-called pseudocritical parameters, which are interpolations of the pure-fluid critical temperatures and densities [24]:

$$\rho_{c,ij}^{-1/3} = \frac{1+d_{ij}}{2}(\rho_{c,i}^{-1/3} + \rho_{c,j}^{-1/3}) \text{ and } T_{c,ij} = \frac{(1-k_{ij})(T_{c,i}T_{c,j})^{1/2}}{1+c/(M_{ij}T)} \quad (12)$$

with $M_{ij}^{-1} = \frac{1}{2}(M_i^{-1} + M_j^{-1})$ and $k_{ij} = 1 - \frac{a_{ij}\rho_{c,ij}}{(\rho_{c,i}\rho_{c,j})^{1/2}}$

Here the M_i denote molar masses of the pure components, M_{ij} an "interaction molar mass", and c is a constant (21.8 K g/mol). It turns out that the adjustable parameters a_{ij} and d_{ij} are very close to zero for a large number of chemical compounds. We have set these two correlation parameters to zero for the hydrogen-oxygen interaction and used the correlations of Estela-Uribe and Jaramillo to predict cross second virial coefficients. The results show a remarkably good agreement with the predictions from quantum mechanics.

IV - CONCLUSION

We conclude that our *ab initio* pair potentials for the hydrogen-oxygen interaction are reliable, and that the calculation of thermodynamic properties from quantum mechanical results can be useful, if experimental data are scarce.

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