

# A computational treatment of the gas-phase thermodynamics of the water dimer in flexible potentials<sup>1</sup>

Zdeněk Slanina<sup>2</sup>

*Max-Planck-Institut für Chemie (Otto-Hahn-Institut), D-W-65 Mainz (Germany)*

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## Abstract

The MCY-type semi-rigid, and the BJH- and MCY-type flexible water–water potentials are used for evaluation of the structure, energetics, vibrations, and thermodynamics of the water dimer. The study includes calculations of the populations of water dimer in the saturated steam above ice and liquid water.

## INTRODUCTION

Water clusters in general [2–5] and the water dimer in particular [6–10] have frequently been treated computationally. Recently, a new type of water–water interaction potentials has been introduced [11–23], the flexible or non-rigid potentials containing, in addition to the intermolecular component, a sophisticated intramolecular component derived from a quartic force-field of the free monomeric units (thus surpassing the simpler (harmonic) free-water molecule potentials [24–26] previously employed, and representing an alternative to the local-mode surfaces [27]). This study employs altogether 12 modifications of the flexible potentials in treating various aspects of the gas-phase thermodynamics of the water dimer, compares the calculations with observed data whenever available [28–35], and suggests recommended theoretical values for further use. In particular, the populations of water dimer in saturated steam over ice or liquid water are evaluated.

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<sup>2</sup> On a leave of absence from the Czechoslovak Academy of Sciences, Prague. Correspondence to Limburgs Universitair Centrum, Departement SBG, Universitaire Campus, Gebouw D, B-3590 Diepenbeek, Belgium.

## THE THERMODYNAMICS AND THE POTENTIALS

The central-force (CF) model of water [11–13], i.e. the potential energy is considered as a function of only two-centre distances, can be viewed as a precursor for the flexible potentials. In this approach, the inter- and intramolecular potential contributions were described in a uniform form, and three modifications (CF [11], CF1 [12], CF2 [13]) of the potential were suggested. In order to enhance the versatility of the potential, Bopp, Jancsó and Heinzinger [14, 15] combined the CF2 intermolecular potential with a quartic spectroscopic force-field of a free water molecule [17]. In such a way, a potential was created, referred to here as BJH/G. A modification of the monomeric force field, adjusted to liquid water conditions, was also suggested [14]. We shall consider the related water–water flexible potential of BJH-type under its acronym BJH/L. Finally, for a sake of completeness, the original CF1 and CF2 intermolecular terms can be combined with the gas-phase intramolecular component (CF1/G and CF2/G potentials). These four potential modifications represent the BJH family of flexible potentials.

There is, however, yet another family of flexible water–water potentials, namely that derived from the MCY intermolecular potentials suggested by Matsuoka et al. [18]. Lie and Clementi [19] created the so-called MCYL potential by combining the MCYII intermolecular potential with a quartic potential of a free water molecule from a quantum-chemical evaluation [21]. Because there are three other available parametric modifications of the MCY intermolecular component (MCYI [18], MCYB [22], MCYC [23]), four members of the MCYL family of flexible potentials can be considered here (referred to as MCY-X, where X is I, L, B or C).

Finally, prior to introduction of the MCY-L flexible potential, a lower degree of flexibility was allowed to the MCY water–water potentials [24–26] by means of a simple harmonic intramolecular force field. In this way, the third potential family (MCY semi-rigid) was created, and its members are labelled MCYI, MCYII, MCYB and MCYC.

The 12 potentials have been treated computationally in a common, unified way that was developed and described recently [36]. The local energy minimum possessing the usual  $C_s$  point group of symmetry was located on the potential hypersurfaces, using their analytically constructed energy derivatives. No a priori geometrical constraint was imposed and a redundancy-free coordinate set was applied. In spite of employing various starting structures, no other local minimum was found in addition to the  $C_s$  one. In the local energy minimum, harmonic vibrational analysis was carried out using the force constants constructed by a numerical differentiation of the analytical energy first derivatives. The calculated energetics, structure, and vibrational frequencies served for construction of the rigid-rotor and harmonic-oscillator (RRHO) partition functions

and then, subsequently, for evaluation of various thermodynamic characteristics.

#### COMPARISON WITH OBSERVATIONS

In terms of the non-rigid potential structural, vibrational and energy data, a complete thermodynamics of the gas-phase light water dimer formation



and of its deuterio analog



have been evaluated employing the partition functions of the RRHO quality. In particular, the comparison with observed data was carried out at the level of the standard enthalpy  $\Delta H_T^\ominus$  and entropy  $\Delta S_T^\ominus$  changes for processes (1) and (2). The observed  $\Delta H_T^\ominus$  and  $\Delta S_T^\ominus$  terms employed here for testing computed values were either obtained from studies of the thermal conductivity of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  vapor [33, 34], or extracted from different evaluations of the second virial coefficient of steam [28, 29, 33]. There are also other, partial observed data available [30–32]; however, for our purposes, they are not sufficiently complete. Table 1 presents the comparison with the MCYL family of flexible potentials as an illustration.

In order to compare the results from different potentials, summations of the squares of the differences between calculations and observations were carried out at five temperatures of observation for the  $\Delta H_T^\ominus$ ,  $\Delta S_T^\ominus$ ,  $T\Delta S_T^\ominus$ , and  $\Delta G_T^\ominus = \Delta H_T^\ominus - T\Delta S_T^\ominus$  terms (the sole observed value for reaction (2) was treated as having the same significance as any one of the results for association (1)). Within the BJH family of potentials, the BJH/G results yield [36] the best agreement with observation for all four levels of comparison. With the MCYL-type potentials, the situation is somewhat more complex: the smallest value of the  $\sum \delta^2 H_i$  term is met for the MCY-B potential; for the two entropy terms, the smallest value is that of the MCY-I potential; and the lowest value of the  $\sum \delta^2 G_i$  term is yielded by the MCY-L approach. Finally, in the MCY semi-rigid family of potentials, the best reproduction of the observed terms was found for the MCYB potential [36].

In order to allow for compensation of possible imperfections of the potentials, a refinement with respect to the observed  $K_p$  values was also considered. It was concluded that the MCYB, BJH/G and MCY-B potentials in the semi-flexible MCY and BJH, and flexible MCY families of potentials, respectively, are preferred for future use. Therefore, these three potentials were applied to the water dimer populations below.

TABLE 1

Comparison of observed standard<sup>a</sup> thermodynamic characteristics of the gas-phase water dimer formation with their flexible MCYL-type potential evaluations

Dimerization to	T/K	$\Delta H_T^\ominus/\text{kJ mol}^{-1}$				
		MCY-I	MCY-L	MCY-B	MCY-C	Obsd.
$(\text{H}_2\text{O})_2(\text{g})^b$	372.4	-17.16	-17.71	-16.80	-18.24	-15.02 <sup>c</sup>
	373.0	-17.15	-17.70	-16.79	-18.23	-13.77 <sup>d</sup>
	423.0	-16.53	-17.10	-16.16	-17.64	-14.31 <sup>d</sup>
	573.15	-14.47	-15.08	-14.06	-15.64	-15.69 <sup>e</sup>
$(\text{D}_2\text{O})_2(\text{g})$	370.75	-17.80	-18.41	-17.40	-18.99	-15.31 <sup>c</sup>
$\Sigma \delta^2 H_i^f$		28.65	40.40	22.73	54.80	
		$\Delta S_T^\ominus/\text{JK}^{-1} \text{mol}^{-1}$				
		MCY-I	MCY-L	MCY-B	MCY-C	Obsd.
$(\text{H}_2\text{O})_2(\text{g})^b$	372.4	-77.11	-80.49	-75.45	-81.96	-77.78 <sup>c</sup>
	373.0	-77.09	-80.47	-75.43	-81.94	-71.42 <sup>d</sup>
	423.0	-75.53	-78.96	-73.83	-80.45	-73.39 <sup>d</sup>
	573.15	-71.36	-74.90	-69.61	-76.43	-74.89 <sup>e</sup>
$(\text{D}_2\text{O})_2(\text{g})$	370.75	-78.27	-81.77	-76.53	-83.27	-78.12 <sup>c</sup>
$\Sigma \delta^2 S_i^g$		49.67	133.7	52.15	206.9	
$\Sigma \delta^2 (TS)_i^f$		9.45	19.82	12.54	31.17	
$\Sigma \delta^2 G_i^h$		15.60	6.72	21.22	7.14	

<sup>a</sup> The standard state, ideal gas phase at 101325 Pa pressure. <sup>b</sup> <sup>1</sup>H isotope in the calculation. <sup>c</sup> Ref. 33. <sup>d</sup> Ref. 33 and data quoted therein. <sup>e</sup> Refs. 28, 29. <sup>f</sup> Sum of the squares of theory – experiment differences, in  $(\text{kJ mol}^{-1})^2$ . <sup>g</sup> Sum of the squares of differences<sup>f</sup> in  $(\text{JK}^{-1} \text{mol}^{-1})^2$ . <sup>h</sup> Sum of the squares of differences<sup>f</sup> in the standard Gibbs energy.

## WATER DIMER POPULATIONS

Let us first consider a simple equilibrium monomer–dimer mixture in terms of mole fractions. The mole fraction of the dimer is given by  $x_2 = n_2/(n_1 + n_2)$  where  $n_1$  and  $n_2$  denote the number of moles, i.e. the mass divided by the molar mass, of the monomer and dimer, respectively, in their mixture. The dimer mole fraction is different from the degree of association or extent of reaction (sometimes denoted by  $\alpha$ ). For the dimer mole fraction [37]

$$x_2 = \frac{2PK_p + 1 - (4PK_p + 1)^{1/2}}{2PK_p} \quad (3)$$

where  $P$  represents the total pressure of the mixture. In a limiting case  $PK_p \ll 1$ , eqn. (3) reduces to a simple form  $x_2 \approx PK_p$ .

In a real situation, however, higher water clusters are also present. In order to account for their effects, an assumption has been introduced [38] that the trimerization, tetramerization, etc., equilibrium-constant values decrease along a geometrical series with a quotient  $z$  (which itself, however, depends on temperature). Within this unlimited cluster dimension model, the dimeric mole fraction becomes

$$x_2 = K_p x_1^2 P \quad (4)$$

where the monomeric mole fraction

$$x_1 = \frac{-Q + [Q^2 + 4P(K_p/z - 1)/z]^{1/2}}{2P(K_p/z - 1)} \quad (5)$$

and

$$Q = 1/z + P \quad (6)$$

In the simple monomer–dimer model, the two mole fractions follow the condition  $x_1 + x_2 = 1$ ; while in the unlimited dimension approach, all clusters are (formally) involved

$$\sum_{i=1}^{\infty} x_i = 1 \quad (7)$$

In this investigation, the total pressure  $P$  is exclusively the saturated pressure of steam over either liquid water [39, 40] or ice [41]. It should be mentioned that the original formula [39] is repeated in ref. 40, although not always consistently. Here, we follow the original form [39], although some minor uncertainties remain, for example, in relation to the practical temperature scale [39] versus the thermodynamic scale. The other formula, the ice formula, was designed [41] for temperatures between the triple point and  $-100^\circ\text{C}$ ; its application here below this lower limit is an extrapolation only.

Table 2 presents change in the dimeric mole fraction  $x_2$  in the saturated steam over a wide temperature interval, from 50 K up to temperatures close to the critical point, evaluated in the three selected potentials (MCYB, BJH/G, and MCY-B). The qualitative picture is the same in each of the three selected potentials. The mole fraction  $x_2$  increases with increasing temperature. In the low temperature region, there is a rapid decrease in the  $x_2$  term with decreasing temperature. This may be surprising but it can easily be rationalized. The  $K_p$  values decrease with temperature for weak molecular complexes. However, the saturated pressure  $P$  increases with temperature. The competition between these two terms decides the final  $x_2$  temperature behavior. The simple monomer–dimer treatment yields somewhat higher  $x_2$  values than the unlimited dimension model (because the latter model has to accommodate all the higher clusters as well).

TABLE 2

Mole fraction <sup>a</sup>  $x_2$  of the water dimer <sup>b</sup> in saturated steam at selected temperatures evaluated in the recommended [12] refined semi-rigid MCYB and BJH/G potentials and the flexible MCY-B potential

T/K	$x_2$		
	MCYB	BJH/G	MCY-B
50	$7.95 \times 10^{-33}$	$4.85 \times 10^{-34}$	$1.15 \times 10^{-32}$
75	$3.04 \times 10^{-21}$	$5.51 \times 10^{-22}$	$3.87 \times 10^{-21}$
100	$2.03 \times 10^{-15}$	$6.36 \times 10^{-16}$	$2.43 \times 10^{-15}$
125	$6.81 \times 10^{-12}$	$2.94 \times 10^{-12}$	$7.82 \times 10^{-12}$
150	$1.60 \times 10^{-9}$	$8.57 \times 10^{-10}$	$1.79 \times 10^{-9}$
175	$8.21 \times 10^{-8}$	$5.10 \times 10^{-8}$	$9.01 \times 10^{-8}$
200	$1.61 \times 10^{-6}$	$1.12 \times 10^{-6}$	$1.75 \times 10^{-6}$
225	$1.67 \times 10^{-5}$	$1.26 \times 10^{-5}$	$1.78 \times 10^{-5}$
250	$1.09 \times 10^{-4}$	$8.87 \times 10^{-5}$	$1.16 \times 10^{-4}$
275	$5.05 \times 10^{-4}$	$4.34 \times 10^{-4}$	$5.30 \times 10^{-4}$
	(0.999)	(1.00)	(0.999)
	[ $1.31 \times 10^{-6}$ ]	[ $1.13 \times 10^{-6}$ ]	[ $1.38 \times 10^{-6}$ ]
300	$1.45 \times 10^{-3}$	$1.31 \times 10^{-3}$	$1.51 \times 10^{-3}$
	(0.999)	(0.999)	(0.998)
	[ $6.06 \times 10^{-6}$ ]	[ $5.46 \times 10^{-6}$ ]	[ $6.32 \times 10^{-6}$ ]
325	$3.44 \times 10^{-3}$	$3.23 \times 10^{-3}$	$3.57 \times 10^{-3}$
	(0.997)	(0.997)	(0.996)
	[ $2.08 \times 10^{-5}$ ]	[ $1.95 \times 10^{-5}$ ]	[ $2.16 \times 10^{-5}$ ]
350	$7.08 \times 10^{-3}$	$6.87 \times 10^{-3}$	$7.32 \times 10^{-3}$
	(0.993)	(0.993)	(0.993)
	[ $5.71 \times 10^{-5}$ ]	[ $5.54 \times 10^{-5}$ ]	[ $5.90 \times 10^{-5}$ ]
400	$2.18 \times 10^{-2}$	$2.23 \times 10^{-2}$	$2.23 \times 10^{-2}$
	(0.978)	(0.977)	(0.977)
	[ $2.64 \times 10^{-4}$ ]	[ $2.70 \times 10^{-4}$ ]	[ $2.71 \times 10^{-4}$ ]
500	$8.93 \times 10^{-2}$	$9.71 \times 10^{-2}$	$9.03 \times 10^{-2}$
	(0.909)	(0.901)	(0.908)
	[ $1.64 \times 10^{-3}$ ]	[ $1.77 \times 10^{-3}$ ]	[ $1.66 \times 10^{-3}$ ]

<sup>a</sup> Evaluated within the unlimited dimension model; it holds for the cluster mole fractions  $\sum_{i=1}^{\infty} x_i = 1$ . <sup>b</sup> The monomeric water mole fraction  $x_1$  and the residuum of the larger clusters  $\sum_{i=3}^{\infty} x_i$  are presented in parentheses and square brackets, respectively, however only if the  $x_1$  term is (in the applied format) different from 1.00.

However, the difference is only noticeable at higher temperatures and is not particularly significant. At higher temperatures, results from the three selected potentials become quite close.

In order to obtain information on higher-cluster populations, Table 2 presents the sum  $\sum_{i=3}^{\infty} x_i$  together with the  $x_1$  term, however, only if the  $x_1$  term differs from 1.00 within the applied format. It should be noticed that, for example, at 400 K the sum is still two orders of magnitude smaller than the  $x_2$  term.

With reference to the applied combination of the sophisticated potentials with the observed data, i.e. the refinement, the  $x_2$  values of this report can be considered as the most reliable so far. There still may be a possibility of further improvement, namely, a reevaluation of the observed data analysis in the cases where an estimation of the  $B_f$  component of the second virial coefficient was applied, i.e. using the most sophisticated  $B_f$  values. Alternatively, newer, independent experimental information would be useful for further refinement of the water potentials. Although associations are widely allowed in the model, each class of clusters is treated as an ideal gas characterized by its partial pressure. Consequently, the equilibrium constants involved are pressure independent which would not be the case at higher pressures, i.e. at higher temperatures in the saturation regime. From this point of view, our results are more reliable at lower temperatures.

The calculations employed the usual rigid-rotor and harmonic-oscillator partition functions. This should not be critical, because the refinement applied should account to some extent for deviations from the model. At higher temperatures, it can be expected that effects of the infinite harmonic-oscillator sum may be influential. However, the information available from diatomic clusters [42, 43] does not yet allow a straightforward conclusion on the magnitude of these effects. Nevertheless, this factor cannot change the results for the proportions of the dimer populations in low-temperature saturated steam, i.e. in the region which is of primary importance in the study of the atmospheres of the earth, the planets or comets.

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