Thermochimica Acta, 180 (1991) 99–106
Elsevier Science Publishers B.V., Amsterdam

THE SECOND VIRIAL COEFFICIENT OF WATER AND HEAVY WATER: A COMPUTATIONAL EVALUATION OF THE ISOTOPIC DIFFERENCE WITHIN THE MCY-TYPE SEMI-RIGID POTENTIALS *

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(Received 13 August 1990)

ABSTRACT

The isotopic difference in the second virial coefficient of steam and deuterated steam is evaluated on the basis of four modifications of the MCY semi-rigid potential (MCYI, MCYII, MCYB, and MCYC) and compared with recently published observed data. Qualitatively the calculations follow the available observation; however, they overestimate the difference. The MCYII and MCYC potential modifications yield the closest approach to the observation. A role of the (usually neglected) component of the second virial coefficient related to the formation of dimeric species is suggested by the results.

INTRODUCTION

Water clusters and the water dimer in particular, have been the subject of constant computational interest [1–91], this being encouraged and stimulated by ever improving observational data. Quite recently Kell et al. [92,93] reported observed differences in the second virial coefficients of water and heavy water $B_2(\mathrm{H}) - B_2(\mathrm{D})$. This new type of information had not been calculated up until now. The present study deals with the problem using the four available modifications of the sophisticated MCY water–water interaction potential [17] in combination with the harmonic intramolecular potential [27,28], i.e. the semi-rigid or semi-flexible MCYI, MCYII, MCYB, and MCYC potentials.

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* Dedicated to Professor Jacob Bigeleisen on the occasion of his 70th birthday.

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0040-6031/91/$03.50

COMPUTATIONAL

The MCY family of water–water (intermolecular) potentials was introduced by Matsuoka et al. [17]. At present four parametric mutations of the ab initio potential are available. Originally two modifications of the MCY potential were derived from the SCF CI results [17] differing in electron-correlation contribution treatment—the full electron correlation, MCYI and the intermolecular electron correlation only, MCYII. The MCYII potential was found [28] to yield a better agreement with observed gas-phase water-dimer data. Later on Bounds [51] found a new solution of the MCYII fitting problem leading to a substantial decrease in the mean standard deviation (MCYB potential). Finally Carravetta and Clementi [55] re-evaluated the electron correlation contribution, creating the fourth (MCYC) potential.

The original MCY potential was rigid, i.e. it considered the intermolecular degrees of freedom only, keeping monomeric unit geometry fixed at their free-state equilibrium positions. In order to allow intramolecular vibrational motions the MCY potentials were combined [27,28] with the observed harmonic force field of the gas-phase water molecule [94]. Within the combined potential (which, with respect to the harmonic character of the intramolecular parts, can be called semi-rigid or semi-flexible) its stationary points were located (especially its minimum) and vibrational analysis in it was carried out (methodology of the treatment was described elsewhere [27,28,67]). In agreement with the contemporary observational and theoretical consensus, the water dimer exhibits C_s point-group symmetry and a near-linear hydrogen bond. In all the potentials the twelve non-trivial vibrational frequencies of the water dimer are real, hence we are dealing with a genuine energy minimum. Using the MCY structural, vibrational and energy data the entire thermodynamics of the gas-phase water-dimer formation can be described, employing the partition functions of the usual rigid rotor and harmonic oscillator quality. The treatment was carried out for both ^{1}H and ^{2}D water-dimer isotopomers. A survey of energetics of the two isotopomeric species is given in Table 1.

This study interest is focused on the second virial coefficient B_2 of water, namely on its isotopic difference $B_2(\mathrm{H}) - B_2(\mathrm{D})$ measured in observation [92]. It has become customary to split the total B_2 term into two parts [95–98]:

$$B_2 = B_{2\mathrm{f}} + B_{2\mathrm{b}} \qquad (1)$$

where the first term $B_{2\mathrm{f}}$ has its origin in the interactions between free molecules not leading to formation of bound dimers, while the second term $B_{2\mathrm{b}}$ reflects the bound species present. Although at medium and higher temperatures $B_{2\mathrm{f}}$ forms a decisive component of B_2 it is not relevant in our case. The latter term, given by an integration of the potential over the whole configurational space, is precisely the same for both isotopic species. This

TABLE 1

Survey [a] of the water dimer energetics [b] in four MCY-type potentials

Potential	H-isotope	Potential energy ΔE	Ground state energy ΔH_0°
MCYI	^{1}H	−23.92	−14.88
	^{2}D		−17.13
MCYII	^{1}H	−24.55	−14.97
	^{2}D		−17.35
MCYB	^{1}H	−23.59	−14.89
	^{2}D		−17.04
MCYC	^{1}H	−25.26	−15.38
	^{2}D		−17.81

[a] The upper and lower line refer to the ^{1}H water-isotopomer dimerization $2H_2O(g) = (H_2O)_2(g)$ and to the ^{2}D water-isotopomer dimerization $2D_2O(g) = (D_2O)_2(g)$, respectively.

[b] Either the potential energy change ΔE or the ground state energy change ΔH_0° is presented, both in kilojoules per mole.

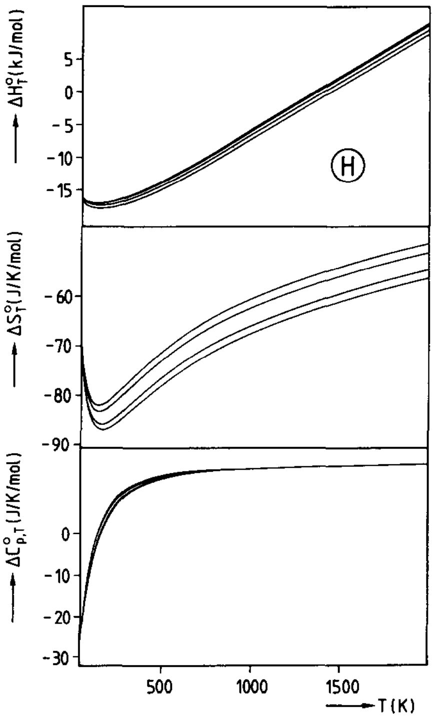

Fig. 1. Temperature dependencies of the standard (ideal gas at 101 325 Pa) changes of enthalpy ΔH_T°, entropy ΔS_T°, and heat capacity at constant pressure $\Delta C_{p,T}^\circ$, for the gas-phase ^{1}H water dimerization $2H_2O(g) = (H_2O)_2(g)$ evaluated in the four MCY potentials (for each presented quantity its values decrease in the order MCYB (the highest curve), MCYI, MCYII, MCYC (the lowest curve)).

exact cancellation follows from the fact that there is no reference to particle mass in the integrand. The B_{2b} term is related to the equilibrium constant K_{p2} of the dimer formation (see for example Ref. 99)

$$B_{2b} = -RTK_{p2} \qquad (2)$$

where R and T have their usual meanings. The K_{p2} terms are clearly different for H and D isotopomer formation owing to the differences in rotational and vibrational partition functions.

RESULTS AND DISCUSSION

Figures 1 and 2 survey thermodynamics of the gas-phase water-dimer formation for H and D isotopic modifications respectively, presenting temperature dependences of the related standard changes in enthalpy, entropy and heat capacity at constant pressure. In a qualitative sense the temperature dependences are quite similar in the two isotopomeric situations

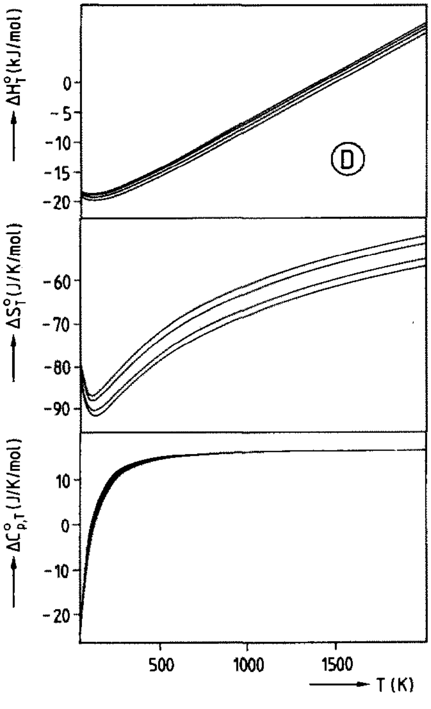

Fig. 2. Temperature dependencies of the standard (ideal gas at 101 325 Pa) changes of enthalpy ΔH_T°, entropy ΔS_T°, and heat capacity at constant pressure $\Delta C_{p,T}^\circ$, for the gas-phase ^{2}D water dimerization $2D_2O(g) = (D_2O)_2(g)$ evaluated in the four MCY potentials (for each presented quantity its values decrease in the order MCYB (the highest curve), MCYI, MCYII, MCYC (the lowest curve)).

TABLE 2

Isotopic differences[a] (B_2(H) − B_2(D)) between the second virial coefficient of water and heavy water evaluated using four MCY-type potentials and their comparison with observation[b]

T (K)	MCYI	MCYII	MCYB	MCYC	Observed[b]
423.15	43.6	36.1	46.5	37.1	15 ±7
448.15	33.0	27.1	35.3	27.5	10 ±5
473.15	25.7	21.0	27.6	21.1	3.9±1
498.15	20.6	16.7	22.2	16.7	3.1±0.5
523.15	17.0	13.6	18.3	13.5	1.8±0.3
548.15	14.2	11.4	15.4	11.2	1.6±0.3
573.15	12.1	9.6	13.1	9.4	0.5±0.4
598.15	10.5	8.3	11.4	8.1	1.7±0.3
623.15	9.2	7.3	10.0	7.0	0.6±0.3
648.15	8.2	6.4	8.9	6.2	0.6±0.3
673.15	7.3	5.7	8.0	5.5	0.6±0.3
698.15	6.6	5.2	7.3	4.9	0.0±0.3
723.15	6.0	4.7	6.6	4.5	0.2±0.2
748.15	5.6	4.3	6.1	4.1	0.1±0.2
773.15	5.1	4.0	5.7	3.7	0.0±0.2

[a] In cubic centimetres per mole.
[b] Ref. 92.

though at lower temperatures the enthalpy and entropy terms for the deuterated species lie substantially lower than for the H isotopomer. Interestingly enough, the four MCY potential modifications considered exhibit the same sequence order in all the situations, namely MCYB, MCYI, MCYII, MCYC, the MCYB and MCYC values being the highest and lowest respectively.

Table 2 presents the isotopic differences in the second virial coefficient of water evaluated using the four potential functions, and compares them with observation [92]. In agreement with the observation the isotopic difference $B_2(\mathrm{H}) - B_2(\mathrm{D})$ is positive in the temperature interval considered and decreases significantly with increasing temperature. However, the absolute values of the terms are considerably overestimated in comparison with observation. In fact, the difference is quite sensitive to the values of some input molecular parameters and thus relatively small changes in the potentials should improve the agreement considerably. An inclusion of anharmonicity contributions, neglected in our treatment, could contribute to improving the theory–experiment agreement too.

The values $B_2(\mathrm{H}) - B_2(\mathrm{D})$ are quite close in the four MCY potential modifications (though the MCYII and MCYC results lie somewhat closer to the observations). This finding can be rationalized as an effect of energy–entropy compensation connected with the above-mentioned uniform sequence order of values from different potential modifications (Figs. 1 and 2).

Finally, the study (representing a first contribution of this type in the field of isotope chemistry [100–111]) indicates a significance of the B_{2b} term which is usually neglected in evaluations of the second virial coefficient.

ACKNOWLEDGEMENTS

The study was completed whilst researching at the Max-Planck-Institut für Chemie (Otto-Hahn-Institut) supported by the Alexander von Humboldt-Stiftung. The support of as well as the valuable discussions with Professor Karl Heinzinger and the kind hospitality shown by him, his group and the Max-Planck-Institut für Chemie are gratefully acknowledged.

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