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CONTENTS OF MOLECULAR COMPLEXES IN GAS PHASE AT HIGHER PRESSURES: A CASE STUDY OF $(H_2O)_2(g)$

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ABSTRACT

The contents of weak molecular complexes have been analysed in equilibrium gaseous mixtures at high pressures, particularly in the region above the critical temperature, and have been illustrated with the water dimer using the most precise quantum-chemical data on the thermodynamics of its formation. The temperature decrease in stability can be overcompensated by the pressure. The competition action of formation of higher clusters has been studied with the model of water vapour composed of oligomers up to (and including) the pentamers.

INTRODUCTION

Both experimental and theoretical studies of gas-phase molecular complexes, e.g. those with a hydrogen bond [1–5], or van der Waals molecules (e.g. refs. 6 and 7), have been intensively developed in close collaboration. Typically, experimental studies of these weak molecular complexes are carried out at low temperatures [6,8] and pressure [6,9] both in the gas phase (inclusive of the expansion in a supersonic jet, e.g. refs. 10–12) and in almost inert matrices (e.g. refs. 13–15). The relatively fast stability decrease of molecular complexes with increasing temperature belongs to their basic features, and it is quantitatively manifested in the temperature dependences of equilibrium constants of formation of these complexes from the corresponding molecular (atomic) subsystems (e.g. refs. 16–18). In contrast to these temperature effects, the pressure effect on stability of the molecular complexes has not been studied systematically. Quite recently, however, attention was attracted by a conference contribution [19] giving the Raman spectra of water at high pressures, which represented a continuation of the previous Raman studies of the group [20,21]. The study [19] was carried out

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at pressures up to 26 GPa (about 256000 atm *) and temperatures up to 1700 K. The possibility of carrying out studies at such extreme conditions naturally evokes the question of the potential existence of (intermolecular) hydrogen bonds in these unusual situations. Although the temperature dependence of the stability of water oligomers (especially the dimer) in the gas phase has been evaluated several times [2,22–30], the pressure effect has not been treated quantitatively before.

COMPUTATIONAL METHODS

The thermodynamics of dimerization of water in the gas phase,

$$2\ H_2O(g) \rightleftharpoons (H_2O)_2(g) \qquad (1)$$

are described by the equilibrium constant

$$K_{p,2} = p_{(H_2O)_2}/p^2_{H_2O} \qquad (2)$$

where $p_{(H_2O)_2}$ and p_{H_2O} mean the partial pressure of the dimers and monomers, respectively, in the equilibrium mixture **. The equilibrium constant (2) can, quite independently of experimental data, be determined by calculation in terms of the partition function of the rigid rotor and harmonic oscillator (RRHO, see, e.g. refs. 22–28) employing the molecular constants derived from the quantum-chemical hypersurface of the pair interaction potential of water [23–27]. The most sophisticated quantum-chemical approach (i.e., the ab initio SCF CI) was used to construct the so-called MCY potential [32] which was modified by Bounds [33] (the MCY-B potential). This newest potential [33] seems to stand [34] so far in the best accordance with various observed data about $(H_2O)_2(g)$. In the present context, the key role is played by the quality of the MCY-B equilibrium constant $K_{p,2}$. Figure 1 presents the temperature dependence of the respective standard change of the Gibbs energy ΔG^0_T for dimerisation of water, and it includes all the observed values (Refs. 35–37, and references cited therein) for both the natural H isotopic mixture and $D_2O(g)$. The agreement with available experimental data is, so far, the best of the results obtained for the calculated ΔG^0_T values. From Fig. 1 it can be seen that the theoretical curve of the temperature dependence of ΔG^0_T would be very close to a suitable fitting of the observed data themselves to an optimum curve.

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* Throughout this paper: 1 atm = 101325 Pa.

** We shall adopt here the usual, although not quite correct, dimensional equilibrium constants. A transition to the more correct dimensionless standard equilibrium constants (cf. ref. 31) would introduce the expression p_X/p_0 instead of p_X into eqn. (2), where p_0 means the standard pressure chosen.

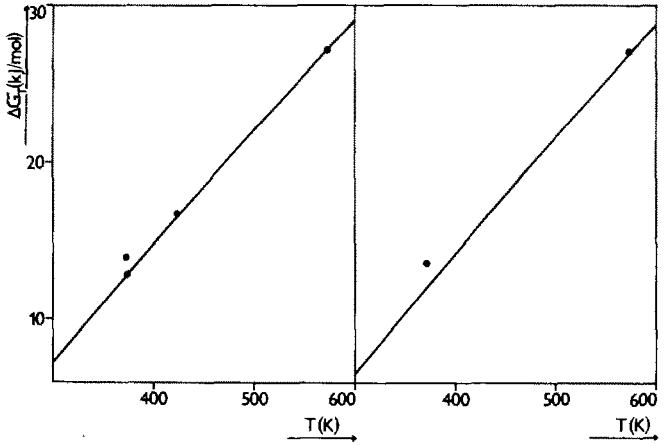

Fig. 1. Temperature dependence of MCY-B Gibbs energy standard change, ΔG_T^0, of $H_2O(g)$ (left, the natural hydrogen isotopic mixture) and $D_2O(g)$ (right) dimerisation together with observed data, (●) see refs. 35–37, and references therein; the standard state, ideal gas phase at 1 atm pressure.

Let us denote the overall equilibrium pressure of the monomer and dimer in the gas phase with the symbol $P(P = p_{H_2O} + p_{(H_2O)_2})$. Then the molar fraction $x_{(H_2O)_2}$ describing the content of the dimer in this equilibrium mixture will be [31]:

$$x_{(H_2O)_2} = \frac{2PK_{p,2} + 1 - (4PK_{p,2} + 1)^{1/2}}{2PK_{p,2}} \tag{3}$$

where the equilibrium constant $K_{p,2}$ and the ΔG_T^0 term from Fig. 1 are connected by the familiar master relation:

$$\Delta G_T^0 = -RT \ln K_{p,2} \tag{4}$$

Formula (3) makes it possible to study the pressure and temperature dependence of composition of the equilibrium water vapour with the presumption that it is only composed of monomers and dimers, i.e. in the range of associates which can, at present, be described by the scope of data extracted so far from the MCY-B potential [34].

More generally, the equilibrium water vapour can be considered to be composed of $H_2O(g)$ and $(H_2O)_i(g)$ associates, with the i value varying from 2 to n. The partial pressures of these associates, $p_{(H_2O)_i}$, fulfil the equilibrium conditions:

$$K_{p,i} = \frac{p_{(H_2O)_i}}{p^i_{H_2O}} \quad (i = 2, \ldots, n) \tag{5}$$

where $K_{p,i}$ means the equilibrium constant of association of i molecules $H_2O(g)$ into a cluster $(H_2O)_i(g)$. Let us consider, besides the temperature T, the overall pressure P of the equilibrium gaseous mixture as the other explicit variable:

$$P = p_{H_2O} + \sum_{i=2}^{n} p_{(H_2O)_i} \tag{6}$$

Equations (5) and (6) represent a set of n equations for n unknown pressures p_{H_2O}, $p_{(H_2O)_i}$. In terms of the molar fraction of $H_2O(g)$ in this n-component mixture, x_{H_2O}, eqns. (5) and (6) are reduced to the algebraic equation of n-th degree for unknown x_{H_2O}:

$$-1 + x_{H_2O} + \sum_{i=2}^{n} K_{p,i} P^{i-1} x_{H_2O}^{i} = 0 \tag{7}$$

In spite of eqn. (7) having n (complex) roots, potential problems of multiplicity of physically meaningful solutions are removed by the existence theorem [38–40] securing only a single solution of eqn. (7) in the interval (0; 1). This unambiguity of solution also simplifies the procedure of its numerical determination. A physically meaningful solution is easily determined with any arbitrary accuracy by the procedure of stepwise halving of the interval and selection of that one of the subintervals produced in the extreme points of which the values of the left-hand expression of eqn. (7) have opposite signs. Knowing the temperature dependence of the equilibrium constants $K_{p,i}$ for $i = 2, \ldots, n$, it is possible to use eqn. (7) to study both the pressure and the temperature dependences of composition of the equilibrium steam modelled as a mixture of monomers and corresponding di- to n-mers.

RESULTS AND DISCUSSION

The very good agreement between the MCY-B and the observed values of the standard Gibbs energy of dimerisation of water, which is presented in Fig. 1, clearly justifies the application of the MCY-B equilibrium constant $K_{p,2}$ to studies of the dimer content in the equilibrium steam. This agreement does not necessarily mean a high accuracy of the MCY-B potential, it is rather a result of happy compensation of errors of the quantum-chemical and statistical–thermodynamic treatments. In any case, the combination of MCY-B potential and RRHO approximation of partition functions represents a reliable device for calculation of $K_{p,2}$ at the temperatures at which the thermodynamics of the dimerisation (1) were experimentally determined. As this device operates reliably in a relatively broad temperature interval of these observations [35–37] (i.e. 100–300°C), its applicability can be presumed also to extrapolations to the regions of both lower and somewhat higher temperatures.

For surveying the pressure and temperature dependences of the dimer

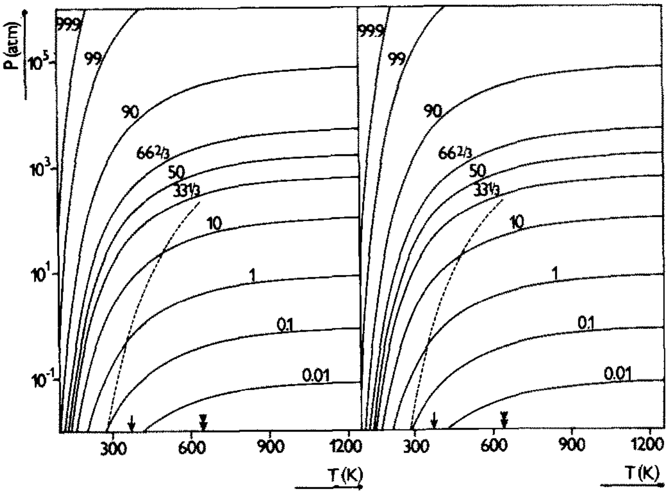

Fig. 2. Temperature dependences of overall pressure *P* of the equilibrium mixture of gas-phase water monomers and dimers leading to a selected value of the water dimer molar fraction (from 0.01 to 99.9% water dimer contents as indicated on the curves): left, MCY-B, the natural hydrogen isotopic mixture; right, MCY-B, deuterated water; the (— — —) temperature course of the saturated vapour pressure; (→) normal boiling point; (⇸) critical temperature.

content in the equilibrium gaseous mixture of the monomer and dimer we have chosen ten representative levels of the dimer content in terms of its molar fraction in a range from 0.01 to 99.9%. For each temperature *T*, the pressure *P* was determined, which was necessary for reaching the prechosen association degree. The dependences are presented in Fig. 2 for a broad interval of temperatures and pressures for both the system $H_2O/(H_2O)_2$ (the natural H isotopic mixture) and the system $D_2O/(D_2O)_2$. Besides the so far considered fulfilling of the requirement of chemical equilibrium, we can also consider the criteria of phase equilibria. Then, of course, a free choice of the pressure value is only possible above the critical temperature. At lower temperatures the pressure should not exceed the liquid–vapour coexistence curve (or solid–vapour). Of course, this only applies to rigorous conditions of the whole thermodynamic equilibrium. In principle, however, we can also consider such situations where the conditions of chemical equilibrium are fulfilled but those of physical equilibrium are not, i.e. particularly the situation where, below the critical temperature, the pressure would be higher than the pressure of the saturated vapour coexisting in equilibrium with the liquid phase (supersaturated vapour). For consideration of this type, Fig. 2 also presents the temperature dependence [41,42] of the saturated vapour pressures for water and deuterated water.

From Fig. 2 it can be seen that in the temperature interval studied even pressures two orders of magnitude lower than those used in the study by

Holmes et al. [19] are sufficient for attaining a marked dimer content in the equilibrium mixture of the monomers and dimers. For example, for attaining a dimer molar fraction of 25% it is sufficient, even at the highest temperature from Fig. 2 (i.e. 1250 K), to apply a pressure lower than 363 and 355 atm for the H and D systems, respectively. Similarly, the molar fractions of 50% are attained by pressures not exceeding 1632 and 1598 atm.

The remarkable increase of the dimer content in the idealised equilibrium monomer–dimer mixture at higher pressures observed even at high temperatures, of course, indicates that a significant role of higher associates must also be generally presumed at these conditions. As the equilibrium constants $K_{p,i}$ $(i > 2)$ of the MCY-B type are not yet available, a judgement of possible proportions needs to apply some lower-quality evaluation of these equilibrium constants. Owicki et al. [24] evaluated the stability of the water oligomers up to the pentamers in terms of the empirical EPEN potential. Their data cannot be considered satisfactory for precise calculations; e.g. their $K_{p,2}$ value at the temperature of 100 K is about 19 and 13 times lower than the MCY-B values for the dimerisation of $H_2O(g)$ and $D_2O(g)$, respectively. These differences are lowered with increasing temperature. Nevertheless, even at e.g. 700 K this underestimation is given by a factor of about 3.5

TABLE 1

Pressure dependence of the equilibrium populations (molar fractions in %) of water oligomers in steam modelled by two- and five-component mixtures at 700 K [a]

Gas-phase cluster	P (atm)						
	1	10	10^2	10^3	10^4	10^5	10^6
	Mixture of monomers and dimers						
H_2O	99.94	99.40	94.59	70.22	33.24	12.07	3.99
	(99.79) [b]	(97.98) [b]	(84.86) [b]	(49.17) [b]	(19.56) [b]	(6.66) [b]	(2.16) [b]
$(H_2O)_2$	0.06	0.60	5.41	29.78	66.76	87.93	96.01
	(0.21) [b]	(2.02) [b]	(15.14) [b]	(50.83) [b]	(80.44) [b]	(93.34) [b]	(97.84) [b]
	Mixture of monomers to pentamers						
H_2O	99.94	99.40	94.56	69.25	29.13	7.46	1.47
$(H_2O)_2$	0.06	0.60	5.40	28.97	51.27	33.60	12.98
$(H_2O)_3$	5×10^{-6}	5×10^{-4}	0.04	1.55	11.55	19.37	14.71
$(H_2O)_4$ [c]	1×10^{-9}	1×10^{-6}	8×10^{-4}	0.23	7.30	31.38	46.82
$(H_2O)_5$ [d]	4×10^{-14}	3×10^{-10}	3×10^{-6}	0.01	0.74	8.19	24.02

[a] Based on $K_{p,i}$ values of Owicki et al. [24] (if not otherwise stated).

[b] Values following from the MCY-B $K_{p,2}$ term are given in parentheses.

[c] A group of three isomeric tetramers treated as one pseudospecies (probably a majority of tetramer energy minima), see ref. 24.

[d] A group of two isomeric pentamers treated as one pseudospecies (probably a minority of pentamer energy minima), see ref. 24.

for each of the two isotopomers. However, the constants $K_{p,i}$ ($i = 2$ to 5) from Ref. 24 represent a useful clue to estimation of populations of the individual oligomers.

Table 1 presents the pressure dependence of the composition of the equilibrium mixture of water monomers to pentamers at the temperature of 700 K based on the equilibrium constants $K_{p,i}$ from ref. 24 (roughly it can be stated that the $K_{p,i}$ value for the standard pressure of 1 atm decreases by four orders of magnitude per each added monomer unit when going from the dimers to pentamers). Whereas at the pressure of 1000 atm the monomer still forms almost 70% of the equilibrium mixture of the monomers to pentamers, at 10000 atm the dimers represent the most significant component, whereas at 10^6 atm the tetramers predominate. For comparison, Table 1 also presents the results obtained for a mere equilibrium mixture of the monomers and dimers. At the pressure of 1000 atm the two models of water vapour (the 2- and 5-component ones) still lead to very close results, at higher pressures the 2-component model progressively overestimates both the dimer and the monomer contents. Moreover, Table 1 also compares the results of the 2-component model based on the equilibrium constant by Owicki et al. [24] with the results based on the MCY-B potential. The former source leads to underestimation of the dimer content as compared with the MCY-B results, this underestimation being decreased with increasing pressure (at high pressures, the therm $1 - x_{(H_2O)_2}$ from eqn. (3) is inversely proportional to $K_{p,2}^{1/2}$).

CONCLUDING REMARKS

The equilibrium constants $K_{p,i}$ are different from zero for every molecular complex (if there is at least one bound quantum state — metastable states are not considered in the present paper, cf. refs. 18, 43 and 44). Obviously, even the least positive value of these constants enables, in principle, an enhancement of population of the corresponding complex in the equilibrium gas phase by application of suitably increased pressure. Different pressures can make associates of different magnitude to be the most significant component of the gaseous mixture, which is important for the choice of suitable conditions of observation of a particular associate. An especially important region for application of high pressures is that above the critical temperature. Finally, in special cases of extreme conditions [19] it can be expected that the associates (and not the monomer) will form the substantial part of the equilibrium gas phase, and hence, that there an intermolecular hydrogen bond will exist at these, so far, unusual conditions.

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