

A CLUSTER MODEL OF THE GAS-PHASE WATER *

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ABSTRACT

Steam has been modelled as an equilibrium mixture of $(\text{H}_2\text{O})_i$ clusters with $i=1-100$. Considerably large fractions of oligomers ($1 < i < 6$) have been found at moderate and high pressures for high temperatures, exhibiting an extreme behaviour in pressure dependency. In contrast, very low fractions of the oligomers have been found, at any pressure, with very low temperatures.

1. INTRODUCTION

The cluster (or supermolecule) approach, e.g. [2–6], is a subject of interest as a model of real gas or liquid phases enabling straightforward studies of environmental effects. In this context, the water dimer, as well as higher water oligomers, have been studied vigorously, e.g. [7–17]. Theoretical thermodynamic and kinetic characteristics of these associates have recently been evaluated [10–13,18–23], data based entirely on quantum-chemical approaches being involved [11,12,20–23], too. However, a study of a whole cluster interplay in the equilibrium steam is still missing. The present paper aims to fill the gap.

2. STEAM AS A CLUSTER MIXTURE

Let us consider the equilibrium water vapour as being composed of $(\text{H}_2\text{O})_i(\text{g})$ associates, $i = 1, 2, \dots, n$. The partial pressures of these associates, $P_i^{(n)}$, fulfil the usual equilibrium conditions:

$$K_{p,i} = P_i^{(n)} / (P_1^{(n)})^i \quad (1)$$

* Dedicated to the 50th anniversary of preparation of the artificial snow crystal by Professor Ukitiro Nakaya at the Hokkaido University on 12 March, 1936 (cf. ref. 1).

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where $K_{p,i}$ denotes the equilibrium constant of association of i water molecules into a cluster:

$$i\text{H}_2\text{O}(\text{g}) = (\text{H}_2\text{O})_i(\text{g}) \quad (2)$$

(for simplicity, we introduce $K_{p,1} = 1$) the superscript (n) reminds us that the partial pressures will generally change with a change of the upper limit, n , of the clusters considered. The total pressure, P , of the cluster system is given as:

$$P = \sum_{i=1}^n P_i^{(n)} \quad (3)$$

The number of variables can easily be reduced to just one: it holds in terms of the mole fraction of the monomer in this n -component mixture, $x_1^{(n)}$:

$$\sum_{i=1}^n K_{p,i} (x_1^{(n)} P)^i = P \quad (4)$$

The mole fractions of higher associates, $x_i^{(n)}$, are given as:

$$x_i^{(n)} = K_{p,i} (x_1^{(n)})^i P^{i-1} \quad (5)$$

Thus, we have an algebraic equation of the n th degree leading to the composition of the equilibrium cluster mixture at any pressure P . It can be proved [24] that equation (4) has just one (real) solution in the interval (0; 1). Using this property, an efficient algorithm for the solution of equation (4) has been set up [25], employing stepwise halving of the interval.

3. ESTIMATION OF THE GIBBS ENERGY TERMS

To describe the cluster system in a complete way, values of the standard changes of Gibbs energy, $\Delta G_{T,i}^0$, connected with equilibria (2) are needed. Their purely quantum-chemical evaluation for large clusters is not possible at present (such sophisticated thermodynamical data are only available [11,15,21] for the water-dimer formation). However, Owicki et al. [20] evaluated within the EPEN potential function the $\Delta G_{T,i}^0$ terms for $i = 2-5$, this being the most comprehensive thermodynamical characterization available for water clusters. Figure 1 presents a useful property of these standard * terms: the value of increment in the $\Delta G_{T,i}^0$ terms per each added water molecule is practically constant within the set. In the first approximation we can use this property for a straightforward extrapolation of the $\Delta G_{T,i}^0$ values of higher clusters. Clearly enough, for a given temperature, equilibrium

* The standard state choice throughout the paper: an ideal gas phase at 1 atm pressure (1 atm = 101325 Pa).

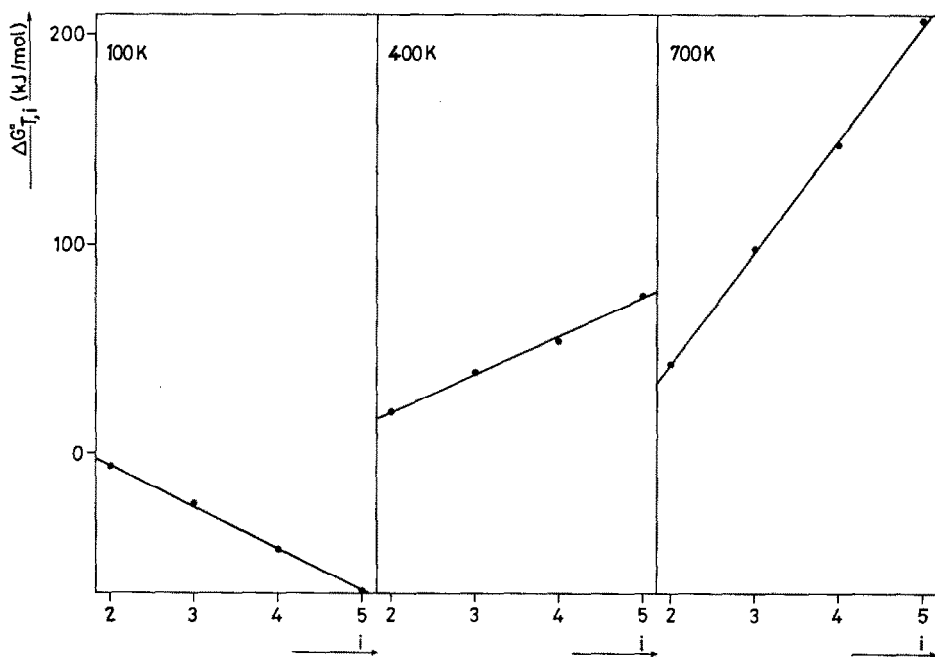


Fig. 1. Plots of the standard changes [19] of Gibbs energy, $\Delta G_{T,i}^0$, upon formation of $(\text{H}_2\text{O})_i(\text{g})$ ($i = 2-5$) versus number of water molecules in the associates (i).

constants ($K_{p,i}$) form, within this equidistant $\Delta G_{T,i}^0$ level spacing, a geometrical series.

4. RESULTS AND DISCUSSION

There are three variable parameters in the model: temperature, T (Owicki et al. [20] considered three distinct temperatures: 100, 400 and 700 K), pressure, P , and dimension of the model, n . Figure 2 sketches the pressure dependences of $x_i^{(n)}$ for the two higher temperatures and $n = 50$. Two different situations can be distinguished here: (i) significant populations of the smallest oligomers only (the region of lower pressure); (ii) continuous increase of populations of just higher clusters with increasing content of water units, i (the region of higher pressure). Between these two pressure regions there is a distinct intermediate situation with all the clusters of $i > 1$ having exactly the same populations. The existence of such a particular pressure point, $\bar{P}^{(n)}$, is a consequence of the equidistant $\Delta G_{T,i}^0$ level spacing: it holds in the point

$$\bar{x}_1^{(n)} \bar{P}^{(n)} = 1/z \quad (6)$$

where z denotes the quotient of the geometrical series:

$$z = K_{p,i+1}/K_{p,i} \quad (7)$$

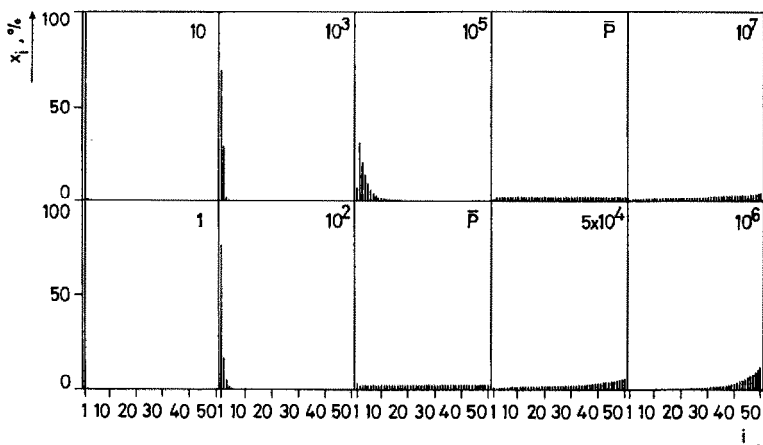


Fig. 2. Populations of the water clusters, x_i (mole fractions in %), evaluated within the set of monomers to oligomers ($n = 50$) for $T = 700$ K (the upper part) and $T = 400$ K (the lower part): the figures in the upper right corner denote the total pressure P in atm. The values $P^{(50)}$ are equal to about 3.34×10^6 and 9.85×10^3 atm for 700 and 400 K, respectively (see equation (6)).

These two types of behaviour can be well rationalized in terms of the following limits (holding for every finite $n > 1$):

$$\lim_{P \rightarrow 0} x_1^{(n)} = 1 \quad (8)$$

$$\lim_{P \rightarrow \infty} x_1^{(n)} = 0 \quad (9)$$

Nevertheless, the term $x_1^{(n)}P$ increases without limitations with increasing P (again considering the above specified values of n):

$$\lim_{P \rightarrow \infty} x_1^{(n)}P = \infty \quad (10)$$

so that even the last term in expansion (4) becomes significant at sufficiently high pressures, and, particularly:

$$\lim_{P \rightarrow \infty} x_n^{(n)} = 1 \quad (11)$$

While for $T = 400$ or 700 K there are pressure regions where small oligomers (i.e., oligomers with $1 < i < 6$) are significantly populated, it is not the case for the lowest temperature studied (Fig. 3). This result may be surprising, however, it is in fact a direct consequence of interplay of $K_{p,i}$ values at this temperature. On the other hand, at higher temperatures, populations of small oligomers can reach very high values for some pressures, as can be seen in Fig. 4. Moreover, the pressure dependencies of the $x_i^{(n)}$ values for these oligomers are not smooth, but exhibit a maximum. Table 1 gives more specific information on coordinates of the water-dimer

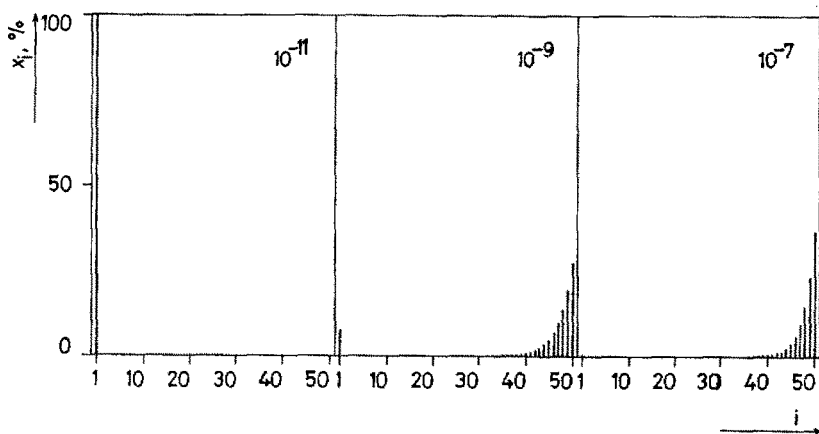


Fig. 3. Populations of the water clusters evaluated at $T=100$ K and $n=50$: $\bar{P}^{(50)} = 5.10 \times 10^{-11}$ atm (see the caption to Fig. 2 for details).

maximum evaluated within the model of $n=100$. Incidentally, it should be noted that the pressure values employed are not terribly high from the experimental point of view. Recently, Walrafen reported [26] Raman spectroscopic studies of water at pressures up to 256 000 atm.

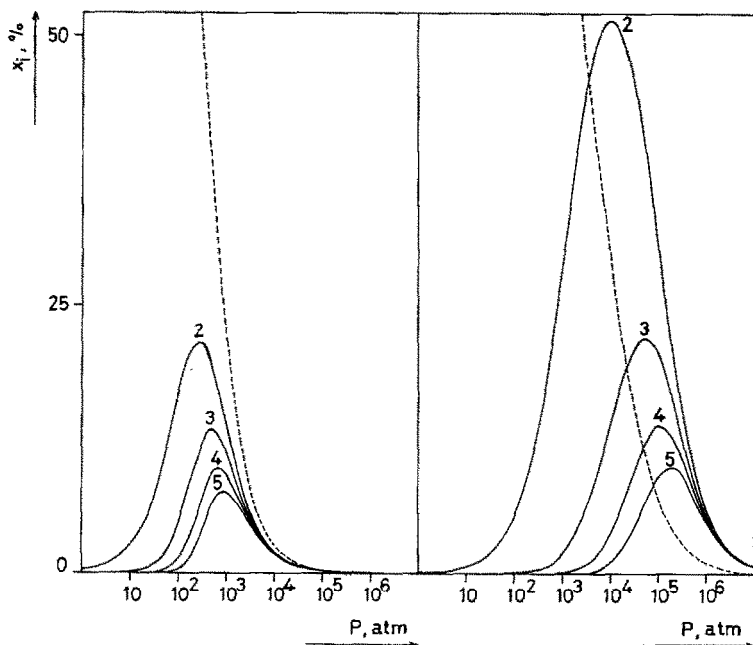


Fig. 4. Pressure dependences of populations of the water oligomers with $i=2-5$, x_i (mole fractions in %), evaluated for $T=400$ K (left) and $T=700$ K (right) within the set of monomers to oligomers ($n=100$): the monomer populations x_1 are shown as dashed lines.

TABLE 1

Examples of situations of relatively high content ^a of the water dimer

T (K) ^b	P (atm)	$x_2^{(100)}$ (%)
700	1×10^4	51.4
400	3×10^2	21.4

^a The points chosen are located in a neighbourhood of the maxima on the $x_2^{(100)}$ (P) curves (cf. Fig. 4).

^b For $T=100$ K the maximum is located close to $P = 6 \times 10^{-11}$ atm and amounts to about 11.9×10^{-6} %; however, the convergency is very slow, e.g. convergency to three digits is not reached until about $n = 7000$.

We have not yet discussed the convergence properties of the model, i.e. the effect of increasing the value of n . The following analytical expression can be derived for the limit:

$$\lim_{n \rightarrow \infty} x_1^{(n)} = x_1^{(\infty)} = \frac{-1/z - P + \left[(1/z + P)^2 + 4P(K_{p,2}/z - 1)/z \right]^{1/2}}{[2P(K_{p,2}/z - 1)]} \quad (12)$$

For a selected temperature the pressure dependency of the convergence properties can be strong, as demonstrated in Table 2. Clearly enough, with increasing pressure, the convergency becomes poorer. However, it is clear that the results related to the water-dimer maximum population (Fig. 4, Table 1) are sufficiently converged (the $x_1^{(100)}$ term with the pressures in question is equal to $x_1^{(\infty)}$, at least for the first five significant digits) so that there would be no significant effect of a further increase of the model dimension.

TABLE 2

An illustration of convergence properties of the monomer mole fraction $x_1^{(n)}$ (%)

n	$T = 400$ K		$T = 700$ K	
	$P = 10^2$ atm	$P = 10^4$ atm	$P = 10^2$ atm	$P = 10^4$ atm
2	81.072	16.979	94.595	33.243
3	77.537	8.5944	94.551	30.040
4	76.645	6.0896		29.383
5	76.398	4.9601		29.219
7	76.306	3.9442		29.163
10	76.298	3.3481		29.158
20		2.8209		
50		2.6082		
100		2.5670		
200		2.5574		
500		2.5563		
∞	76.298	2.5563	94.551	29.158

The quality of $K_{p,i}$ equilibrium constants entirely determines the accuracy of the $x_i^{(n)}$ results. The available experimental information on the equilibrium constants is rather limited—there are observed data on the $K_{p,2}$ term only. However, it is clear that the $K_{p,2}$ values by Owicki et al. [20] we have employed are somewhat underestimated compared [25] to the observed data. This is the first line of improving the input $K_{p,i}$ data set. Moreover, the equidistant $\Delta G_{T,i}^0$ level spacing we have applied is questionable for higher i values. One could expect a more rapid decrease of stability of higher associates, instead. So, there is a clear need for a more precise evaluation of the $K_{p,i}$ terms for higher associates, too. Of course, with higher clusters, phenomenological potentials will still be a preferred tool for such purposes. Studies along these lines are in progress.

With the $K_{p,i}$ set having a sufficient precision, we could match the results of the cluster model to observed information on steam properties, including the behaviour in vicinity of the critical temperature and pressure. Finally, there is, at least in principle, a possibility to include not only temperature but also pressure dependence of the $K_{p,i}$ terms, viz. through pressure dependence (originated in a pressure dependent structure of environment) of quantum states of clusters.

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